Polymerization of Ethylene by the Electrophilic Mixed Cyclopentadienylpyridylalkoxide Complexes $[CpM\{NC_5H_4(CR_2O)\text{-}2\}Cl_2]$ ($M = Ti, Zr, R = Ph, Pr^i$)

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*Summary: The group 4 mixed-ligand compounds $[CpM\{NC_5H_4(CR_2O)\text{-}2\}Cl_2]$ ($M = Ti$; $R = Pr^i$ (**1a**), Ph (**1b**); $M = Zr$, $R = Pr^i$ (**2a**), Ph (**2b**)) have been prepared and characterized. Single-crystal X-ray analyses reveal that **1a** and **2b** adopt four-legged piano-stool structures in which the cyclopentadienyl ligand is asymmetrically bonded and the pyridylalkoxide is bidentate. Toluene solutions of $[CpM\{NC_5H_4(CR_2O)\text{-}2\}Cl_2]$ and methylaluminoxane catalyze the polymerization of ethylene, generating high molecular weight polymers with narrow molecular weight distributions. The activity of the titanium- and zirconium-based catalysts are comparable.*

Since the discovery of homogeneous Ziegler−Natta catalysis by group 4 metallocenes[1] considerable effort has been devoted to catalyst modification in order to improve polymerization activity and control polymer properties such as stereoregularity, co-monomer incorporation, and microstructure.[2] As a result, metallocene-based chemistry has undergone significant developments, including the synthesis of single-site cationic catalysts with high olefin polymerization activities,[3] the stereospecific polymerization of propylene by C_2-symmetric *ansa*-metallocenes,[4] and the synthesis of thermoplastic elastomeric polypropylene using a nonbridged metallocene catalyst.[5] Researchers at Dow and Exxon have recently shown that constrained-geometry catalysts that contain one cyclopentadienyl ligand and one amido group, such as $\{SiMe_2(C_5H_4)NR\}MCl_2$ ($M = Ti$, Zr, Hf), are active and selective for the copolymerization of ethylene and α-olefins.[6] The most recent strategy in catalyst design and modification has been the development of noncyclopentadienyl-based derivatives of the early transition metals, with the focus of attention on nitrogen- and/or oxygen-containing ligands. In this regard, the electronic relationship between the $\sigma{-}2\pi$ cyclopentadienide fragment and single-faced π-donor ligands such as NR_2, NR, and OR has been discussed.[7] A number of chelating diamide[8] and dialkoxide[9] complexes of the group 4 metals, mixed organoimido−cyclopentadienyl derivatives[10] of group 5, and bisimido[11] complexes of group 6 have now been prepared, many of which can be activated to yield catalysts for the polymerization of α-olefins. Notably, some of these complexes show high olefin polymerization activities while others can be activated for the living polymerization of 1-hexene.[8]

Given the impact of ligand design on catalyst performance, we have recently begun to explore the potential of mixed-ligand complexes of the type $CpM(L)X_2$, where L represents a monoanionic mono- or multidentate ligand, as α-olefin polymerization precatalysts. In comparison to conventional metallocene initiators Cp_2MX_2, monocyclopentadienyl complexes $CpM(L)X_2$ offer the advantage of catalyst modification by changing the nature of the spectator ligand, L. Herein, we report preliminary ethylene polymerization activities for the electrophilic mixed-ligand complexes $[CpM\{NC_5H_4\text{-}$

