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Selective Oligomerization of Ethylene to Linear α-Olefins by Tetrahedral Cobalt(II) Complexes with 6-(Organyl)-2-(imino)pyridyl Ligands: Influence of the Heteroatom in the Organyl Group on the Catalytic Activity

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Summary: The oligomerization of ethylene to α-olefins has been obtained by MAO activation of tetrahedral Co^{II} complexes of iminopyridines substituted in the 6-position of the pyridine ring by thiophen-2-yl, furan-2-yl, or phenyl groups. An intriguing heteroatom effect has been noticed on both activity and selectivity, together with a change in the Co^{II} spin state upon activation of the dichloride precursors with MAO.

The use of tetrahedral Co^{II} complexes to catalyze the insertion polymerization of ethylene is limited to a few *o*-bis(imino)benzene precursors reported in a patent and claimed to produce polyethylene.[1,2] The present work shows, for the first time, that pyridinimine ligands bearing appropriate substituents in the 6-position of the pyridine ring can form, in conjunction with $CoCl_2$ and methylaluminoxane (MAO), very efficient catalysts for the oligomerization of ethylene to α-olefins. An intriguing heteroatom effect has been noticed on both oligomerization activity and selectivity.

The new pyridinimines N_2^{Th}, N_2^{ThE}, and N_2^{Fu} were prepared via Stille coupling between 6-bromo-2-((2,6-diisopropylphenyl)imino)pyridine and thiophen-2-yl stannane, 5-ethylthiophen-2-yl stannane, and furan-2-yl stannane, respectively (Scheme 1).

The phenyl-substituted pyridinimine N_2^{Ph} was obtained by a Suzuki reaction between 6-bromo-2-acetyl ketone and $PhB(OH)_2$, followed by condensation of the resultant 6-phenyl-2-acetyl ketone with the aniline.

The Co^{II} complexes $CoCl_2N_2^{Th}$ (**1**), $CoCl_2N_2^{ThE}$ (**2**), $CoCl_2N_2^{Fu}$ (**3**), and $CoCl_2N_2^{Ph}$ (**4**) were obtained as green crystals in high yield by reacting 1 equiv of the ligand with $CoCl_2·6H_2O$ in refluxing *n*-BuOH. All complexes are high spin in the solid state with μ_{eff} at 20 °C ranging from 4.7 to 4.9 μ_B, which is typical for a d^7 metal ion in a tetrahedral coordination geometry.[3] Single crystals of **2** and **4** were grown by slow evaporation of the solvent from CH_2Cl_2 and CH_2Cl_2/ethyl acetate solution, respectively. The cobalt atom in each complex is tetrahedrally coordinated by two nitrogen atoms from the pyridinimine ligand and by two chlorine atoms. ORTEP drawings are reported in Figure 1.

The distortion from a regular tetrahedron is remarkable in the two geometries, as shown by the angle originated by the chelating dinitrogen ligand N1−Co−N2, which is much smaller than the regular tetrahedral angle, while the N2−Co−Cl2 angles are remarkably large, which reflects the presence of a sterically demanding substituent at the 6-position of the pyridine ring. The Co−N$_{imine}$ bonds are slightly shorter than the Co−N$_{pyridine}$ bonds, which is opposite to what is observed in related 2,6-bis(imino)pyridyl Co^{II} dichlorides.[4] The thiophenyl sulfur atom in **2** does not show any bonding interaction to cobalt, being actually oriented away from it.

The reflectance spectra of all complexes in the visible and near-IR region, showing three d−d absorption bands in the spectral regions 5500−6100, 7000−7500, and 9500−10 100 cm^{-1}, respectively, and three or two higher intensity bands in the region 14 500−18 000 cm^{-1}, are consistent with a high-spin tetrahedral coordination of the Co^{II} ion.[3] The electronic spectra in CH_2Cl_2 solution are fully comparable to the reflectance spectra, indicating that the primary stereochemistry is the same in both the solid state and solution. This would exclude a bonding interaction between cobalt and the sulfur atom in **2** even in solution. The ^{1}H NMR spectra of **2** and **4** in CD_2Cl_2, being very similar to each other, confirm indirectly the nonbonding nature of the sulfur atom.

As expected, the presence of three unpaired electrons in each complex makes all compounds EPR silent in the X-band at room temperature in both the solid state and solution.[5] Surprisingly, however, *clean EPR signals*

