Synthesis of a New Polydentate Ligand Obtained by Coupling 2,6-Bis(imino)pyridine and (Imino)pyridine Moieties and Its Use in Ethylene Oligomerization in Conjunction with Iron(II) and Cobalt(II) Bis-halides

Claudio Bianchini,*[,†] Giuliano Giambastiani,*[,†] Itzel Guerrero Rios,[†] Andrea Meli,[†] Werner Oberhauser,[†] Lorenzo Sorace,[‡] and Alessandro Toti[†]

Istituto di Chimica dei Composti Organometallici (ICCOM-CNR), Via Madonna del Piano 10, 50019 Sesto Fiorentino (Firenze), Italy, and Dipartimento di Chimica and UdR INSTM, Università di Firenze, Via della Lastruccia 3, 50019 Sesto Fiorentino (Firenze), Italy

Received June 28, 2007

In this paper are described the synthesis, characterization, and coordinating properties of a new potentially pentadentate nitrogen ligand, $^{CyAr2}\mathbf{N_5}$, that combines in the same molecular structure 2,6-bis(imino)-pyridine and (imino)pyridine moieties. This ligand reacts with 1 or 2 equiv of anhydrous MCl_2 (M = Fe, Co) to give paramagnetic mononuclear or homodinuclear complexes of the formula $^{CyAr2}\mathbf{N_5MCl_2}$ and $^{CyAr2}\mathbf{N_5M_2Cl_4}$. In the dinuclear complexes, one metal center is five-coordinate, while the other is four-coordinate. Ligand and metal complexes have been characterized, both in the solid state and in solution, by a variety of techniques, including single-crystal X-ray diffraction analyses, magnetic susceptibility determinations, IR, vis−NIR, ^{1}H NMR, and X-band EPR spectroscopies. On activation by methylaluminoxane (MAO) in toluene, the Fe^{II} and Co^{II} complexes generate effective catalysts for the oligomerization of ethylene to α-olefins with productivities and Schulz−Flory parameters depending on the type and number of the coordinated metals. In an attempt to rationalize the surprisingly high activity of the Co^{II} precursors, and in particular that of the dinuclear derivative $^{CyAr2}\mathbf{N_5Co_2Cl_4}$, which is 4 times higher than that of the mononuclear analogue $^{CyAr2}\mathbf{N_5CoCl_2}$, a Co^{II} complex has been synthesized where the supporting ligand is sterically similar to $^{CyAr2}\mathbf{N_5}$, yet it contains only the three nitrogen donor atoms of the 2,6-bis-(imino)pyridine moiety. From this study, it is concluded that all five nitrogen atoms of $^{CyAr2}\mathbf{N_5}$ play an active role under catalytic conditions, even when the precursor contains a free (imino)pyridine moiety.

Introduction

The success of iron and cobalt bis-chloride catalysts supported by either 2,6-bis(imino)pyridine[1−3] or (imino)pyridine[4,5] ligands in ethylene oligomerization is stimulating much research aimed at developing analogous catalytic systems with improved productivity and selectivity. Some active precursors for the oligomerization of ethylene to α-olefins with a Schulz−Flory distribution are shown in Scheme 1.

The advantages of 2,6-bis(arylimino)pyridine or (imino)-pyridine Fe^{II} and Co^{II} catalysts over other types of early and late transition metal systems for ethylene oligomerization are manifold, spanning from the ease of preparation and handling, to the use of cheap metals with reduced environmental impact. Another intriguing feature of these catalyst precursors is provided by the facile tuning of their activity by simple structural modifications such as the number, size, nature, and regiochemistry of the substituents either in the pyridine ring or in the arylimino groups.[1,4] Moreover, due to the good compatibility with other catalytic systems, 2,6-bis(arylimino)pyridine[6] and (imino)pyridine[4c,7] Fe^{II} and Co^{II} dihalides can be used as oligomerization catalysts in tandem reactions for the production of branched polyethylene (PE) as well as in reactor blending processes to give PE with controlled molecular weight distribution and rheology.[8]

* To whom correspondence should be addressed. E-mail: claudio.bianchini@iccom.cnr.it.

† ICCOM-CNR.

‡ Università di Firenze and UdR INSTM-Firenze.

(1) (a) Bianchini, C.; Giambastiani, G.; Guerrero Rios, I.; Mantovani, G.; Meli, A.; Segarra, A. M. *Coord. Chem. Rev.* **2006**, *250*, 1391. (b) Gibson, V. C.; Redshaw, C.; Solan, G. A. *Chem. Rev.* **2007**, *107*, 1745.

(2) (a) Small, B. L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 7143. (b) Britovsek, G. J. P.; Bruce, M.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; McTavish, S. J.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1998**, 849. (c) Britovsek, G. J. P.; Mastroianni, S.; Solan, G. A.; Baugh, S. P. D.; Redshaw, C.; Gibson, V. C.; White, A. J. P.; Williams, D. J.; Elsegood, M. R. J. *Chem.−Eur. J.* **2000**, *6*, 2221.

(3) (a) Bianchini, C.; Mantovani, G.; Meli, A.; Migliacci, F.; Zanobini, F.; Laschi, F.; Sommazzi, A. *Eur. J. Inorg. Chem.* **2003**, 1620. (b) Bianchini, C.; Giambastiani, G.; Guerrero Rios, I.; Meli, A.; Passaglia, E.; Gragnoli, T. *Organometallics* **2004**, *23*, 6087.

(4) (a) Bianchini, C.; Mantovani, G.; Meli, A.; Migliacci, F.; Laschi, F. *Organometallics* **2003**, *22*, 2545. (b) Bianchini, C.; Giambastiani, G.; Mantovani, G.; Meli, A.; Mimeau, D. *J. Organomet. Chem.* **2004**, *689*, 1356. (c) Bianchini, C.; Frediani, M.; Giambastiani, G.; Kaminsky, W.; Meli, A.; Passaglia, E. *Macromol. Rapid Commun.* **2005**, *26*, 1218. (d) Bianchini, C.; Gatteschi, D.; Giambastiani, G.; Guerrero Rios, I.; Ienco, A.; Laschi, F.; Mealli, C.; Meli, A.; Sorace, L.; Toti, A.; Vizza, F. *Organometallics* **2007**, *26*, 726.

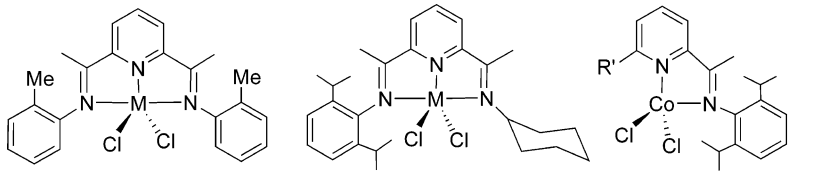
(5) (a) Britovsek, G. J. P.; Baugh, S. P. D.; Hoarau, O.; Gibson, V. C.; Wass D. F.; White, A. J. P.; Williams, D. J. *Inorg. Chim. Acta* **2003**, *345*, 279. (b) Tang, X.; Sun, W.-H.; Gao, T.; Hou, J.; Chen, J.; Chen, W. *J. Organomet. Chem.* **2005**, *690*, 1570.

(6) (a) Quijada, R.; Rojas, R.; Bazan, G.; Komon, Z. J. A.; Mauler, R. S.; Galland, G. B. *Macromolecules* **2001**, *34*, 2411. (b) Wang, H.; Ma, Z.; Ke, Y.; Hu, Y. *Polym. Int.* **2003**, *52*, 1546. (c) Zhang, Z.; Lu, Z.; Chen, S.; Li, H.; Zhang, X.; Lu, Y.; Hu, Y. *J. Mol. Catal. A* **2005**, *236*, 87.

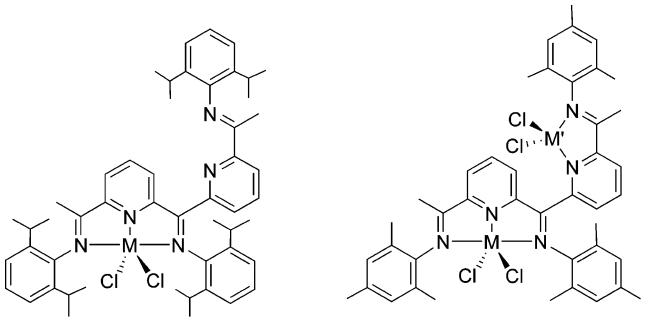
(7) Musikabhumma, K.; Spaniol, T. P.; Okuda, J. *J. Polym. Sci. Part A: Polym. Chem.* **2003**, *41*, 528.

10.1021/om7006503 CCC: $37.00
Publication on Web 08/25/2007

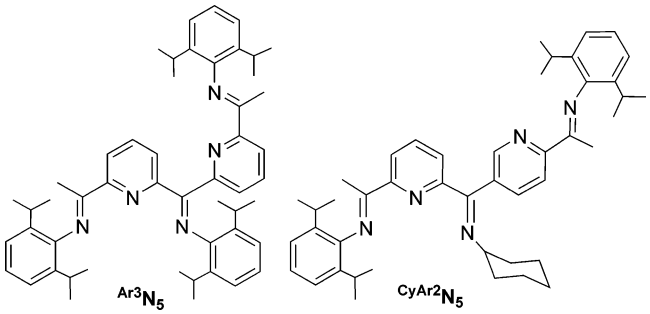
Scheme 1



Scheme 2



Scheme 3



For these reasons, the search for new molecular architectures of either 2,6-bis(imino)pyridine or (imino)pyridine ligands is a topic of much current interest. Among the many possible structural variations, great interest is being stirred up by the incorporation of 2,6-bis(imino)pyridine and (imino)pyridine moieties into the same molecular structure.[1,5a,9,10] Such polydentate nitrogen ligands are expected to generate polymetallic catalysts with diverse applications in homogeneous catalysis, with particular regard to ethylene oligomerization/polymerization. Indeed, homo- or heteropolymetallic catalysts may (i) produce unconventional mixtures of PEs and/or α-olefins, (ii) exhibit increased activity due to favorable steric and electronic metal−metal interactions, and (iii) produce tailored materials via chain transfer from one metal to the other with or without a shuttling agent.

The coupling of a 2,6-bis(imino)pyridyl moiety with an (imino)pyridyl fragment has been recently described, and the corresponding Fe^{II} and Co^{II} mono- and dinuclear complexes have been successfully used for the polymerization of ethylene to high-density PE (Scheme 2).[10]

In this paper, we describe the synthetic route to a new molecule, $^{CyAr2}\mathbf{N_5}$ (Scheme 3), that combines in the same molecular structure two ligands, each of which is independently capable of generating an effective Fe^{II} or Co^{II} catalyst for the oligomerization of ethylene.[3,4] The $^{CyAr2}\mathbf{N_5}$ ligand differs from any other previously described related molecule, for example $^{Ar3}\mathbf{N_5}$ shown in Scheme 3,[10] for the position of the (imino)-pyridine fragment with respect to the central imine group as well as the presence of a cyclohexyl substituent on the latter group. As it will be shown in this paper, $^{CyAr2}\mathbf{N_5}$ allows for the formation of mononuclear and dinuclear Fe^{II} and Co^{II} bis-chloride complexes that, upon activation with methylaluminoxane (MAO), convert ethylene into α-olefins with productivities and Schulz−Flory parameters depending on the type and the number of coordinated metals.

Experimental Section

General Considerations. All air- and/or water-sensitive reactions were performed under either nitrogen or argon in flame-dried flasks using standard Schlenk-type techniques. Anhydrous toluene, THF, and Et_2O were obtained by means of an MBraun solvent purification systems, while CH_2Cl_2 and MeOH were distilled over CaH_2 and Mg, respectively. Solid MAO for polymerization was prepared by removing toluene and $AlMe_3$ under vacuum from a commercially available MAO solution (10 wt % in toluene, Sigma-Aldrich). The MAO solution was filtered on a D4 funnel and evaporated to dryness at 50 °C under vacuum. The resulting white residue was heated further to 50 °C under vacuum overnight. A stock solution of MAO was prepared by dissolving solid MAO in toluene (100 mg mL^{-1}). The solution was used within three weeks to avoid self-condensation effects of the MAO. All the other reagents and solvents were used as purchased from commercial suppliers. Solid compounds were collected on sintered-glass frits and washed with appropriate solvents before being dried in a stream of nitrogen. Ethylene oligomerization reactions and reactions under high CO pressure were performed in stainless steel reactors (500 and 100 mL for ethylene and CO, respectively), constructed at the ICCOM-CNR (Firenze, Italy), equipped with a magnetic drive stirrer, and a Parr 4842 temperature and pressure controller. The reactor was connected to an ethylene reservoir to maintain a constant pressure throughout the catalytic runs. Deuterated solvents for NMR measurements were dried over 4 Å molecular sieves. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker ACP 200 (200.13 and 50.32 MHz, respectively) and Bruker Avance DRX-400 (400.13 and 100.62 MHz, respectively) spectrometers equipped with variable-temperature control units accurate to ±0.1 °C. Chemical shifts are reported in ppm (δ) relative to TMS or referenced to the chemical shifts of residual solvent resonances (^1H and ^{13}C). The number of protons attached to the carbon nuclei was determined by means of both $^{13}C\{^1H\}$ DEPT 135 and J-modulated spin−echo NMR pulse programs. The assignments of the signals was achieved with the aid of 1D spectra, 2D ^1H COSY, ^1H NOESY, and proton-detected $^1H-^{13}C$ correlations (HMQC) using nonspinning samples. 2D NMR spectra were recorded with pulse sequences suitable for phase-sensitive representations using TPPI. ^1H NOESY measurements[11] were recorded with 1024 increments of size 2 K (with 8

(8) De Souza, R. F.; Casagrande, O. L., Jr. *Macromol. Rapid Commun.* **2001**, *22*, 1293.