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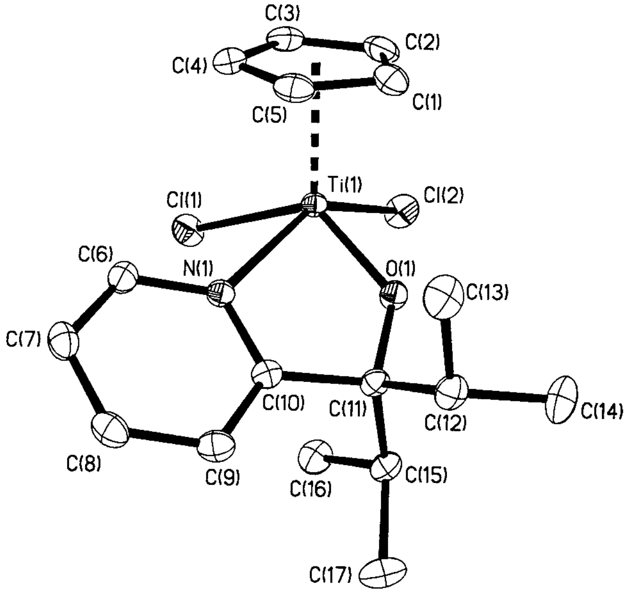
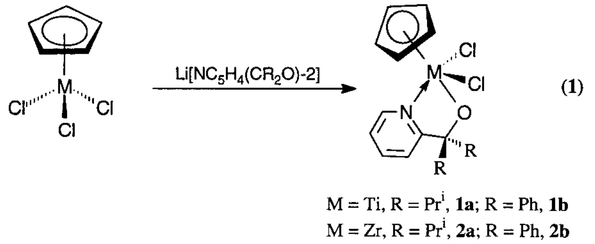


Figure 1. Molecular structure of [CpTi{$NC_5H_4(CPr^i{}_2O)$-2}Cl_2], **1a**. H-atoms omitted for clarity.

(CR_2O)-2}Cl_2] that contain one cyclopentadienyl and one chelating pyridylalkoxide ligand.

Compounds **1a,b** and **2a,b** are readily synthesized via slow addition of a toluene solution of Li[$NC_5H_4(CR_2O)$-2] (R = Pr^i, Ph) to a toluene solution of $CpTiCl_3$ or $CpZrCl_3$(dme), respectively[12] (eq 1). In the $^{13}C\{^1H\}$ NMR spectrum of **1a**,[13] the isopropyl methyl groups appear as two singlets, which suggests that the pyridylalkoxide is coordinated in a bidentate manner. Similar features are apparent in the $^{13}C\{^1H\}$ NMR spectrum of **2a**.[14] Single-crystal X-ray analyses of **1a** and **2b** were undertaken in order to provide precise structural details.[15,16]



The molecular structure shown in Figure 1 reveals **1a** to be monomeric, with a coordination geometry best described as square-based pyramidal with the centroid of the C_5H_5 ring occupying the apical site and the pyridyl alkoxide and chlorides occupying the basal positions. Interestingly, the Ti−C bond lengths differ significantly, ranging from 2.3482(14) to 2.4154(14) Å (ΔTi−C = 0.0672 Å), with one short, two medium, and two long bonds. Notably, the shortest Ti−C bond length (Ti(1)−C(1) = 2.3482(4) Å) is trans to Ti(1)−Cl(1), suggesting that the difference in Ti−C bond lengths may reflect the different trans influence of the donor atoms in the basal plane. A similar bond length pattern has recently been suggested to reflect a tendency toward three-electron η^3-coordination.[17] Surprisingly, the Ti−Cl bond trans to the pyridyl nitrogen is considerably longer (Ti(1)−Cl(2) = 2.3482(4) Å) than that trans to the alkoxide (Ti(1)−Cl(1) = 2.3396(4) Å, ΔTi−Cl = 0.0389 Å), contrary to what is expected based solely on trans influence trends. For comparison, we have prepared and structurally characterized CpTi(tmhd)Cl_2, which contains a symmetrically chelating 2,2,6,6-tetramethylheptanedionate ligand.[18] The Ti−C bond length differences in CpTi(tmhd)Cl_2 (ΔTi−C = 0.033(3) Å) are less pronounced than those in **1a** as are the differences in the Ti−Cl bond lengths (ΔTi−Cl = 0.0041(6) Å). The Ti−O bond length in **1a** (Ti(1)−O(1) = 1.8267(9) Å) is slightly shorter than that recently reported by Marks and co-workers[19] for the phenolate constrained geometry catalyst [{C_5Me_4-2-Me-C_6H_3O}Ti($CH_2Ph)_2$] (1.851(7) Å), which may reflect O(pπ)−Ti(dπ) donation to the metal.