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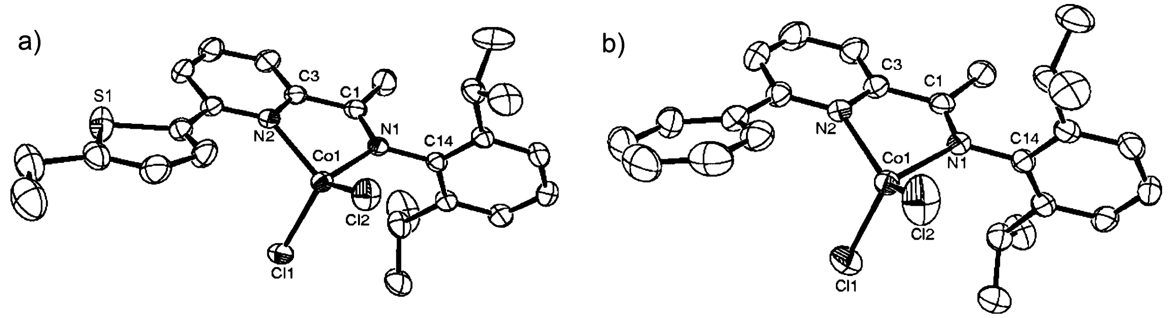
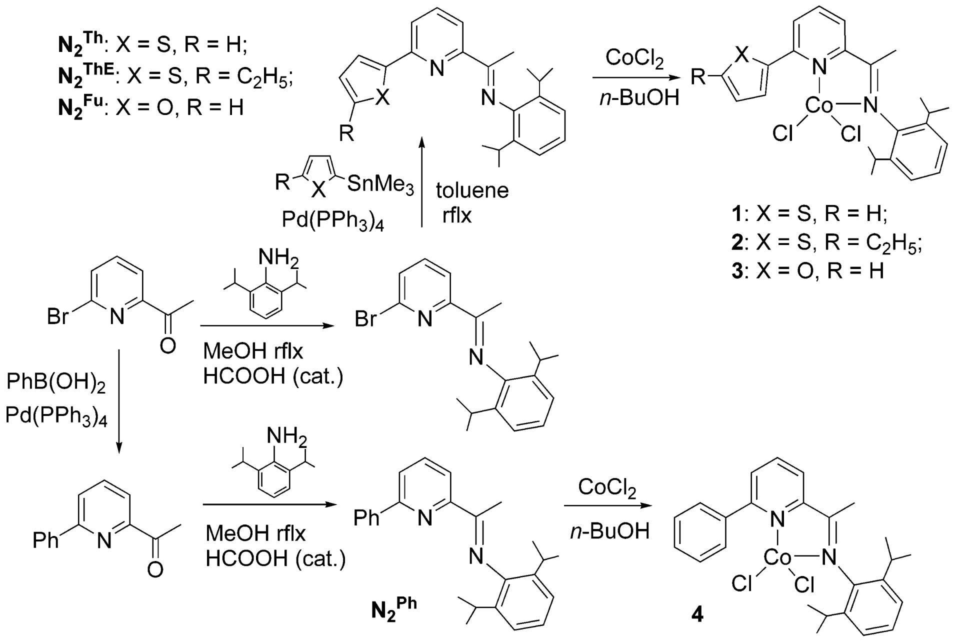


Figure 1. ORTEP drawings for **2** (a) and **4** (b). Selected bond lengths (Å) and angles (deg) for **2** and **4**, respectively: Co−N2 = 2.074(3), 2.084(4); Co−N1 = 2.031(2), 2.049(4); Co−Cl1 = 2.221(1), 2.206(2); Co−Cl2 = 2.213(1), 2.205(2); N1−Co−N2 = 81.53, 80.71; N2−Co−Cl2 = 127.05, 129.78.

Scheme 1



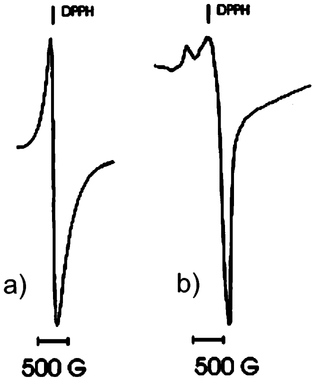


Figure 2. X-Band EPR spectra of **2** in toluene: (a) in the presence of 50 equiv of MAO at room temperature under N_2; (b) at 8 K.

appeared on treatment of the dichloride precursors ***1−4*** *with an excess of MAO at room temperature.* Figure 2a shows the X-band EPR spectrum of **2** in toluene at room temperature in the presence of an excess of MAO.

The spectrum with $g_{iso} = 2.00(5)$ does not show any hyperfine splitting at room temperature, yet a partially resolved axial structure was observed at 8 K with $g_{\|} = 2.33(5)$ and $g_{\perp} = 1.90(5)$ ($\langle g \rangle = 2.05(5)$) (Figure 2b). Values of g_{iso} for the other systems are as follows: **2**/MAO, $g_{iso} = 2.04(5)$; **3**/MAO, $g_{iso} = 2.12(8)$; **4**/MAO, $g_{iso} = 2.05(8)$.