(9) (a) Wang, L.; Sun, W.-H.; Han, L.; Yang, H.; Hu, Y.; Jin, X. *J. Organomet. Chem.* **2002**, *658*, 62. (b) Champouret, Y. D. M.; Maréchal J.-D.; Dadhiwala, I.; Fawcett, J.; Palmer, D.; Singh, K.; Solan G. A. *Dalton Trans.* **2006**, 2350. (c) Zhang, S.; Vystorop, I.; Tang, Z.; Sun, W.-H. *Organometallics* **2007**, *6* 2456.

(10) Barbaro P.; Bianchini, C.; Giambastiani, G.; Guerrero Rios, I.; Meli, A.; Oberhauser, W.; Segarra, A. M.; Sorace, L.; Toti, A. *Organometallics*, in press.

scans each) covering the full range in both dimensions and with mixing times of 800 and 300 ms. $^1H-^{13}C$ HMQC correlations[12] were recorded by use of the standard sequence with decoupling during acquisition. Vis−NIR spectra (range 25 000−4550 cm^{-1}) in both solid-state (reflectance) and CH_2Cl_2 solution (absorption) were recorded on a Perkin-Elmer Lamda 9 spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer Spectrum BX FT-IR spectrophotometer using samples mulled in Nujol between KBr plates. Magnetic moments were measured at 22 °C with a Cryogenic SQUID S600 magnetometer at three different applied magnetic fields (0.5, 1, and 2 T). Raw data were corrected for the diamagnetism of the sample holder, measured in the same conditions, and for the intrinsic diamagnetism of the sample, estimated through Pascal's constants. X-band EPR spectra of both powder and frozen solution (CH_2Cl_2) samples were recorded on a Bruker Elexsys E500 spectrometer equipped with a ^4He continuous flow cryostat for operation at cryogenic temperature (4−20 K). Elemental analyses were performed using a Carlo Erba model 1106 elemental analyzer with an accepted tolerance of ±0.4 unit on carbon (C), hydrogen (H), and nitrogen (N). Melting points were recorded on a Stuart Scientific SMP3 apparatus. Conductivity measurement was obtained with an ORION model 990101 conductance cell connected to a model 101 conductivity meter. The conductivity data[13] were obtained at sample concentrations of ca. 10^{-3} M in 1,2-dicholoethane solution. GC analyses of the reaction products were performed on a Shimadzu GC-17 gas chromatograph equipped with a flame ionization detector and a Supelco SPB-1 fused silica capillary column (30 m length, 0.25 mm i.d., 0.25 μm film thickness) for the C6−C20 fraction or a HP-PLOT Al_2O_3 KCl column (50 m length, 0.53 mm i.d., 15 μm film thickness) for the C4−C6 fraction. The GC/MS analyses were performed on a Shimadzu QP2010S apparatus equipped with a column identical with that used for GC analysis.

Synthesis of 1-(6-Bromopyridin-2-yl)ethanone.[14] To a stirred solution of 2,6-dibromopyridine (7.11 g, 30.0 mmol) in Et_2O (130 mL) at −78 °C was added dropwise a 1.7 M solution of ^{t}BuLi (18.8 mL, 30.0 mmol) in *n*-pentane over 10 min. After 30 min stirring at −78 °C, *N*,*N*-dimethylacetamide (3.1 mL, 33.0 mmol) was added and stirring maintained for 1.5 h. The resulting mixture was allowed to warm to room temperature and treated with water (30 mL). The formed layers were separated, and the organic phase was washed with water (2 × 30 mL). The aqueous layer was extracted with Et_2O (3 × 30 mL). The combined organic layers were dried over Na_2SO_4. Removal of the solvent under reduced pressure gave a yellow oil that was dissolved in petroleum ether and cooled to −20 °C. After 6 h, small pale yellow crystals were separated by filtration (yield 90%). Mp: 44 °C. IR (KBr): ν 1695 cm^{-1} (C═O). ^1H NMR ($CDCl_3$): δ 2.70 (s, 3H, C(O)Me), 7.68 (m, 2H, CH), 7.98 (dd, J = 6.5, 2.1, 1H, CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 26.4 (1C, C(O)*Me*), 121.1 (1C, CH), 132.4 (1C, CH), 139.8 (1C, CH), 142.0 (1C, C), 154.9 (1C, C), 198.5 (1C, *C*(O)Me). Anal. Calcd (%) for C_7H_6BrNO (200.03): C, 42.03; H, 3.02; N, 7.00. Found: C, 42.09; H, 2.90; N, 7.02.

Synthesis of 6-Bromo-2-(2′-methyl-1′,3′-dioxolan-2′-yl)pyridine (I).[15] A solution of 1-(6-bromopyridin-2-yl)ethanone (1.0 g, 5 mmol), 1,2-ethanediol (0.34 mL, 6 mmol), and *p*-toluenesulfonic acid monohydrate (PTSA, 0.1 g, 0.5 mmol) in 15 mL of distilled benzene was heated for 24 h under reflux in a Dean-Stark apparatus. The mixture was cooled to room temperature and then treated with 5 mL of a 0.5 M aqueous NaOH solution. The formed layers were separated. The aqueous phase was washed with Et_2O (2 × 5 mL), and the combined organic extracts were dried over $NaSO_4$. After removal of the solvent under reduced pressure a white solid was obtained in pure form (yield >99%). Mp: 40−42 °C. ^1H NMR ($CDCl_3$): δ 1.80 (s, 3H, Me), 3.95−4.20 (m, 4H, CH_2), 7.49 (dd, J = 7.7, 1.3, 1H, CH Ar), 7.58−7.65 (2H, m, CH Ar). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 25.6 (1C, Me); 65.6 (2C, CH_2); 108.5 (1C, C Ar); 118.9 (1C, CH Ar); 128.1 (1C, CH Ar); 139.6 (1C, CH Ar); 142.5 (1C, CH Ar); 163.0 (1C, CH Ar). Anal. Calcd (%) for $C_9H_{10}BrNO_2$ (244.09): C, 44.29; H, 4.13; N, 5.74. Found: C, 44.09; H, 4.22; N, 5.69.

Synthesis of 2-Cyano-5-bromopyridine. To a solution of 2,5-dibromopyridine (5.0 g, 21.1 mmol) in DMF (40 mL) were added in sequence CuCN (1.5 g, 16.75 mmol) and NaCN (0.85 g, 17.34 mmol). The reaction mixture was stirred at reflux temperature for 4 h. After cooling to room temperature, water was added and the reaction mixture was extracted three times with AcOEt (3 × 20 mL). The collected organic layers were dried over Na_2SO_4, filtered, and evaporated under reduced pressure to give a pale yellow semisolid material. Chromatographic purification over silica (AcOEt/*n*-pentane, 5:95) gave a white solid in 82% yield. ^1H NMR ($CDCl_3$): δ 7.59 (d, J = 10.5 Hz, 1H), 8.00 (dd, J = 10.5, 2.7 Hz, 1H), 8.79 (s, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 116.9 (1C, C≡N), 125.4 (1C, CH), 129.6 (1C, CH), 132.4 (1C, CH), 140.1 (1C, CH), 152.9 (1C, CH). Anal. Calcd (%) for $C_6H_3BrN_2$ (183.01): C, 39.38; H, 1.65; N, 15.31. Found: C, 39.09; H, 1.5; N, 15.52.

Synthesis of 5-Bromo-2-[(trimethylsilyl)ethynyl]pyridine. A solution of 2,5-dibromopyridine (5.0 g, 21.1 mmol) and trimethylsilylacetylene (2.21 g, 22.5 mmol) in NEt_3/MeCN (1:1, 40 mL) at room temperature was treated with dichlorobis(triphenylphosphine)palladium(II) ($PdCl_2(PPh_3)_2$, 298 mg, 0.425 mmol) and CuI (81 mg, 0.425 mmol). After 1 h stirring the slurry solution formed was concentrated. The salts formed were filtered off, and the solution was evaporated under reduced pressure. The dark orange oil obtained was purified by a chromatographic filtration over a silica gel pad using *n*-hexane/AcOEt (97:3) as eluent, providing a yellow oil. The oil was then dissolved in CH_2Cl_2 and treated with activated carbon. Filtration over a Celite pad and evaporation of the solvent afforded a colorless oil, which solidifies upon standing at room temperature (96%). ^1H NMR ($CDCl_3$): δ 0.26 (s, 9H), 7.48 (d, J = 8.5 Hz, 1H), 7.77 (dd, J = 8.4, 2.1 Hz, 1H), 8.62 (d, J = 2.1 Hz, 1H). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ −0.1, 96.1, 103.5, 120.7, 129.0, 139.8, 140.7, 151.2.

Synthesis of 1-(5-Bromo-2-pyridinyl)ethanone. A solution of 5-bromo-2-[(trimethylsilyl)ethynyl]pyridine (9.8 g, 38.5 mmol) in acetone/H_2O (8:1, 150 mL) at room temperature was treated with $Hg(OAc)_2$ (12.9 g, 40.4 mmol). After 15 min stirring, the reaction was treated with H_2SO_4 (3 M, 38.8 mL) and heated to reflux for 1 h. The mixture was cooled in an ice bath, neutralized with 2 M NaOH, and extracted with AcOEt. The combined organic layers were dried (Na_2SO_4) and evaporated to dryness. The residue was purified by silica gel chromatography (*n*-hexane/AcOEt, 97:3) to provide the product as a white crystalline solid (yield 75%). IR (KBr): ν 1697 cm^{-1} (C═O). ^1H NMR ($CDCl_3$): δ 2.69 (s, 3H, Me), 7.92 (d, J = 7.5 Hz, 1H, Py-H_m), 7.98 (dd, J = 7.2, 2.1 Hz, 1H, Py-H_p), 8.73 (d, J = 1.2, 1H, Py-H_o). ^{13}C NMR ($CDCl_3$): δ 26.1 (1C, C(O)*Me*), 123.2 (1C, CH), 125.6 (1C, C), 139.9 (1C, CH), 150.5 (1C, CH), 152.1 (1C, C), 199.5 (1C, *C*(O)Me). Anal. Calcd (%) for C_7H_6BrNO (200.03): C, 42.03; H, 3.02; N, 7.00. Found: C, 42.09; H, 2.90; N, 7.02.

Synthesis of 5-Bromo-2-(2-methyl-1,3-dioxolan-2-yl)pyridine (II). To a solution of 1-(5-bromo-2-pyridinyl)ethanone (7.3 g, 36.6 mmol) and ethylene glycol (43.9 mmol) in 80 mL of distilled benzene was added a catalytic amount of PTSA. The solution was warmed to reflux temperature using a Dean-Stark apparatus. After 36 h the reaction was cooled to room temperature and 50 mL of

(11) (a) Sklener, V.; Miyashiro, H.; Zon, G.; Miles, H. T.; Bax, A. *FEBS Lett.* **1986**, *208*, 94. (b) Jeener, J.; Meier, B. H.; Bachmann, P.; Ernst, R. R. *J. Chem. Phys.* **1979**, *71*, 4546.

(12) Bax, A. A.; Griffey, R. H.; Hawkins, B. L. *J. Magn. Reson.* **1983**, *55*, 301.

(13) Geary, W. J. *J. Coord. Chem. Rev.* **1971**, *7*, 81. (b) Morassi, R.; Sacconi, L. *J. Chem. Soc. A* **1971**, 492.

(14) Bolm, C.; Ewald, M.; Schilingloff, G. *Chem. Ber.* **1992**, *125*, 1169.

(15) Constable, E. C.; Heirtzler, F.; Neuburger, N.; Zehnder, M. *J. Am. Chem. Soc.* **1997**, *119*, 5606.

H_2O was added slowly. The phases were separated, and the aqueous layer was extracted with 2 × 50 mL of Et_2O. The combined organic layers were dried over Na_2SO_4. The solvent was removed under reduced pressure, and the white solid obtained was used without further purification (yield 98%). ^{1}H NMR (CD_2Cl_2): δ 1.70 (s, 3H, Me), 3.88 (m, 2H, CH_2), 4.08 (m, 2H, CH_2), 7.49 (d, J = 8.3 Hz, 1H, Py-H$_m$), 7.86 (dd, J = 8.3, 2.4 Hz, 1H, Py-H$_p$), 8.68 (d, J = 2.1 Hz, 1H, Py-H$_o$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 35.03 (1C, Me), 75.36 (2C, CH_2), 118.63 (1C, C), 130.24 (1C, C), 131.37 (1C, CH), 149.28 (1C, CH), 160.60 (1C, CH), 170.05 (1C, C).