Complex **2b** crystallizes in the noncentrosymmetric space group $P2_12_12_1$ as a single enantiomer.[16] The molecular structure, shown in Figure 2, revealed that the zirconium center has a pseudosquare-based pyramidal geometry. While the gross structural features of **2b** are similar to those of **1a**, there are several noteworthy differences, the most striking of which is the smaller variation in M−C bond lengths, which lie between 2.486(3) and 2.525(3) Å (ΔZr−C = 0.039 Å). As in **1a**, the M−Cl bond trans to the pyridine (Zr(1)−Cl(2) = 2.4528(8) Å) is longer than that trans to the alkoxide (Zr(1)−Cl(1) = 2.4439(8) Å), although these differences are somewhat smaller than those in **1a** (ΔZr−Cl = 0.0089 Å). The chelate O(1)−Zr(1)−N(1)

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(12) **Preparation of 1a**: A solution of Li[$NC_5H_4(CPr^i{}_2O)$-2], prepared by the addition of ^{n}BuLi (2.20 mL, 5.5 mmol) to a toluene solution of the pyridyl alcohol (1.07 g, 5.5 mmol), was added to a rapidly stirred suspension of $CpTiCl_3$ (1.20 g, 5.5 mmol) in toluene. The reaction mixture was stirred overnight and filtered, and the solvent was removed under reduced pressure to give a yellow-orange solid residue. The product was crystallized by slow diffusion of hexane into a dichloromethane solution of **1a**. Compounds **1b** and **2a**,**b** were prepared following a procedure similar to that described above.

(13) Spectroscopic data for **1a**: $^{13}C\{^1H\}$ NMR (125.65 MHz, $CDCl_3$, δ): 170.2 (s, C_5N), 150.3 (s, C_5N), 138.8 (s, C_5N), 123.7 (s, C_5N), 121.7 (s, C_5N), 121.4 (s, C_5H_5), 107.1 (s, Py−*C*−O), 37.1 (s, *C*H($CH_3)_2$), 19.5 (s, CH(*C*$H_3)_2$), 17.9 (s, CH(*C*$H_3)_2$). Anal. Calcd for $C_{17}H_{23}Cl_2NOTi$: C, 54.25; H, 6.12; N, 3.72. Found: C, 54.19; H, 6.17; N, 3.71.

(14) Spectroscopic data for **2a**: $^{13}C\{^1H\}$ NMR (125.65 MHz, $CDCl_3$, δ): 170.0 (s, C_5N), 149.8 (s, C_5N), 138.7 (s, C_5N), 122.9 (s, C_5N), 121.5 (s, C_5N), 116.6 (s, C_5H_5), 98.6 (s, Py−*C*−O), 35.6 (s, *C*H($CH_3)_2$), 18.1 (s, CH(*C*$H_3)_2$), 17.3 (s, CH(*C*$H_3)_2$). Compound **2b**: $^{13}C\{^1H\}$ NMR (125.65 MHz, $CDCl_3$, δ): 169.9 (s, C_5N), 149.8 (s, C_6H_5), 144.9 (s, C_5N), 139.0 (s, C_5N), 128.1 (s, C_6H_5), 128.0 (s, C_6H_5), 127.4 (s, C_6H_5), 125.4 (s, C_5N), 123.4 (s, C_5N), 116.1 (s, C_5H_5), 96.0 (s, Py−*C*−O).