The simple substitution of the chlorides in the precursor with stronger methyl ligands by MAO can hardly account for the appearance of an EPR signal at room temperature without a concomitant change in the coordination geometry from tetrahedral (high spin irrespective of the donor atom set) to low-spin square planar or five-coordinate.[5] A square-planar coordination is more likely in view of the fact that an EPR-active species was observed also when **4**, devoid of any potential donor atom in the phenyl substituent, was treated with MAO. Moreover, square-planar Co^{II} complexes with nitrogen ligands such as $Co(CN)_2(py)_2$ and $[Co(py)_4]Cl(PF_6)$ are low spin (py = pyridine).[3a,6] On the other hand, it is worth noting that the Co^{II} complex CoI[PhBP$_3$] is pseudotetrahedral and exhibits a doublet ground state ($PhBP_3 = PhB(CH_2PPh_2)_3^-$).[7]

The thiophenyl-containing Co^{II} complexes **1** and **2** were active catalysts for the production of low-molecular-weight α-olefins (C_4−C_{12}) with Schulz−Flory distri-

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Table 1. Ethylene Oligomerization with the Co^{II} Catalysts[a]

entry	precatalyst/ amt (μmol)	pressure (psi)	overall TOF[b] ($\times 10^{-5}$)	TOF[c] ($\times 10^{-5}$) C_8,C_6	α[d]	β[d]	sel α-olefins (%)
1	**1**/0.8	60	4.62	0.42	0.06	15.6	90
2	**1**/12	60	1.20	0.20	0.11	8.1	66
3	**2**/0.8	60	5.10	0.48	0.09	10.1	93
4	**2**/12	60	1.33	0.24	0.13	6.7	67
5	**3**/0.8	60	1.10[e]	0.03	-		f
6	**4**/0.8	60	1.12[e]	<0.01	-		f
7	**1**/0.8	120	8.70	0.80	0.06	15.6	94
8	**1**/0.8	200	15.2	1.37	0.06	15.6	95
9[g]	**2**/12	60	2.70	0.44	0.11	8.1	71
10[h]	**2**/12	60	0.52	0.10	0.16	5.2	61

[a] Reaction conditions: toluene 100 mL, MAO 200 equiv, 30 min, 25 °C. [b] Mol of C_2H_4 converted (mol of Co)$^{-1}$ h^{-1} determined by GC at appropriate temperatures. [c] Mol of C_2H_4 converted (mol of Co)$^{-1}$ h^{-1} into C_6 and C_8 olefins. [d] Schulz-Flory parameters: α = mol of C_{n+2} (mol of C_n)$^{-1}$; $\beta = (1 - \alpha)/\alpha$. [e] Almost exclusively butenes produced. [f] Not determined. [g] 5 min. [h] 180 min.

butions.[4,8] Selected data are reported in Table 1. In all cases, the addition of ethylene to the catalyst/cocatalyst mixture resulted in a rapid exotherm, indicative of no induction period. Experiments with precursor **1** in the C_2H_4 pressure range from 60 to 200 psi (entries 1, 7, and 8) showed a linear dependence of activity with the pressure, while the α factor was independent of the pressure, indicating that the propagation and chain-transfer rates are first order in ethylene.[4,8] The TOF observed at 200 psi (1.52×10^6 mol of C_2H_4 converted (mol of Co)$^{-1}$ h^{-1}) is remarkable, at least 2 orders of magnitude higher than those reported for 2,6-bis(imino)pyridyl Co^{II} catalysts under comparable conditions.[4,9]

The furanyl- and phenyl-substituted precursors **3** and **4** were much less active than either thiophenyl-substituted catalyst and produced essentially butenes (entries 5 and 6). In the reactions catalyzed by **1** or **2**, the selectivity in α-olefins decreased with time (entries 4, 9, and 10) due to isomerization to internal olefins (predominantly with *E* configuration), while the α factor increased due to the reincorporation of α-olefin products into oligomers made later in the reaction.[8] The occurrence of both olefin isomerization and reincorporation was confirmed by independent experiments in which the oligomerization of ethylene with **1** was carried out in the presence of an excess of 1-undecene. Odd-carbon oligomers were formed together with various undecenes, in fact. No saturated hydrocarbon was produced, which indicates the absence of chain transfer to aluminum.[4]

Given the comparable size of the furanyl and phenyl groups as compared to thiophenyl, steric factors cannot account for the remarkably different activity and selectivity of **1** and **2** vs **3** and **4**. It is therefore likely that the sulfur atom plays an active role during the oligomerization of ethylene. In view of the EPR study discussed above, the oligomerization process may involve square-planar Co^{II} initiators. Interestingly, theoretical calculations suggest the occurrence of a spin state changeover in the propagation and chain transfer of ethylene polymerization by 2,6-bis(imino)pyridyl Fe^{II} catalysis.[10] It is also worth mentioning that square-planar Co^{I} complexes, formed by reduction of 2,6-bis(imino)pyridyl Co^{II} precursors with MAO, can initiate the polymerization of ethylene, yet it is not clear whether the active catalysts are Co^{I} or Co^{III} species.[11,12]

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Supporting Information Available: Text giving the synthesis and characterization of the pyridinimine ligands N_2^{Th}, N_2^{ThE}, and N_2^{Fu} and of the Co^{II} complexes **1**−**4**, text giving details of the oligomerization procedure, and text and tables giving crystallographic data for compounds **2** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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