Synthesis of 6-(2-Methyl[1,3]dioxolan-2-yl)nicotinic Acid Propyl Ester (III). The reaction was carried out in a 200 mL stainless steel reactor provided by magnetic stirring and a pressure controller. The reactor was charged with a solution of **II** (2 g, 8.19 mmol) and $Pd(PPh_3)_2Cl_2$ (0.4 g, 0.57 mmol) in 40 mL of a mixture of EtOH/NEt_3 (7:3). It was stirred and warmed to 80 °C for 24 h under a CO atmosphere (4 bar). The reactor was cooled to room temperature and depressurized. The solution was concentrated under reduced pressure, the resulting suspension was dissolved with CH_2Cl_2, and water was added. The phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were dried over Na_2SO_4, and the removal of solvent under reduced pressure gave a crude orange oil, which was purified by silica gel chromatography using *n*-hexane/AcOEt (8:2, v/v) and 5% NEt_3 as eluent, to provide a yellow oil (yield 96%). IR (KBr): ν 1695 cm^{-1} (C═O). ^{1}H NMR (CD_2Cl_2): δ 1.42 (t, J = 7.15 Hz, 3H, C(O)OCH$_2$*Me*), 1.73 (s, 3H, Me), 3.89 (m, 2H, C*H*$_2$), 4.10 (m, 2H, C*H*$_2$), 4.42 (q, J = 7.15 Hz, 2H, C(O)OC*H*$_2$Me), 7.66 (dd, J = 8.16, 0.74 Hz, 1H, Py-H$_m$), 8.31 (dd, J = 8.16, 2.11 Hz, 1H, Py-H$_p$), 9.19 (pseudo-t, J = 2.11, 0.74 Hz, 1H, Py-H$_o$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 14.01 (1C, C(O)OCH$_2$*Me*), 24.67 (1C, Me), 61.32 (C(O)OCH$_2$Me), 65.01 (1C, CH_2), 65.06 (1C, CH_2), 108.43 (1C, *C*), 119.00 (1C, CH), 125.60 (1C, C), 137.45 (1C, CH), 150.37 (1C, CH), 164.93 (1C, C), 165.05 (1C, *C*(O)OCH$_2$Me). Anal. Calcd (%) for $C_{12}H_{15}NO_4$ (237.26): C, 60.75; H, 6.37; N, 5.90. Found: C, 60.80; H, 6.35; N, 5.94.

Synthesis of [6-(2-Methyl[1,3]dioxolan-2-yl)pyridin-2-yl][6-(2-methyl[1,3]dioxolan-2-yl)pyridin-3-yl]methanone (IV). A solution of **I** (2 g, 8.0 mmol) in 60 mL of THF was cooled to −78 °C and treated dropwise with a 1.7 M solution of ^{t}BuLi in *n*-pentane (5.22 mL, 8.9 mmol). After 30 min a solution of **III** (2.1 g, 8.9 mmol) in 10 mL of THF was added slowly at −78 °C by cannula. After 1 h stirring, the mixture was allowed to warm to room temperature. After standing overnight, 25 mL of H_2O was added portionwise. The phases were separated, and the aqueous layer was extracted with 2 × 30 mL of Et_2O. The combined organic layers were dried over Na_2SO_4. The solvent was removed under reduced pressure, and the yellow oil obtained was purified by silica gel chromatography (*n*-hexane/AcOEt, 65:35 and 3% NEt_3) to provide a pure pale yellow oil (yield 83%). Mp: 94−96 °C. IR (KBr): ν 1675 cm^{-1} (C═O). ^{1}H NMR (CD_2Cl_2): δ 1.77 (s, 3H, Me), 1.78 (s, 3H, Me), 3.94 (m, 4H, CH_2), 4.12 (m, 4H, CH_2), 7.72 (dd, J = 8.21, 0.55 Hz, 1H, Py-H$_m$), 7.84 (dd, J = 7.81, 1.11 Hz, 1H, Py-H$_m$), 7.98 (pseudo-t, J = 7.81, 7.71 Hz, 1H, Py-H$_p$), 8.09 (dd, J = 7.72, 1.12 Hz, 1H, Py-H$_m$), 8.53 (dd, J = 8.28, 1.95 Hz, 1H, Py-H$_p$), 9.39 (dd, J = 1.85, 0.59 Hz, 1H, Py-H$_o$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 34.93 (1C, Me), 35.11 (1C, Me), 75.44 (1C, CH_2), 75.52 (1C, CH_2), 118.75 (1C, CH), 118.84 (1C, CH), 129.09 (1C, CH), 132.96 (1C, CH), 133.86 (1C, CH), 141.53 (1C, C), 148.23 (1C, CH), 149.36 (1C, CH), 162.35 (1C, CH), 163.93 (1C, C), 170.68 (1C, C), 174.73 (1C, C), 201.67 (1C, C═O). Anal. Calcd (%) for $C_{19}H_{20}N_2O_5$ (356.38): C, 64.04; H, 5.66; N, 7.86. Found: C, 63.59; H, 5.74; N, 7.80.

Synthesis of 1-[5-(6-Acetylpyridine-2-carbonyl)pyridin-2-yl]-ethanone (V). A sample of **IV** (1.50 g, 4.21 mmol) was suspended in 2 M HCl (15 mL) and stirred at 80−85 °C for 2 h. The resulting mixture was then cooled in an ice bath, diluted with ice water (15 mL), and neutralized portionwise with solid $NaHCO_3$. A standard extractive workup with AcOEt (3 × 50 mL) gave after removal of solvent a crude, slightly brown solid, which was purified by filtration over a silica gel pad (AcOEt/petroleum ether, 95:5) to afford the expected compound as pure yellow crystals (yield 94%). Mp: 98−99 °C. IR (KBr): ν 1701 cm^{-1} (C═O), ν 1664 cm^{-1} (C═O). ^{1}H NMR ($CDCl_3$): δ 2.68 (s, 3H, Me), 2.78 (s, 3H, Me), 8.12 (pseudo-t, J = 7.57, 7.81, 1H, Py-H$_p$), 8.17 (d, J = 8.09, 1H, Py-H$_m$), 8.29 (d, J = 7.82, 1H, Py-H$_m$), 8.40 (d, J = 7.57, 1H, Py-H$_m$), 8.59 (dd, J = 8.06, 1.95, 1H, Py-H$_p$), 9.43 (d, J = 1.95, 1H, Py-H$_o$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 25.79 (1C, C(O)*Me*), 26.05 (1C, C(O)*Me*), 120.79 (1C, CH), 124.89 (1C, CH), 127.78 (1C, CH), 134.21 (1C, C), 138.62 (1C, CH), 139.13 (1C, CH), 151.27 (1C, CH), 152.32 (1C, C), 152.52 (1C, C), 155.16 (1C, C), 190.62 (1C, C═O), 198.81 (1C, *C*(O)Me), 199.53 (1C, *C*(O)Me). Anal. Calcd (%) for $C_{15}H_{12}N_2O_3$ (268.27): C, 67.16; H, 4.51; N, 10.44. Found: C, 67.10; H, 4.60; N, 10.39.

Synthesis of {6-[1-(2,6-Diisopropylphenylimino)ethyl]pyridin-2-yl}{6-[1-(2,6-diisopropylphenylimino)ethyl]pyridin-3-yl}-methanone (VI). A solution of **V** (1.0 g, 3.7 mmol), 2,6-bis(isopropylphenyl)amine (2.8 mL, 14.9 mmol, 4 equiv), and a few drops of formic acid in MeOH (30 mL) were refluxed for 28 h. The reaction mixture was cooled to room temperature under stirring overnight to give a solid, which was filtered and washed several times with cold MeOH. Recrystallization from boiling MeOH gave a yellow solid in 82% yield. IR (KBr): ν 1669 cm^{-1} (C═O), ν 1639 cm^{-1} (C═N). ^{1}H NMR (CD_2Cl_2): δ 1.20−1.15 (m, 24H, CH*Me*$_2$), 2.24 (s, 3H, C(N-Ar)Me), 2.26 (s, 3H, C(N-Ar)Me), 2.79−2.74 (m, 4H, C*H*Me$_2$), 7.14−7.12 (m, 2H, CH-Ar), 7.21−7.19 (m, 4H, CH−Ar), 8.14 (pseudo-t, J = 7.84, 7.80 Hz, 1H, Py-H$_p$), 8.34 (dd, 1H, J = 7.80, 1.09 Hz, Py-H$_m$), 8.51 (d, J = 8.32 Hz, 1H, Py-H$_m$), 8.67 (dd, 1H, J = 8.32, 1.98 Hz, Py-H$_p$), 8.68 (dd, 1H, J = 7.84, 1.09 Hz, Py-H$_m$), 9.51 (d, J = 1.98 Hz, 1H, Py-H$_o$). ^{13}C NMR (CD_2Cl_2): δ 17.03 (1C, Me), 17.15 (1C, Me), 22.51 (2C, Me), 22.95 (2C, Me), 22.97 (1C, Me), 28.25 (2C, CH), 28.30 (2C, CH), 120.33 (1C, CH), 122.98 (1C, CH), 122.99 (1C, CH), 123.75 (1C, CH), 123.76 (1C, CH), 124.43 (1C, CH), 125.59 (1C, CH), 132.73 (1C, C), 135.59 (1C, CH), 135.63 (1C, CH), 135.64 (1C, CH), 137.89 (1C, CH), 138.63 (1C, CH), 146.20 (1C, C), 146.31 (1C, C), 151.20 (1C, CH), 152.91 (1C, C), 155.34 (1C, C), 158.67 (1C, C), 166.28 (1C, C═N), 166.88 (1C, C═N), 191.37 (1C, C═O). Anal. Calcd (%) for $C_{39}H_{46}N_4O$ (586.82): C, 79.82; H, 7.90; N, 9.55. Found: C, 79.79; H, 7.94; N, 9.50.

Synthesis of (1-{6-[Cyclohexylimino(6-(2,6-diisopropylphenylimino)ethylpyridin-3-yl)methyl]pyridin-2-yl}ethylidene)(2,6-diisopropylphenyl)amine (^{CyAr2}N$_5$). A mixture of **VI** (0.5 g, 0.86 mmol) and cyclohexylamine (86.4 mmol, 1 mL) was heated at 100 °C without stirring for 24 h. The excess of cyclohexylamine was removed under reduced pressure. The solid formed was dissolved in CH_2Cl_2, cooled to 0 °C and cold MeOH was added to induce crystallization. After 5 h at −20 °C, pale yellow crystals separated, which were filtered and washed with cold MeOH (yield 75%). IR (KBr): ν 1646 cm^{-1} (C═N). ^{1}H NMR (CD_2Cl_2): δ 1.17−1.11 (m, 24H, CH*Me*$_2$), 1.39−1.26 (m, 3H, Cy), 1.76−1.65 (m, 5H, Cy), 1.86−1.81 (m, 2H, Cy), 1.88 (s, 3H, C(N)Me), 2.22 (s, 3H, C(N)Me), 2.80−2.66 (m, 4H, C*H*Me$_2$), 3.50−3.55 (m, 1H, CH Cy), 7.19−7.08 (m, 6H, CH Ar), 7.79 (d, J = 8.00 Hz, 1H, Py-H$_m$), 7.95 (t, J = 7.80 Hz, 1H, Py-H$_p$), 8.37 (d, J = 7.80 Hz, 1H, Py-H$_m$), 8.39 (d, J = 7.80 Hz, 1H, Py-H$_m$), 8.45 (d, J = 8.00 Hz, 1H, Py-H$_p$), 8.60 (s, 1H, Py-H$_o$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 166.87, 166.85, 162.43, 156.20, 155.57, 154.77, 153.56, 148.67, 147.58, 146.45, 146.41, 136.98, 136.83, 136.71, 135.74, 135.72, 135.66, 135.44, 133.44, 124.34, 123.65, 123.53, 123.44, 122.98, 122.95, 122.87, 122.50, 121.21, 120.83, 120.52, 120.03, 61.90, 33.93, 28.23, 25.65, 24.16, 23.04, 22.90, 22.55, 22.50, 22.46, 17.04, 17.00, 16.48. Anal. Calcd (%) for $C_{45}H_{57}N_5$ (667.98): C, 80.91; H, 8.60; N, 10.48. Found: C, 80.88; H, 8.57; N, 10.53.

Synthesis of Methyl 4-(1-Phenylprop-1-en-2-yl)benzoate (X).[15] A suspension of benzyltriphenylphosphonium chloride (2.43 g, 5.61 mmol) in THF (30 mL) at −5 °C was treated under stirring with ^{n}BuLi (1.6 M in hexane, 3.7 mL, 5.92 mmol). When the ylide was formed, an intense red color appeared. The ylide was transferred via cannula under N_2 atmosphere to a separate vessel containing a cooled solution (0 °C) of methyl-4-acetylbenzoate (1 g, 5.61 mmol) in 20 mL of dry and degassed THF. After 30 min stirring, the mixture was warmed to 50 °C and stirred overnight. Afterward, it was cooled to room temperature and treated with water (40 mL). The resulting phases were separated, and the acqueous layer was extracted with Et_2O (3 × 30 mL). The collected organic phases were dried over Na_2SO_4, and after removal of solvent, a yellow crude solid was obtained. The crude material was purified by flash chromatography (silica, hexane/EtOAc (95:5)) to afford a white solid as a mixture of two inseparable diastereoisomers in 45(*E*):55(*Z*) ratio (yield 55%). IR (KBr): ν 1718 cm^{-1} (C═O); 1601 cm^{-1} (C═C). ^{1}H NMR (CD_2Cl_2): δ 2.24 (d, 3 H(*E*), J = 1.5 Hz, Me), 2.33 (d, 3 H(*Z*), J = 1.3 Hz, Me), 3.91 (s, 3 H(*E*), Me), 3.93 (s, 3 H(*Z*), Me), 6.59 (d, 1 H(*E*), J = 1.5 Hz, CH), 6.98 (d, 1 H(*Z*), J = 1.3 Hz, CH), 6.95 (2 H, Ar), 7.12 (2 H, Ar), 7.29 (2 H, Ar), 7.42 (5 H, Ar), 7.64 (3 H, Ar), 7.95 (2 H, Ar), 8.04 (2 H, Ar). ^{13}C{^{1}H} NMR (CD_2Cl_2): (selected data) δ 166.71, 148.37, 147.16, 137.87, 137.24, 136.46, 129.59, 129.50, 129.34, 129.17, 128.94, 128.80, 128.72, 128.37, 128.21, 127.90, 127.57, 126.83, 126.36, 125.88, 51.92, 26.37, 17.07. Anal. Calcd (%) for $C_{17}H_{16}O_2$ (252.31): C, 80.93; H, 6.39. Found: C, 81.03; H, 6.41.