(15) Crystal data for **1a**. $C_{17}H_{23}Cl_2NOTi$, M_r = 376.16, monoclinic, $P2_1/c$, a = 7.4335(5) Å, b = 16.8859(12) Å, c = 13.9126(10) Å, β = 97.577(2)°, V = 1731.1(2) Å^3, Z = 4, D_{calcd} = 1.443 g cm^{-3}, μ = 0.804 mm^{-1}, (Mo Kα, λ = 0.710 73 Å), F(000) = 784; 10 734 reflections (θ_{max} = 28.83°) measured on a Bruker SMART CCD area detector diffractometer at 160 K, 4023 unique data (R_{int} = 0.0197) were corrected semiempirically for absorption (transmission 0.862−0.725 for crystal size 0.50 × 0.23 × 0.18 mm); structure solution by direct methods, refinement on F^2 with statistics-based weighting scheme, anisotropic displacement parameters for all non-H atoms, and constrained isotropic H atoms; final wR2 = $\{\Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]\}^{1/2}$ = 0.0673 for all data, conventional R = 0.0245 on F values for 3550 reflections having $F_o{}^2 > 2\sigma(F_o{}^2)$, S = 1.038 on F^2 for all data and 204 refined parameters; final difference map extremes +0.420 and −0.314 e Å^{-3}.

(16) Crystal data for **2b**. $C_{23}H_{19}Cl_2NOZr$, M_r = 487.51, orthorhombic, $P2_12_12_1$, a = 9.277(2) Å, b = 14.377(3) Å, c = 15.795(4) Å, V = 2106.7(8) Å^3, Z = 4, D_{calcd} = 1.537 g cm^{-3}, μ = 0.789 mm^{-1}, (Mo Kα, λ = 0.710 73 Å), F(000) = 984; 11 663 reflections (θ_{max} = 28.93) at 173 K, 4876 unique data (R_{int} = 0.0380), transmission 0.746−0.564 for crystal size 0.39 × 0.36 × 0.33 mm; refinement as for **1a**; final wR2 = 0.0558 for all data, R = 0.0298 on F values for 4144 reflections having $F_o{}^2 > 2\sigma(F_o{}^2)$, S = 0.966 on F^2 for all data and 254 refined parameters; final difference map extremes +0.325 and −0.467 e Å^{-3}.

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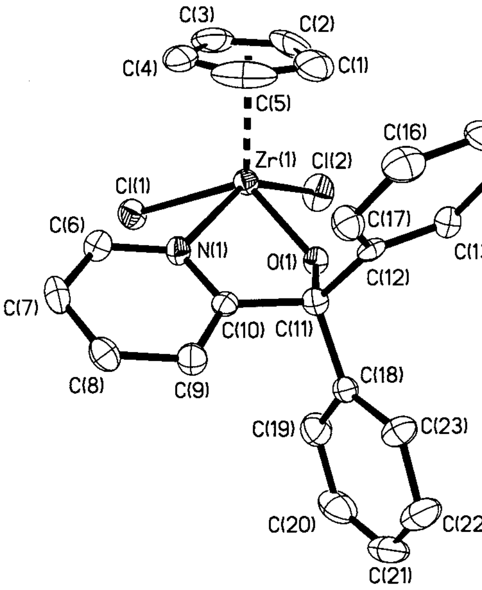

Figure 2. Molecular structure of [CpZr{$NC_5H_4(CPh_2O)$-2}Cl_2], **2b**. H-atoms omitted for clarity.

angle of 69.70(7)° is acute and similar to the previously reported values of 69.2(1)° and 70.1(1)° in the pyridylalkoxide-substituted zirconium complex [$(NC_5H_4CMe_2O)_2$-$Zr(CH_2Ph)_2$].[20] The Zr(1)−O(1)−C(11) angle of 130.05(15)° suggests that O(1) is sp^2 hybridized, while the Zr(1)−O(1) distance of 1.9544(16) Å is substantially shorter than those in [$(NC_5H_4CMe_2O)_2Zr(CH_2Ph)_2$], which contains a *trans*-O−Zr−O and *cis*-N−Zr−N arrangement of the pyridylalkoxide ligands with Zr−O bond lengths of 1.995(3) and 2.004(3) Å and Zr−N bond lengths of 2.429(3) and 2.391(3) Å. This bond length shortening may reflect greater O(pπ)−Zr(dπ) donation trans to a chloride compared to that when trans to another alkoxide or Coulombic stabilization by an ionic contribution to the zirconium−oxygen bond, i.e., Zr^+−O^-, as discussed recently by Parkin and co-workers in a structural comparison within the series [$(\eta^5\text{-}C_5Me_5)_2$-$Zr(EPh)_2$] (E = O, S, Se, Te).[21]