Synthesis of (6-(2-Methyl-1,3-dioxolan-2-yl)pyridin-2-yl)(4-(1-phenylprop-1-en-2-yl)phenyl)methanone (XI). A solution of 6-bromo-2-(2′-methyl-1′,3′-dioxolan-2′-yl)pyridine (0.87 g, 3.6 mmol) in 25 mL of THF at −78 °C was treated dropwise with 2.34 mL of a 1.7 M solution of ^{t}BuLi in *n*-pentane. After 30 min stirring, the mixture was warmed to −55 °C and a solution of **X** (1 g, 4 mmol) in 15 mL of THF was added via cannula portionwise. After 30 min stirring, the resulting solution was allowed to warm to room temperature and then stirred for a further 2 h. Water (50 mL) was added, the phases were separated, and the acqueous layer was extracted with Et_2O (3 × 50 mL). The collected organic phases were dried over Na_2SO_4, and after removal of solvent a yellow crude oil was obtained. The product was purified by flash chromatography (silica, hexane/EtOAc (4:1, v/v) + 3% (v/v) NEt_3) to afford a mixture of inseparable diastereoisomers (45(*E*):55(*Z*) ratio) as a yellow oil (yield 51%). IR (CH_2Cl_2): ν 1661 cm^{-1} (C═O); 1601 cm^{-1} (C═C). ^{1}H NMR (CD_2Cl_2): δ 1.74 (s, 3 H(*E*), Me), 1.79 (s, 3 H(*Z*), Me), 2.29 (s, 3 H(*E*), Me), 2.37 (s, 3 H(*Z*), Me), 4.02 (m, 8 H, CH_2), 6.63 (s, 1 H(*E*), CH), 7.03 (2 H, Ar), 7.04 (bs, 1 H(*Z*), CH), 7.14 (3 H, Ar), 7.34 (2 H, Ar), 7.44 (5 H, Ar), 7.70 (2 H, Ar), 7.78 (2 H, Ar), 7.96 (4 H, Ar), 8.06 (2 H, Ar), 8.18 (2H, Ar). ^{13}C{^{1}H} NMR (CD_2Cl_2): (selected data) δ 24.54 (1 C, C(C)-*Me*), 26.35 (1 C, Me), 65.14 (4 C, CH_2), 108.43, 121.92, 123.51, 123.54, 126.38, 127.95, 128.21, 129.00, 131.33, 134.76, 137.04, 137.64, 137.90, 147.05, 154.65, 159.94, 192.66 (1 C, C═O). Anal. Calcd (%) for $C_{25}H_{23}NO_3$ (385.46): C, 77.90; H, 6.01; N, 3.63. Found: C, 77.92; H, 5.98, N, 3.50.

Synthesis of 1-(6-(4-(1-Phenylprop-1-en-2-yl)benzoyl)pyridin-2-yl)ethanone (XII). A solution of **XI** (0.4 g, 1 mmol) in acetone/water (15:1, v/v; 16 mL) was treated with PTSA (0.04 g, 0.21 mmol) and refluxed for 40 h. The solution was cooled to room temperature and neutralized with a saturated solution of K_2CO_3. Then 10 mL of water was added and the phases were sepparated. The aqueous phase was extracted with Et_2O (2 × 15 mL), and the collected organic layers were dried over Na_2SO_4. After solvent removal the resulting yellow, crude oil was isolated and purified over a silica gel pad (hexane/EtOAc, 85:15) to give a mixture of inseparable diastereoisomers (45(*E*):55(*Z*) ratio) as a pale yellow oil (yield 95%). IR (CH_2Cl_2): ν 1701, 1661 cm^{-1} (C═O); 1601 cm^{-1} (C═C). ^{1}H NMR (CD_2Cl_2): δ 2.30 (d, 3 H(*E*), J = 1.3 Hz, Me), 2.38 (d, 3 H(*Z*), J = 1.0 Hz, Me), 2.67 (s, 3 H(*E*), Me), 2.74 (s, 3 H(*Z*), Me), 6.65 (bs, 1 H(*E*), CH), 7.03 (2 H, Ar), 7.07 (bs, 1 H(*Z*), CH), 7.14 (3 H, Ar), 7.38 (2 H, Ar), 7.44 (5 H, Ar), 7.74 (3 H, Ar), 8.11 (4 H, Ar), 8.26 (5 H, Ar). ^{13}C{^{1}H} NMR ($CDCl_3$): (selected data) δ 17.05, 25.54, 25.59. 26.23, 123.62, 125.57, 126.43, 126.91, 127.60, 127.87, 127.93, 128.09, 128.25, 129.01, 129.21, 129.68, 131.28, 131.34, 138.26, 134.47, 134.51, 136.44, 137.32, 137.81, 137.85, 147.25, 148.48, 152.06, 152.11, 154.19, 154.35, 191.76 (1 C, C═O), 192.04 (1 C, C═O), 199.19 (1 C, C═O), 199.23 (1 C, C═O). Anal. Calcd (%) for $C_{23}H_{19}NO_2$ (341.4): C, 80.92; H, 5.61; N, 4.10. Found: C, 80.93; H, 5.60; N, 4.12.

Synthesis of (6-(1-(2,6-Diisopropylphenylimino)ethyl)pyridin-2-yl)(4-((*Z*)-1-phenylprop-1-en-2-yl)phenyl)methanone (XIII). A solution of **XII** (0.2 g, 0.6 mmol) and 2,6-diisopropylaniline (0.22 mL, 1.2 mmol) in dry ^{n}BuOH (1.5 mL) was treated with a catalytic amount of formic acid and warmed to 65 °C overnight. The excess of solvent and aniline were removed under reduced pressure, gently warming the mixture. The remaining oil was dissolved in hot MeOH and precipitated with *n*-pentane. The precipitate was filtered and recrystallized from MeOH to afford yellow pale microcrystals of the *Z*-isomer (yield 34%). IR (CH_2Cl_2): ν 1659 cm^{-1} (C═O); 1647 cm^{-1} (C═N); 1601 cm^{-1} (C═C). ^{1}H NMR (CD_2Cl_2): δ 1.17 (d, 6 H, J = 6.9 Hz, CH*Me*$_2$), 1.19 (d, 6 H, J = 6.9 Hz, CH*Me*$_2$), 2.22 (s, 3 H, Me), 2.36 (d, 3 H, J = 1.3 Hz, Me), 2.78 (sept, 2 H, J = 6.9 Hz, C*H*Me$_2$), 7.04 (d, 1 H, J = 1.3 Hz, CH), 7.12 (1 H, Ar), 7.20 (2 H, Ar), 7.43 (5 H, Ar), 7.71 (2 H, Ar), 8.09 (t, 1 H, J = 7.8 Hz, Py-H$_p$), 8.20 (dd, 1 H, J = 7.8, 1.1 Hz, Py-H$_m$), 8.28 (2 H, Ar), 8.61 (dd, 1 H, J = 7.8, 1.1 Hz, Py-H$_m$). ^{13}C{^{1}H} NMR ($CDCl_3$): (selected data) δ 16.96 (1 C, Me); 17.01 (1 C, Me), 22.51 (1 C, Me), 22.96 (1 C, Me), 28.27 (1 C, Me), 122.97 (CH Ar), 123.57 (CH Ar), 123.67 (CH Ar), 125.47 (CH Ar), 125.53 (CH Ar), 126.84 (CH Ar), 127.98 (CH Ar), 128.20 (CH Ar), 128.95 (CH Ar), 129.16 (CH Ar), 129.53 (CH Ar), 131.33 (CH Ar), 134.88 (C), 135.68 (CH Ar), 136.50 (C), 137.56 (CH Ar), 137.88 (C), 146.31 (C), 148.28 (C), 154.09 (C), 155.07 (C), 166. 60 (CN), 192.19 (*C*O). Anal. Calcd (%) for $C_{35}H_{36}N_2O$ (500.67): C, 83.96; H, 7.25; N, 5.60. Found: C, 83.94; H, 7.23; N, 5.63.

Synthesis of (*E*)-*N*-(1-(6-((*E*)-(cyclohexylimino)(4-((*E*)-1-phenylprop-1-en-2-yl)phenyl)methyl)pyridin-2-yl)ethylidene)-2,6-diisopropylbenzenamine ($^{CyAr}N_3^H$). A mixture of **XIII** (0.12 g, 0.24 mmol) and cyclohexylamine (0.28 mL, 2.41 mmol) was heated at 100 °C for 40 h without stirring. The excess of cyclohexylamine was removed under reduced pressure, and the remaining oil was crystallized from *n*-pentane/MeOH (40:60, v/v) to afford the ligand as pale yellow crystals (yield 30%). IR (CH_2Cl_2): ν 1647 cm^{-1} (C═N); 1601 cm^{-1} (C═C). ^{1}H NMR (CD_2Cl_2): δ 1.11 (d, 12 H, J = 6.6 Hz, CH*Me*$_2$), 1.29 (m, 3 H, Cy), 1.66 (m, 5 H, Cy), 1.80 (m, 2 H, Cy), 2.15 (s, 3 H, CH(C)*Me*), 2.33 (s, 3 H, C(N)Me), 2.70 (sept, 2 H, J = 6.6 Hz, C*H*Me$_2$), 3.51 (m, 1 H, Cy), 6.97 (s, 1 H, C*H*(C)Me), 7.07 (1 H, Ar), 7.14 (2 H, Ar), 7.30 (2 H, Ar), 7,41 (5 H, Ar), 7.64 (2 H, Ar), 7.90 (t, 1 H, J = 7.8 Hz, Py-H$_p$), 8.29 (d, 1 H, J = 7.8 Hz, Py-H$_m$), 8.35 (d, 1 H, J = 7.8 Hz, Py-H$_m$). ^{13}C{^{1}H} NMR (CD_2Cl_2): (selected data) δ 16.48, 17.07, 22.56, 22.90, 23.06, 24.31, 25.74, 28.19, 33.97, 61.66, 120.03, 120.55, 122.98, 123.35, 123.61, 125.34, 126.82, 128.14, 128.32, 129.13, 135.66, 135.79, 136.68. Anal. Calcd (%) for $C_{41}H_{47}N_3$ (581.83): C, 84.64; H, 8.14; N, 7.22. Found: C, 84.62; H, 8.15; N, 7.23.

Synthesis of $^{CyAr2}N_5FeCl_2$. A suspension of $FeCl_2$ (0.21 mmol) in THF (3 mL) was transferred by a cannula into a stirred solution of $^{CyAr2}N_5$ (0.23 mmol) in THF (5 mL) at room temperature. A blue solution formed immediately. After stirring the solution overnight, the solvent was partially evaporated, leading to the precipitation of the product as a blue solid, which was filtered on a sintered-glass frit, washed with *n*-pentane, and dried under a stream of nitrogen (yield 82%). IR (KBr): ν 1640 cm^{-1} (C═N), ν 1617 cm^{-1} (C═N). μ_{eff}: 5.10 μ_B (22 °C). Electronic spectra:

Table 1. Crystallographic Data

	VI·0.8CH_2Cl_2	**$^{CyAr2}N_5$**
empirical formula	$C_{39.80}H_{47.60}Cl_{1.60}N_4O$	$C_{45}H_{57}N_5$
fw	654.74	667.96
temperature [K]	180(2)	180(2)
wavelength [Å]	0.71073	0.71073
cryst syst, space group	triclinic, $P\bar{1}$	monoclinic, $C2/c$
a [Å]	11.613(5)	31.166(5)
b [Å]	12.353(5)	11.873(5)
c [Å]	14.453(5)	25.816(5)
α [deg]	74.867(5)	
β [deg]	77.213(5)	120.733(5)
γ [deg]	71.924(5)	
V [Å^3]	1880.3(13)	8211(4)
Z, D_c [g m^{-3}]	2, 1.156	8, 1.081
absorp coeff [mm^{-1}]	0.179	0.063
F(000)	699	2896
cryst size [mm]	0.30 × 0.20 × 0.20	0.30 × 0.20 × 0.20
θ range for data collection [deg]	4.22−36.25	4.36−32.12
limiting indices	$-14 \le h \le 16$	$-45 \le h \le 33$
	$-20 \le k \le 15$	$0 \le k \le 17$
	$-23 \le l \le 17$	$0 \le l \le 37$
no. of reflns collected/unique	15524/6675	8429/8429
GOF on F^2	1.066	1.211
no. of data/restraints/params	6675/0/434	8429/0/461
final R indices [I > 2σ(I)]	R1 = 0.0717, wR2 = 0.1847	R1 = 0.0948, wR2 = 0.2475
R indices (all data)	R1 = 0.1007, wR2 = 0.2022	R1 = 0.1813, wR2 = 0.3015
largest diff peak and hole [e Å^{-3}]	0.443 and −0.323	0.487 and −0.298

(reflectance) 13 900, 4900sh cm^{-1}; (absorption) 14 100 (ϵ 700), 4850 (ϵ 36) cm^{-1}. Anal. Calcd (%) for $C_{45}H_{57}Cl_2FeN_5$ (794.73): C, 68.01; H, 7.23; Fe, 7.03; N, 8.81. Found: C, 68.04; H, 7.20; Fe, 7.05; N, 8.78.

Synthesis of $^{CyAr2}N_5Fe_2Cl_4$. Employing a procedure analogous to that described above, except using $FeCl_2$ (0.46 mmol), gave the product as a blue solid in 80% yield. IR (KBr): ν 1617 cm^{-1} (C═N). μ_{eff}: 6.82 μ_B (22 °C). Electronic spectra: (reflectance) 13 900, 11 900sh, 5000sh cm^{-1}. Anal. Calcd (%) for $C_{45}H_{57}Cl_4Fe_2N_5$ (921.49): C, 58.65; H, 6.23; Fe, 12.12; N, 7.60. Found: C, 58.68; H, 6.20; Cl, 15.42; Fe, 12.10; N, 7.63.

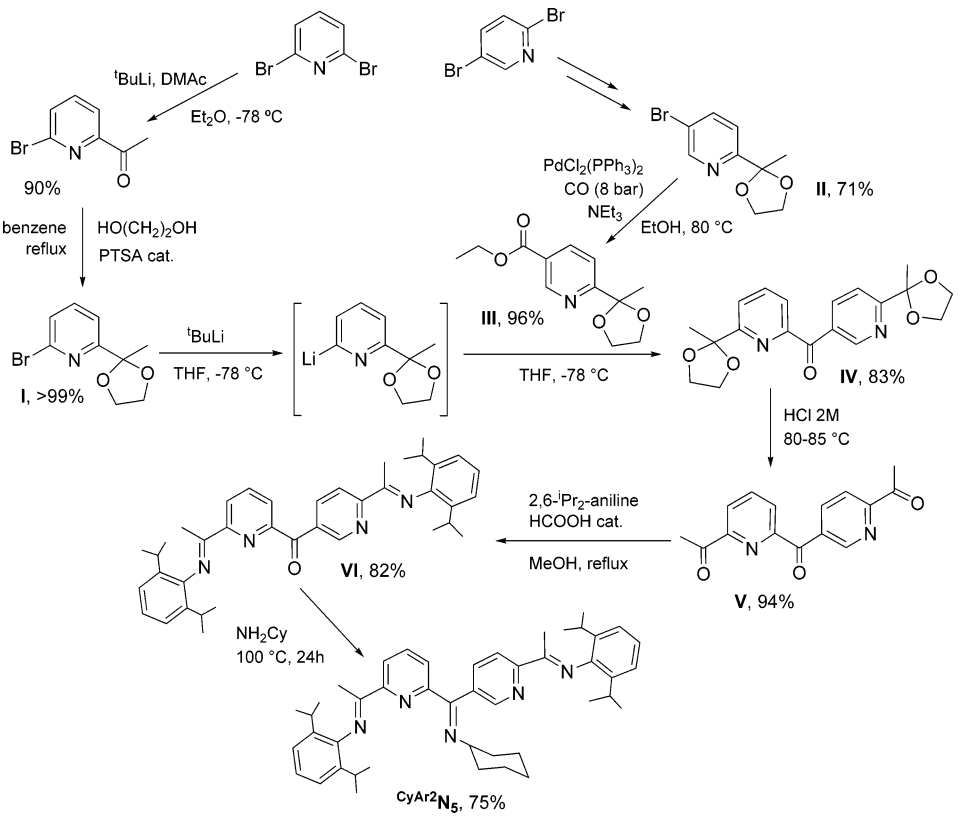
Synthesis of $^{CyAr2}N_5CoCl_2$. Addition of a suspension of $CoCl_2$ (0.21 mmol) in THF (3 mL) to a stirred solution of the ligand $^{CyAr2}N_5$ (0.23 mmol) in a 5:1 mixture of Et_2O/THF (15 mL) at room temperature gave immediately a dark brown solution. After 30 min, the precipitation of a small crop of product as a green solid occurred. The mixture was allowed to stand overnight and then was concentrated to small volume under vacuum. The product was filtered on a sintered-glass frit, washed with Et_2O, and dried under a stream of nitrogen (yield 84%). IR (KBr): ν 1637 cm^{-1} (C═N), ν 1616 cm^{-1} (C═N). μ_{eff}: 4.75 μ_B (22 °C). Electronic spectra: (reflectance) 16 600sh, 15 150, 10 300, 7700, 5050sh cm^{-1}; (absorption) 16400sh, 14 800 (ϵ 109), 10 950 (ϵ 10), 7750 (ϵ 15), 5050sh cm^{-1}. Anal. Calcd (%) for $C_{45}H_{57}Cl_2CoN_5$ (797.82): C, 67.75; H, 7.20; Co, 7.39; N, 8.78. Found: C, 67.78; H, 7.19; Co, 7.41; N, 8.81.

Synthesis of $^{CyAr2}N_5Co_2Cl_4$. Employing an analogous procedure to that described above except using $CoCl_2$ (0.46 mmol) gave the product as a brown solid in 88% yield. IR (KBr): ν 1617 cm^{-1} (C═N). μ_{eff}: 6.33 μ_B (22 °C). Electronic spectra: (reflectance) 18 000sh, 16 600sh, 15 150, 10 900, 8500sh, 7200, 5050sh cm^{-1}. Anal. Calcd (%) for $C_{45}H_{57}Cl_4Co_2N_5$ (927.66): C, 58.26; H, 6.19; Co, 12.71; N, 7.55. Found: C, 58.29; H, 6.21; Co, 12.74; N, 7.59.

Synthesis of $^{CyAr}N_3{}^{H}CoCl_2$. The solid ligand $^{CyAr}N_3{}^{H}$ (0.07 mmol) was added in one portion to a solution of $CoCl_2$ (0.07 mmol) in THF (3 mL) at room temperature. The resulting green solution was stirred at room temperature for 2 h. Bubbling *n*-pentane vapors overnight led to the precipitation of green microcrystals, which were filtered on a sintered-glass frit, washed with Et_2O, and dried under a stream of nitrogen (yield 84%). IR (KBr): ν 1595 cm^{-1} (C═N). μ_{eff}: 4.80 μ_B (22 °C). Electronic spectra: (reflectance) 16 800sh, 15 350, 10 400, 8100, 5800 cm^{-1}; (absorption) 16 500sh, 14 900 (ϵ 129), 10 600 (ϵ 74), 7800 (ϵ 100), 5600 (ϵ 90) cm^{-1}. Anal. Calcd (%) for $C_{41}H_{47}Cl_2CoN_3$ (711.68): C, 69.20; H, 6.66; Co, 8.28; N, 5.90. Found: C, 68.78; H, 6.59; Co, 8.18; N, 5.84.

General Procedure for Ethylene Oligomerization. A 500 mL stainless steel reactor was heated at 60 °C under vacuum overnight and then cooled to room temperature under a nitrogen atmosphere. The solid precatalyst (12 μmol) was charged into the reactor, which was sealed and placed under vacuum. An appropriate solution of MAO (1440 equiv/M), prepared by adding a stock toluene solution of solid MAO in toluene (100 mg mL^{-1}) into toluene, was introduced into the reactor by suction. The reaction mixture was stirred at room temperature for about 1 min. The reactor was then pressurized with ethylene to 4 bar and stirred at 1500 rpm. Ethylene was continuously fed to maintain the reactor pressure at the desired value. The temperature inside the reactor increased due to the exothermicity of the reaction and reached a maximum value within 5−7 min. After 15 min, the reaction was stopped by cooling the reactor to −20 °C, depressurizing, and introducing 2 mL of acidic MeOH (5% HCl). Depending on the oligomerization products, two different procedures were followed. For reactions yielding mixtures of α-olefins, *n*-heptane was injected into the reactor as the GC internal standard and the reactor contents were stirred for 10 min. The solution was analyzed by GC and GC/MS. The moles of the C6 and C8 fractions were determined by GC using calibration curves with standard toluene solutions containing concentrations of 1-hexene and 1-octene as close as possible to those in the sample under analysis. Schulz−Flory α constants were determined by the molar ratio of the couple C8/C6. The moles of C4 were calculated by the Schulz−Flory α constant and the moles of C6 by the formula moles(C4) = moles(C6)/α, whereas the moles of the oligomers in the C10−C34 range were calculated by the Schulz−Flory α constant and the moles of C8 by the formula moles(Ci) = moles(C8) × $\alpha^{i-8/2}$. The total moles of converted ethylene was obtained by the formula moles(C_2H_4) = $\sum$moles(Ci) × i/2 with i = 4−34; therefore, the TOFs were obtained. For reactions yielding exclusively butenes, the reactor contents, after cooling to −50 °C, were transferred into a flask immersed in a bath at −50 °C. Oligomers were distilled over a Vigreux column (70 °C), condensed into a cooling trap (−196 °C) containing isobutane as the GC internal standard, and analyzed by GC.[4]

Scheme 4



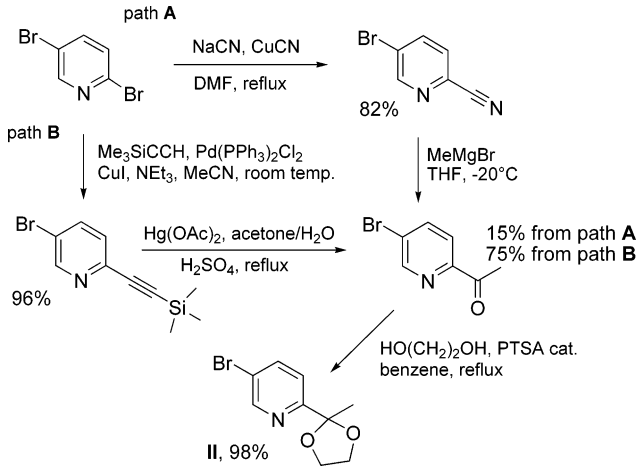
X-ray Diffraction Data. Crystallographic data of **VI**·$0.8CH_2Cl_2$ and $^{CyAr2}N_5$ are reported in Table 1. X-ray diffraction intensity data were collected on an Oxford Diffraction CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) using ω-scans. Details of data collection, refinement, and crystal data are listed in Table 1. Cell refinement, data reduction, and empirical absorption corrections were carried out with the Oxford diffraction software and SADABS.[16] All structure determination calculations were performed with the WINGX package[17] using SIR-97,[18] SHELXL-97,[19] and ORTEP-3 programs.[20] Final refinements based on F^2 were carried out with anisotropic thermal parameters for all non-hydrogen atoms, which were included using a riding model with isotropic U values depending on the U_{eq} of the adjacent carbon atoms.

Results and Discussion

Synthesis and Characterization of the $^{CyAr2}N_5$ Ligand. Scheme 4 illustrates the stepwise procedure developed to prepare the desired $^{CyAr2}N_5$ ligand in good yield. Since this synthesis work has not been technically trivial and may be useful to design other molecular architectures containing pyridine and imine groups, a description of the most relevant reaction steps is given in the following.

The ethylenedioxy ketal building block **I** was straightforwardly synthesized by lithiation of 2,6-dibromopyridine with a slight excess of ^{t}BuLi in ether at −78 °C, followed by monoacetylation with *N*,*N*-dimethylacetamide (DMAc).[21] The protection of the acetyl group of 2-acetyl-6-bromopyridine as ethylenedioxy ketal was achieved in benzene by reaction with ethane-1,2-diol in the presence of a catalytic amount of PTSA using a Dean-Stark apparatus.[15,22]

Scheme 5



Two different strategies, summarized in Scheme 5, have been developed to prepare the ethylenedioxy ketal of 2-acetyl-5-bromo pyridine **II**.

The regioselective cyanation of 2,5-dibromopyridine, followed by reductive alkylation with MeMgBr (path A),[23] gave only modest yields of the desired 2-ketone-5-bromopyridine, due to the low selectivity of the reductive alkylation step. A much

(16) Sheldrick, G. M. *SADABS*, Program for Empirical Absorption Corrections; University of Göttingen: Göttingen, Germany, 1986.
(17) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.
(18) Altomare, A.; Burla, M. C.; Cavalli, M.; Cascarano, G. L.; Giacovazzo, C.; Gagliardi, A.; Moliterni, G. G;. Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115.
(19) Sheldrick, G. M. *SHELX-97*; University of Göttingen, 1997.
(20) Burnett, M. N.; Johnson, C. K. *ORTEP-3*, Report ORNL-6895; Oak Ridge National Laboratory: Oak Ridge, TN, 1996.
(21) (a) Parks, J. E.; Wagner, B. E.; Holm, R. H. *J. Organomet. Chem.* **1973**, *56*, 53. (b) Bolm, C.; Ewald, M.; Felder, M.; Schlingloff, G. *Chem. Ber.* **1992**, *125*, 1169. (c) Peterson, M. A.; Mitchell, J. R. *J. Org. Chem.* **1997**, *62*, 8237.
(22) Kocieński, P. J. *Protecting Groups*, 3rd ed.; George Thieme Verlag: New York, 2004; p 49.

higher yield was obtained by transformation of 2,5-dibromopyridine into the 5-bromo-2-trimethylsilyl acetylene derivative via a regioselective Sonogashira protocol,[24,25] followed by a mercury(II)-catalyzed hydrolysis.[25,26] 2-Ketone-5-bromopyridine was finally protected in the *O*,*O*-ketal form via the acid-catalyzed dioxolanation method[15,22] to give **II** in 98% yield (overall yield 71%).

After several attempts to couple the two pyridine rings of **I** and **II** via formyl derivatives (*vide infra*), the target bis(pyridine)ketone **IV** was best obtained by coupling the lithium salt of **I** with the ethyl ester building block **III**, in turn prepared by methoxycarbonylation of **II**.[27] Acid hydrolysis of **IV** gave the tris(ketone) bis(pyridine) intermediate **V** in almost quantitative yield, which was transformed into the bis(iminodipyridine)-ketone **VI** by formic acid-catalyzed condensation with 2,6-diisopropylaniline in refluxing MeOH. Notably, the central ketone group of **V** remained intact even by treatment with a large excess of 2,6-diisopropylaniline, irrespective of the solvent and the reaction temperature.[3] Likewise, aniline and other anilines such as 2,6-dimethylaniline did not react with **VI** even when used as solvents at reflux temperature. In contrast, a selective reaction occurred with neat cyclohexylamine at 100 °C to give the desired $^{CyAr^2}\mathbf{N_5}$ ligand in 75% yield. Apparently, the attack by primary amines at the central C═O group of **VI** is primarily governed by electronic factors rather than by steric factors, which is consistent with the nonsterically congested structure of **VI** in the solid state, provided this is maintained in solution.

Yellow needles of $\mathbf{VI{\cdot}0.8CH_2Cl_2}$, suited for a single-crystal X-ray analysis, were obtained from a CH_2Cl_2 solution of the bis(iminopyridine)ketone **VI** on standing at −5 °C for 3 days. An ORTEP drawing of the molecule is shown in Figure 1, while crystallographic data and selected bond distances and angles are given in Tables 1 and 2, respectively.

The two pyridine units attached to the central carbonyl carbon atom C(20) are not coplanar, as put in evidence by torsion angles with the C═O unit of 29.47(0.52)° (pyridine ring with N(2)) and of 34.88(0.39)° (pyridine ring with N(3)), respectively. The hydrogen atom H(17) shows an intramolecular distance of 2.676 Å to the pyridine nitrogen atom N(3). Both ^{i}Pr rings bearing the *ipso* carbon atoms C(1) and C(28) exhibit a torsion angle with the nearest pyridine unit of 61.44(0.24)° and 89.92(0.24)°, respectively.

Well-shaped pale yellow crystals of the ligand $^{CyAr^2}\mathbf{N_5}$ were obtained by recrystallization of the crude product from a CH_2Cl_2/MeOH mixture at 0 °C. An ORTEP drawing of the molecule of $^{CyAr^2}\mathbf{N_5}$ in the asymmetric unit is shown in Figure 2, while crystallographic data and selected bond distances and angles are given in Tables 1 and 2, respectively.

The two pyridine units attached through the C(18) and C(27) carbon atoms to the central imine fragment (C(20)−N(3)) are not coplanar, the latter group showing a torsion angle of 80.66(0.41)° and of 10.21(0.37)°, respectively. Both ^{i}Pr rings with the *ipso* carbon atoms C(1) and C(34) exhibit torsion angles with the nearest pyridine unit of 72.37(0.35)° and 75.45(0.27)°, respectively. The three C═N bond lengths are comparable to each other and are in the typical range for imine groups.[28]

Table 2. Selected Bond Lengths (Å) and Angles (deg) for the Two Ligands

	$\mathbf{VI{\cdot}0.8CH_2Cl_2}$	$^{CyAr^2}\mathbf{N_5}$
C(13)−N(1)	1.280(3)	1.262(4)
C(20)−N(3)		1.269(4)
C(26)−N(4)	1.281(3)	
C(32)−N(5)		1.273(4)
C(1)−N(1)−C(13)	121.7(2)	123.6(3)
C(20)−N(3)−C(21)		120.2(3)
C(32)−N(5)−C(34)		121.1(3)
C(28)−N(4)−C(26)	120.4(2)	

Prior to the synthetic procedure reported in Scheme 4, the ketal-protected tris(ketone) **IV** was prepared by an alternative method involving the reaction of the formyl derivative **VII** with the lithium salt derived from **II** (Scheme 6). This protocol was soon abandoned due to its low yield. Nevertheless, it is worth commenting upon, as it opens the door to a different building block, namely, the dipyridine methane derivative **IX**, which may be useful to synthesize poly(imino)pyridine structures.

Indeed, the direct coupling of the lithiated form of **II** with the formyl **VII** produced a chromatographically separable mixture of **IX** and of the ketal-protected tris(ketone) **IV**, due to disproportionation of the benzydryl intermediate **VIII**.[29]

Synthesis and Characterization of the Mono- and Dinuclear Complexes with $^{CyAr^2}\mathbf{N_5}$. The mono- and dinuclear complexes with the ligand $^{CyAr^2}\mathbf{N_5}$ were prepared in good yields by the reaction of the ligand with 1 or 2 equiv of the appropriate anhydrous Fe^{II} or Co^{II} dihalide in THF at room temperature (Scheme 7).

All the mononuclear complexes are sparingly soluble in aromatic hydrocarbons, while they dissolve fairly well in organic solvents such as THF, CH_2Cl_2, and 1,2-dichloroethane. In the last solvent they behave as nonelectrolytes. All compounds are fairly air-stable in the solid state, whereas they decompose in solution unless protected by a nitrogen or argon atmosphere. Magnetic data at room temperature and relevant IR and vis−NIR absorptions (range 25 000−4550 cm^{-1}) for each complex are reported in the Experimental Section.

The IR spectra of the mononuclear compounds are identical both in the solid state and in solution and show two ν(C═N) bands, one for the coordinated C═N groups at ca. 1617 cm^{-1} and another for the uncoordinated C═N group at ca. 1640 cm^{-1} (ν(C═N) in the free ligand falls at 1646 cm^{-1}), which indicates that not all of the imine nitrogen atoms of the ligand are engaged in bonding a metal center.[5a,9b,30]

The mononuclear complexes exhibit high-spin electronic configurations with μ_{eff} values of 5.10 and 4.75 μ_B at room temperature for $^{CyAr^2}\mathbf{N_5FeCl_2}$ and $^{CyAr^2}\mathbf{N_5CoCl_2}$, respectively. These data are comparable to those reported for other iron(II) and cobalt(II) complexes with quintuplet and quartet ground states, respectively.[10]

(23) Jo, Y. W.; Im, W. B.; Rhee, J. K.; Shim, M. J.; Kim, W. B.; Choi, E. C. *Bioorg. Med. Chem.* **2004**, *12*, 5909.
(24) Tilley, J. W.; Zawoiski, S. *J. Org. Chem.* **1988**, *53*, 386.
(25) Matulenko, M. A.; Lee, C. H.; Jiang, M.; Frey, R. R.; Cowart, M. D.; Bayburt, E. K.; Di Domenico, S., Jr.; Gfesser, G. A.; Gomtsyan, A.; Zheng, G. Z.; Mc Kie, J. A.; Stewart, A. O.; Yu, H.; Kohlhaas, K. L.; Alexander, K. M.; McGaraughty, S.; Wismer, C. T.; Mikusa, J.; Marsh, K. C.; Snyder, R. D.; Diehl, M. S.; Kowaluk, E. A.; Jarvisa, M. F.; Bhagwata, S. S. *Bioorg. Med. Chem.* **2005**, *13*, 3705.
(26) Reed, M. W.; Moore, H. W. *J. Org. Chem.* **1988**, *53*, 4166.
(27) Mameri, S.; Charbonniere, L. J.; Ziessel, R. F. *Synthesis* **2003**, *17*, 2713.
(28) (a) Pelascini, F.; Wesolek, M.; Peruch, F.; Lutz, P. J. *Eur. J. Inorg. Chem.* **2006**, 4309. (b) Bart, S. C.; Chlopek, K.; Bill, E.; Bouwkamp, M. W.; Lobkovsky, E.; Neese, F.; Wieghardt, K.; Chirik, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 13901.
(29) (a) Bisaro, F.; Prestat, G.; Vitale, M.; Poli, G. *Synlett* **2002**, *11*, 1823. (b) Gautert, P.; El-Ghammarti, S.; Legrand, A.; Couturier, D.; Rigo, B. *Synth. Commun.* **1996**, *26*, 707. (c) Balfe, M. P.; Kenyon, J.; Thain, E. M. *J. Chem. Soc.* **1952**, 790. (d) Burton, H.; Cheesman, G. W. H. *J. Chem. Soc.* **1953**, 986. (e) Bartlett, P.; McCollum, J. D. *J. Am. Chem. Soc.* **1956**, *78*, 1441.
(30) Britovsek, G. J. P.; Gibson, V. C.; Spitzmesser, S. K., Tellmann, K. P.; White, A. J. P.; Williams, D. J. *Dalton Trans.* **2002**, 1159.

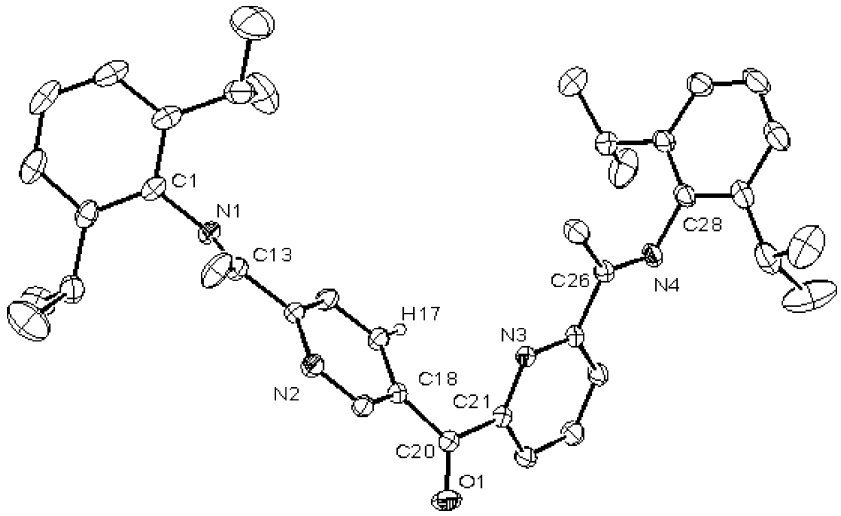


Figure 1. ORTEP drawing of **VI·0.8CH$_2$Cl$_2$**. Hydrogen atoms and solvent molecules are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level.

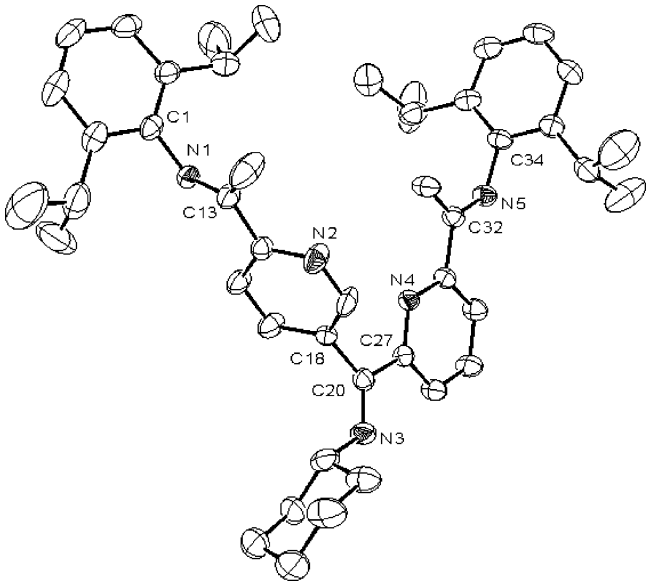
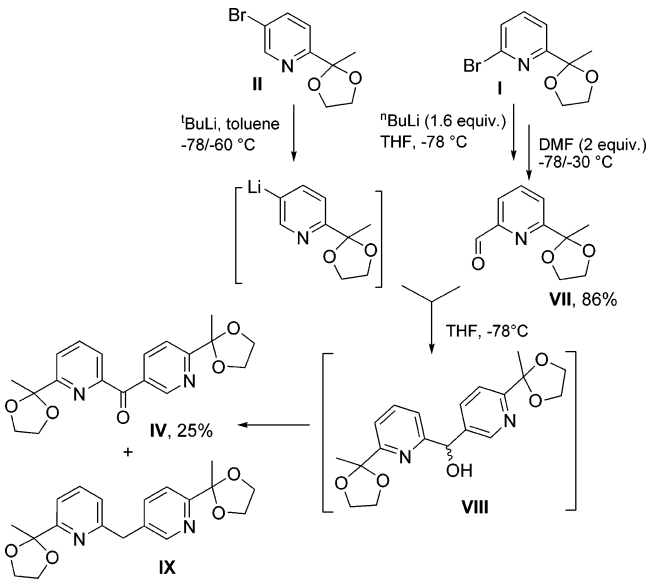


Figure 2. ORTEP drawing of ^{CyAr2}**N$_5$**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level.

Scheme 6



The electronic spectra of the mononuclear complexes show bands that are typical of the N_3MCl_2 chromophores (M = Fe, Co) in five-coordinate structures with an intermediate geometry between a square pyramid and a trigonal bipyramid.[3a,30−32] The reflectance spectra of the solids closely resemble those of the complexes in solution. Accordingly, no significant change in the stereochemistry of the complexes should occur on going from solid state to solution. The absorption spectrum of ^{CyAr2}**N$_5$CoCl$_2$** consists of five bands at 5050sh, 7750 (ϵ 15), 10 950 (ϵ 10), 14 800 (ϵ 109), and 16 400sh cm^{-1}. The first three bands are assignable to transitions between states originating from splitting of the ^4F term of the d^7 configuration in the field of D_{3h} symmetry. The first band is assignable to a $^4A_2'(F) \rightarrow {}^4E''(F)$ transition and the other two to the two components of the $^4A_2'(F) \rightarrow {}^4E'(F)$ transition in a field of lower symmetry. The fact that the latter transition is split into two components with an energy difference of ca. 3000 cm^{-1} is indicative of a high distortion in these complexes. The other two bands are due to transitions from the fundamental state $^4A_2'$-(F) to the states originating from splitting of the ^4P term ($^4A_2'$-(P) and $^4E''(P)$). The absorption spectrum of ^{CyAr2}**N$_5$FeCl$_2$** displays, in the visible region, a broad and strong absorption (ϵ 700) at 14 100 cm^{-1}, which is probably due to a ligand to metal charge transfer.[10−30] However, in the NIR region, the spectrum seems to contain also a low-intensity band (ϵ 36) at 4850 cm^{-1}. Generally, high-spin five-coordinate Fe^{II} complexes with an N_3Cl_2 donor atom set show two low-intensity absorption bands, one, in the 10 000−7000 cm^{-1} region, attributed to the spin-allowed d−d transition from the quintet ground state $^5E''$ to the excited state $^5A_1'$, and another below ca. 5000 cm^{-1} for the $^5E'' \rightarrow {}^5E'$ transition.[3a,10,30−32] It is very likely that the latter transition is responsible for the band observed at 4850 cm^{-1}, whereas the transition $^5E'' \rightarrow {}^5A_1'$ could be masked by the broad absorption centered at 14 100 cm^{-1}, which covers spectral frequencies up to 8500 cm^{-1}.

Useful information for assigning the solution structure of the mononuclear complexes was obtained by ^{1}H NMR spectroscopy. The ^{1}H NMR spectra have been acquired in CD_2Cl_2 solutions at 22 °C, and the data obtained are collected in Table 3. All

(31) (a) Sacconi, L.; Morassi, R.; Midollini, S. *J. Chem. Soc. A* **1968**, 1510. (b) Sacconi, L.; Bertini, I.; Morassi, R. *Inorg. Chem.* **1967**, *6*, 1548. (c) Ciampolini, M.; Speroni, G. P. *Inorg. Chem.* **1966**, *5*, 45.

(32) (a) Morassi, R.; Bertini, I.; Sacconi, L. *Coord. Chem. Rev.* **1973**, *11*, 343. (b) Ciampolini, M.; Gelsomini, J. *Inorg. Chem.* **1967**, *6*, 1821.

Scheme 7

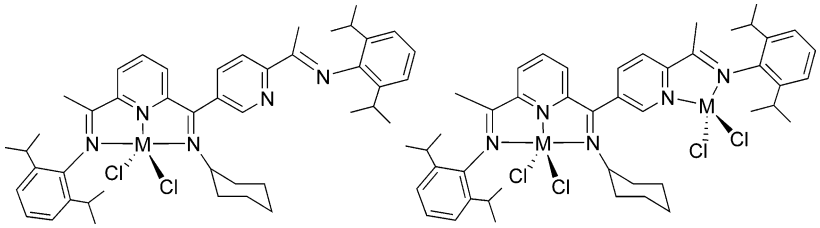


Table 3. ^{1}H NMR Assignments for Iron(II) and Cobalt(II) Complexes with $^{CyAr}N_3$ and $^{CyAr2}N_5$ (CD_2Cl_2, 22 °C, 400.13 MHz)

	$^{CyAr2}N_5CoCl_2$		$^{CyAr2}N_3CoCl_2$		$^{CyAr2}N_5FeCl_2$		$^{CyAr}N_3FeCl_2$	
position	δ	int	δ	int	δ	int	δ	int
			Coordinated Portion					
Py-H_m	109.35	1,1	108.18, 103.73	1,1	80.92 70.20	1,1	89.11 68.55	1,1
	107.58							
Py-H_p	34.54	1	25.92	1	52.44	1	35.97	1
N=CMe	−5.84	3	−4.63, −15.41	3,3	−25.41	3	−12.79 −33.57	3,3
^{i}Pr-Me	−11.12	3,3	−12.14, −17.81	6,6	1.24 −5.23	6,6	3.08 −5.38	6,6
	−14.81							
	−19.72	3,3						
	−20.20							
^{i}Pr-CH	−71.41	1,1	−73.80	2	−26.06	2	−14.94	2
	−74.61							
Ar-H_m	2.12	2	1.15	2	2.85	2	20.69	2
Ar-H_p	−10.83	1	−12.69	1	−1.10	1	−1.70	1
Cy	174.81	1	143.42	1			1.28	1
Cy	15.53	1	17.63	1			−2.99	2
Cy	−84.79	1	4.10	2			−4.72	1
Cy	−85.61	1	0.25	1			−6.74	1
Cy			−3.72	2			−7.85	2
Cy			−14.75	2			−29.10	2
Cy			−71.05	2			−37.18	2
			Uncoordinated Portion					
N=CMe	0.45	3			−3.41	3		
^{i}Pr-Me	2.12	6,6			2.41 1.24	6,6		
	−1.25							
			Unassigned Peaks					
	6.79	1			19.44	1		
	−7.74	1			18.71	1		
	−12.74	1			12.28	1		
	3.84	2			2.41	2		
	7.32	2			1.95	2		
	6.22	1			4.33	1		
	4.52	2			19.77	1		
	−0.58	1			15.45	1		
	−6.61	1			−1.10	2		
	−16.77	3			−2.71	1		
					−2.91	1		
					−6.95	1		
					−7.68	1		
					−14.10	1		
					−18.12	1		
					−29.30	1		

protons have been found to resonate at remarkably different chemical shifts as compared to the corresponding protons in the free ligands, which is consistent with the paramagnetic nature of the metal complexes. All resonances appear as broad singlets, and their assignment has been carried out on the basis of their relative intensities and line-widths (correlated to the proximity to the paramagnetic metal center), COSY experiments, and a comparison with analogous Fe^{II} and Co^{II} complexes with the 2-(arylimino)-6(cyclohexylimino)pyridine ligand 2-(2,6-^{i}Pr$_2$-C_6H_3N=CMe)-6-(cyclo-C_6H_{11}N=CMe)C_5H_3N (^{CyAr}**N$_3$**) (Scheme 1).[3a]

In line with the presence of a five-coordinate metal center in ^{CyAr2}**N$_5$CoCl$_2$**, 12 proton resonances are assigned to the coordinated bis(imino)pyridine portion of the ligand (Scheme 7). The ^{1}H NMR spectrum of the complex also shows four different methyl signals and two different methine signals for the $CHMe_2$ group, as expected for the hindered rotation of the ^{i}Pr-substituted aryl of the coordinated imino nitrogen.[10] In contrast, the ^{1}H NMR spectrum of ^{CyAr2}**N$_5$FeCl$_2$** shows two methyl signals and one methine signal for the coordinated imine moiety, which suggests a less rigid structure in solution for this iron derivative.

Unlike the mononuclear complexes, which are fairly soluble in chlorinated solvents, the dinuclear complexes dissolve only in very polar solvent like DMF, with decomposition however. For this reason, the dinuclear complexes have been exclusively characterized by solid-state techniques. The IR spectra contain

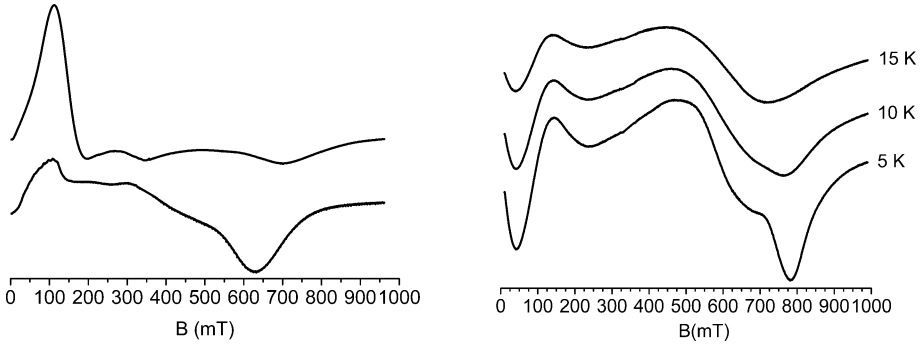


Figure 3. (a) Solid-state (upper trace) and CH_2Cl_2 solution (lower trace) EPR spectra of $^{CyAr2}N_5CoCl_2$ at 5 K. (b) Variable-temperature solid-state EPR spectra of $^{CyAr2}N_5Co_2Cl_4$.

only one ν(C═N) absorption, at 1617 cm^{-1}, consistent with the coordination of all nitrogen atoms.

The magnetic properties and the spectral parameters of the dinuclear complexes are strongly indicative of the presence of two high-spin metal centers in either square-pyramidal or tetrahedral geometry (μ_{eff} values of 6.82 and 6.33 μ_B in $^{CyAr2}N_5Fe_2Cl_4$ and $^{CyAr2}N_5Co_2Cl_4$, respectively). Since μ_{eff} values of 7.6 and 6.7 μ_B are expected for noninteracting high-spin couples of Fe^{II} and Co^{II} ions, respectively,[9b,33] one may reasonably conclude that the metal centers behave almost as separated entities with negligible magnetic interaction.

The reflectance spectrum of the dinuclear iron complex $^{CyAr2}N_5Fe_2Cl_4$ shows no additional absorption with respect to the mononuclear parent, which is likely due to the fact that tetrahedral N_2FeX_2 chromophores exhibit only one spin-allowed d−d transition observable beyond the low-energy limit of our spectrophotometer (4550 cm^{-1}). The reflectance spectrum of $^{CyAr2}N_5Co_2Cl_4$ is more complex than that of its mononuclear congener $^{CyAr2}N_5CoCl_2$ and exhibits additional absorptions at ca. 18 000 cm^{-1} and in the region 10 000−7000 cm^{-1}, which are typical of a N_2CoX_2 chromophore in a tetrahedral environment.[4d]

The EPR spectra of $^{CyAr2}N_5CoCl_2$ and $^{CyAr2}N_5Co_2Cl_4$ were recorded at 5 K due to the fast spin−lattice relaxation time, which makes high-spin Co^{II} centers detectable only at very low temperature.[34] As for the Fe^{II} complexes, the large zero field splitting of their integer ground state ($S = 2$) makes them EPR silent in the X-band even at the lowest temperature attained.

$^{CyAr2}N_5CoCl_2$ shows a typical EPR spectrum for an effective $S_{eff} = 1/2$ spin Hamiltonian with a rhombic g factor, $g_1 = 5.9$, $g_2 = 2.02$, $g_3 = 0.96$ (Figure 3a). This pattern is in agreement with the literature data for Co^{II} centers in a distorted square-pyramidal geometry[35] and, in particular, with the pattern exhibited by bis(imino)pyridine Co^{II} complexes.[10] Interestingly, a similar rhombic pattern of g values was observed for the frozen CH_2Cl_2 solution spectrum ($g_1 = 6.6$, $g_2 = 1.7$, $g_3 = 1.06$) that shows a hyperfine structure for the low-field signal. The observed differences in the g factors between the solid-state and frozen solution spectra can be reasonably attributed to differences in the intermolecular interactions of the two phases.

A fairly different EPR spectrum was obtained for the dinuclear complex $^{CyAr2}N_5Co_2Cl_4$ (Figure 3b), as three different transitions were actually observed: the first close to zero field, the second at $g = 1.14$ (perpendicular type), and the third at $g = 0.85$ (parallel type). Notably, the temperature dependence of the spectra is compatible with the presence of two different paramagnetic centers, as both the transition occurring close to zero field and that around $g = 0.85$ decreased in intensity on increasing the temperature from 5 to 15 K. Conversely, the perpendicular type transition at ca. $g = 1.13$ was not significantly affected by the temperature variation. The two sets of transitions can then be reasonably attributed to two Co^{II} ions in different coordination environments, hence with different relaxation behavior as well as different g patterns. Finally, we note that the spectra of the mono- and dinuclear complexes $^{CyAr2}N_5CoCl_2$ and $^{CyAr2}N_5Co_2Cl_4$ do not contain any signals in coincident positions. This suggests that the addition of a second cobalt ion to $^{CyAr2}N_5CoCl_2$ affects somehow the coordination environment of the first cobalt center, likely by increasing the degree of distortion from the idealized geometries.

Synthesis and Characterization of the $^{CyAr}N_3^H$ Ligand and of Its Mononuclear Complex $^{CyAr}N_3^HCoCl_2$. Scheme 8 illustrates the stepwise procedure developed to prepare the $^{CyAr}N_3^H$ ligand, which is sterically comparable to $^{CyAr2}N_5$, yet with only three nitrogen donor atoms like $^{CyAr}N_3$. The reasons that prompted us to synthesize $^{CyAr}N_3^H$ will be accounted for in a following section dealing with our efforts to correlate catalytic activity and ligand structure.

The 4-vinyl benzoate **X**, straightforwardly prepared in fairly good yield as a mixture of two inseparable diasteroisomers via a Wittig protocol,[36] was reacted with the lithiated form of 2-ethylenedioxy ketal-6-bromopyridine to afford the intermediate **XI** as a mixture of *E*/*Z* isomers. The deprotection of the ethylenedioxy ketal **XI**, followed by an acid-catalyzed imination with 2,6-diisopropylaniline, gave the monoimine−monoketone **XIII**, which was recrystallized from hot methanol in its *Z*, pure form. On reaction in hot cyclohexylamine, **XIII** was converted to the target $^{CyAr}N_3^H$ ligand. It is noteworthy that, besides exhibiting similar steric properties, $^{CyAr2}N_5$ and $^{CyAr}N_3^H$ share a similar network of single and double bonds, which should contribute to make a comparison of the catalytic performance of their Co^{II} complexes as reliable as possible.

The cobalt complex $^{CyAr}N_3^HCoCl_2$ was finally prepared by the reaction of the $^{CyAr}N_3^H$ with 1 equiv of anhydrous $CoCl_2$ in THF at room temperature (Scheme 8). Like all its congeners described in this paper, $^{CyAr}N_3^HCoCl_2$ is fairly air-stable in the solid state, whereas it decomposes in solution unless protected by an inert atmosphere. The complex shows a good solubility in organic solvents such as THF, CH_2Cl_2, and 1,2-dichloroethane. In the latter solvent it behaves as a nonelectrolyte. Since the magnetic data and the relevant IR and vis−NIR absorptions of $^{CyAr}N_3^HCoCl_2$ are fully comparable to those of the five-

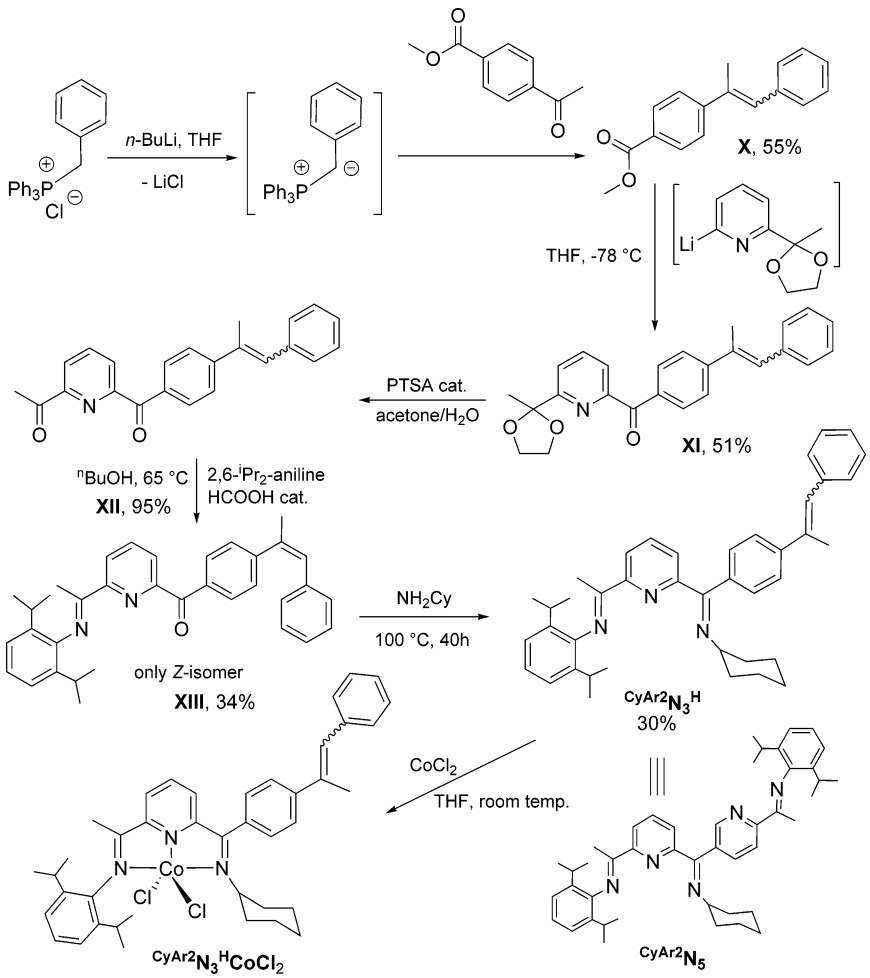
(33) Gerli, A.; Hagen, K. S.; Marzilli, L. G. *Inorg. Chem.* **1991**, *30*, 4673.

(34) Abragam, A.; Bleaney, B. *Electron Paramagnetic Resonance of Transition Ions*; Dover: New York, 1986.

(35) Bencini, A.; Gatteschi, D. In *Transition Metal Chemistry*; Figgis, B. N., Melson, G., Eds.; Marcel Dekker: New York, 1982; Vol. 8.

(36) Nakamura, Y.; Yamazaki, T.; Nishimura, J. *Org. Lett.* **2005**, *7*, 3259.

Scheme 8



coordinate $^{CyAr2}\mathbf{N_5}$ congener (see Experimental Section), no further comment is given here.

Ethylene Oligomerization Catalyzed by Mono- and Dinuclear Precursors with the $^{CyAr2}\mathbf{N_5}$ Ligand. The mono- and dinuclear Co^{II} and Fe^{II} complexes with $^{CyAr2}\mathbf{N_5}$ have been scrutinized as catalyst precursors for the oligomerization of ethylene in toluene under standard experimental conditions, using MAO as activator.[1,37] No attempt of optimizing the catalytic performance was carried out, this study being essentially concerned with a preliminary screening of the potential of $^{CyAr2}\mathbf{N_5}$ metal complexes in homogeneous catalysis. Comparative reactions were performed with known oligomerization Fe^{II} and Co^{II} catalysts modified with the more conventional 2,6-bis(imino)pyridine ligand $^{CyAr}\mathbf{N_3}$ (Scheme 1). Table 4 reports the experimental conditions and the results obtained.

Upon activation by MAO, all Co^{II} and Fe^{II} complexes with the $^{CyAr2}\mathbf{N_5}$ ligand gave α-olefins with a Schulz−Flory distribution (Table 4). Irrespective of the supporting ligand, the chain length of the oligomers showed a clear dependence on the nature of the metal center, as C_4-C_{14} α-olefins ($\alpha = 0.18-0.12$) were produced with the Co^{II} catalysts, whereas the Fe^{II} derivatives gave a broader oligomer distribution ($\alpha = 0.71-0.63$). The ability of the Fe^{II} precursors to produce higher molecular weight oligomers as compared to Co^{II} analogues is typical of systems supported by 2,6-bis(imino)pyridine ligands where one nitrogen atom bears an aryl substituent and the other a cyclohexyl substituent.[3a] Unlike classical 2,6-bis(imino)pyridine ligands, $^{CyAr2}\mathbf{N_5}$ forms Fe^{II} and Co^{II} oligomerization catalysts with comparable activities.[1,2] Unexpectedly, however, it turned out that the catalyst generated by $^{CyAr2}\mathbf{N_5CoCl_2}$ was more than 1 order of magnitude more active than that supported by the ligand $^{CyAr}\mathbf{N_3}$.[3a] More surprisingly, the activity of the mononuclear precursor $^{CyAr2}\mathbf{N_5CoCl_2}$ was 4 times lower than that of the dinuclear analogue $^{CyAr2}\mathbf{N_5Co_2Cl_4}$ (2.5 vs 10.4 g, entries 3, 4). This result cannot be simply related to the presence of a double proportion of metal in the latter precursor, as one may suggest to explain the activity of the Fe^{II} catalyst $^{CyAr2}\mathbf{N_5Fe_2Cl_2}$, which actually gives twice as much α-olefins than its mononuclear

Table 4. Ethylene Oligomerization with $^{CyAr2}\mathbf{N_5}$ and $^{CyAr}\mathbf{N_3}$ Iron(II) and Cobalt(II) Catalyst Precursors[a]

run	precatalyst	Δ*T* (°C)	oligomers (g)	TOF[b,c] (×10⁻⁴)	α[d]	α-olefin selectivity[b] (%)
1	$^{CyAr}\mathbf{N_3CoCl_2}$	1	0.1	0.1	*e*	96
2	$^{CyAr}\mathbf{N_3^HCoCl_2}$	1	0.1	0.1	*e*	96
3	$^{CyA2r}\mathbf{N_5CoCl_2}$	5	2.5	2.9	0.18	98
4	$^{CyAr2}\mathbf{N_5Co_2Cl_4}$	17	10.2	6.1	0.12	96
5	$^{CyAr}\mathbf{N_3FeCl_2}$	17	5.5	6.5	0.74	96
6	$^{CyAr2}\mathbf{N_5FeCl_2}$	13	5.3	6.3	0.63	98
7	$^{CyAr2}\mathbf{N_5Fe_2Cl_4}$	29	11.2	6.7	0.71	99

[a] Reaction conditions: precatalyst, 12 μmol; MAO, 1440 equiv/M; C_2H_4 pressure, 4 bar; toluene, 100 mL; initial temperature, 25 °C; reaction time, 15 min; stirring, 1500 rpm. [b] Determined by GC. [c] In units of mol of C_2H_4 converted (mol of M)$^{-1}$ h^{-1}. Average values over at least three reactions. [d] Schulz−Flory parameter, α = rate of propagation (rate of propagation + rate of chain transfer)$^{-1}$ = mol of C_{n+2} (mol of C_n)$^{-1}$. [e] Not determined. Almost exclusively butenes produced.

(37) Chen, E. Y.-X.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391.

analogue $^{CyAr2}N_5FeCl_2$ (entries 6, 7) and is also as active as its 2,6-bis(imino)pyridine counterpart $^{CyAr}N_3FeCl_2$ (entries 5, 6).

In an attempt to address the superior activity of $^{CyAr2}N_5CoCl_2$, some oligomerization reactions were carried out in the presence of the precursor $^{CyAr}N_3{}^{H}CoCl_2$ containing a ligand sterically comparable to $^{CyAr2}N_5$, yet with only three nitrogen donor atoms as in $^{CyAr}N_3$. Indeed, we thought that a comparison between the catalytic activity of $CoCl_2$ modified with either $^{CyAr}N_3$ or $^{CyAr}N_3{}^{H}$ would have been useful to assess whether a group of the same size as that borne by the (cyclohexyl)imine carbon atom in $^{CyAr2}N_5$ might account for so large an increase in productivity. Indeed, steric interactions between the R and R′ substituents on the RC═NR′ moiety of 2,6-bis(imino)pyridine ligands are crucial to control the chain-transfer rate of ethylene oligomerization/polymerization reactions by late transition metal complexes.[1−4]

Under the experimental conditions reported in Table 4, $^{CyAr}N_3{}^{H}CoCl_2$ generated a poorly active oligomerization catalyst, comparable to $^{CyAr}N_3CoCl_2$ (entries 1, 2). In light of this result, we are inclined to rule out any merely steric role of the uncoordinated (imino)pyridyl group to account for the greater catalytic activity of $^{CyAr2}N_5CoCl_2$ versus $^{CyAr}N_3CoCl_2$. This means that the two additional nitrogen atoms in $^{CyAr2}N_5$ may play a substantial role once the precursor is activated by MAO. These nitrogen atoms may interact with the metal center, leading to more active species, or generate more active forms of the activator. Indeed, the possible reactions of MAO with the Fe^{II} and Co^{II} complexes of the type described in this paper are manifold, spanning from the formation of square-planar Co^{II} methyl compounds, either diamagnetic Co^{I} or paramagnetic low-spin Co^{II} species,[4,38] to adducts where the residual $AlMe_3$ or MAO itself reacts with the nitrogen atoms or is able to alkylate and even reduce the C═N bonds,[39] to species where the π-electrons of the C═N-aryl rings interact with the metal center.[40] In the absence of an in-depth investigation, any of these options is equally possible. Likewise, we have no reliable explanation for the largely superior activity of the dinuclear analogue $^{CyAr2}N_5Co_2Cl_4$ as compared to the mononuclear derivative $^{CyAr2}N_5CoCl_2$ as well as for the fact that the ligand $^{CyAr2}N_5$ increases the catalytic activity of the Co^{II} derivatives more than the Fe^{II} ones. Perhaps an accurate analysis of the products formed by the reaction of the precursors with MAO might contribute to unravel these questions. Studies in this direction are in progress in our laboratory.

Conclusions

A new potentially pentadentate ligand, $^{CyAr2}N_5$, has been synthesized through a protocol that will allow one to prepare many other structurally similar molecules for use in organometallic chemistry and homogeneous catalysis.

This ligand joins 2,6-bis(imino)pyridyl and (imino)pyridyl moieties and, as such, can accommodate one or two metal centers with different coordination geometries. Moreover, the geometry of $^{CyAr2}N_5$, with the second pyridine ring linked in the 3-position, makes very unlikely the formation of octahedral mononuclear complexes, as it has been found to occur for analogous $^{Ar3}N_5$ derivatives (Scheme 3).[10]

In the present work, $^{CyAr2}N_5$ has been used to prepare mono- and homodinuclear Fe^{II} and Co^{II} bis-chloride complexes that have been characterized by a variety of analytical and spectroscopic techniques. On activation by MAO in toluene, $FeCl_2$ and $CoCl_2$ modified with $^{CyAr2}N_5$ generate effective catalysts for the oligomerization of ethylene to α-olefins with productivities and Schulz−Flory parameters depending on the type and number of coordinated metals. In particular, unlike separate 2,6-bis(imino)pyridine and (imino)pyridine ligands, their coupling, as in $^{CyAr2}N_5$, results in comparably active Fe^{II} and Co^{II} catalysts, with the latter yielding shorter oligomers. A model study has allowed us to rule out any significant role of steric effects in increasing the catalytic activity of the mononuclear Co^{II} complex $^{CyAr2}N_5CoCl_2$ versus its 2,6-bis(imino)pyridine counterpart, while no rationale has been reached to explain why the dinuclear derivative $^{CyAr2}N_5Co_2Cl_4$ is 4 times more active than its mononuclear analogue $^{CyAr2}N_5CoCl_2$.

Acknowledgment. Thanks are due to the European Community (STREP project no. 516972−NANOHYBRID; Network of Excellence no. NMP3-CT-2005-0011730−IDECAT), Ministero dell'Istruzione, dell'Università e della Ricerca (FIRB project no. RBNE03R78E−NANOPACK), and Firenze-HYDROLAB project for financial support. L.S. acknowledges Prof. D. Gatteschi for useful discussion on the EPR spectra and the financial support of Ente Cassa di Risparmio di Firenze.

Supporting Information Available: Text and tables giving crystallographic data for $VI{\cdot}0.8CH_2Cl_2$ and $^{CyAr2}N_5$. This material is available free of charge via the Internet at http://pubs.acs.org.

OM7006503

(38) (a) Humphries, M. J.; Tellmann, K. P.; Gibson, V. C.; White, A. J. P.; Williams, D. J. *Organometallics* **2005**, *24*, 2039. (b) Knijnenburg, Q.; Hetterscheid, D.; Kooistra, T. M.; Budzelaar, P. H. M. *Eur. J. Inorg. Chem.* **2004**, 1204.

(39) (a) Bruce, M.; Gibson, V. C.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1998**, 849. (b) Gibson, V. C.; Redshaw, C.; White, A. J. P.; Williams, D. J. *J. Organomet. Chem.* **1998**, *550*, 453. (c) Milione, S.; Cavallo, G.; Tedesco, C.; Grassi, A. *Dalton Trans.* **2002**, 1839. (d) Knijnenburg, Q.; Smits, J. M. M.; Budzelaar, P. H. M. *Organometallics* **2006**, *25*, 1036.

(40) Archer, A. M.; Bouwkamp, M. W.; Cortez, M.-P.; Lobkovsky, E.; Chirik, P. J. *Organometallics* **2006**, *25*, 4269.