The results of preliminary studies on ethylene polymerization activities and polymer properties are summarized in Table 1.[22] Toluene solutions of **1a**,**b**, **2a**,**b**, and methylaluminoxane (MAO) are active catalysts for the polymerization of ethylene, generating high molecular weight polymers with a narrow molecular weight distribution. Under these conditions, stable polymerization profiles with little evidence for catalyst decay were observed in all four cases, suggesting that the active species are stable under these conditions. Interestingly, the nature of the R groups on the alkoxide ligand has a significant effect on productivity, the Pr^i-substituted systems being about twice as active as the Ph-substituted derivatives. This could possibly represent a steric effect and/or greater π-donation to the metal center by the oxygen atom in the more electron-rich alkoxide complexes **1a** and **2a**, although the geometry of the chelate ring would seem to preclude strong π-donation analogous to that seen in cationic alkoxide complexes of group 4.[23,24] A number of monocyclopentadienylmetal complexes of group 4 have been shown to polymerize ethylene. To compare, Chien and coworkers have reported that $CpTiCl_3$/MAO has an ethylene polymerization activity of 6.2 × 10^4 g of polymer (mol of Ti)$^{-1}$ h^{-1}, substantially lower than ($\eta^5\text{-}C_5H_4CH_2$-CH_2NMe_2)$TiCl_3$/MAO mixtures which showed activities as high as high as 5 × 10^6 g of polymer (mol of Ti)$^{-1}$ h^{-1} under similar conditions. The molecular weights (MW) of the PE produced using **1a**,**b** and **2a**,**b** also exhibited some variation, although considerably less so than that observed for catalyst activities; in general, the Pr^i-substituted systems provided lower MW PE than the Ph derivatives, suggesting faster rates of chain transfer for the former. Given the uncertainty in active site concentrations in these experiments, the evaluation of single-component versions of these catalyst systems should prove more informative in this regard.

Table 1. Summary of Ethylene Polymerization Results Using Complexes 1a,b and 2a,b

entry	precatalyst	temp/ °C	activity/g of PE (mol of cat)$^{-1}$ h^{-1}	M_w	M_n	M_w/M_n
1	**1a**	30	80 000	450 000	225 000	2.00
2	**1b**	30	320 000	544 000	292 000	1.86
3	**2a**	30	430 000	567 000	261 000	2.17
4	**2a**	30	710 000	862 000	250 000	3.44
5	**2b**	30	370 000	658 000	378 000	1.74

In summary, mixed-ligand complexes of the group 4 transition metals containing one cyclopentadienyl ligand and one anionic pyridylalkoxide spectator ligand have been prepared. In the presence of MAO, these compounds are active for the polymerization of ethylene, generating high molecular weight polymers with narrow molecular weight distributions. The influence of ligand modification on the structure and activity of these new precatalysts, the synthesis of single-site cationic derivatives of the type $[CpM(L)R]^+$, and their applications as Lewis-acid catalysts are currently under investigation.

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Supporting Information Available: A table giving spectroscopic and analytical data for **1a**,**b** and **2a**,**b** and tables giving details of the crystal structure analyses of **1a** and **1b** (12 pages). Ordering information is given on any current masthead page.

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[22] **Polymerization procedure:** Ethylene polymerizations were conducted in a toluene slurry in a 1 L stirred autoclave at 75 psig of C_2H_4 at 30 °C. In a typical procedure, solid MAO (Al:M 1000:1) dissolved in 25 mL of toluene was added via pressurized sample vessel to 450 mL of toluene at the desired process temperature, and the solution was then saturated with monomer, stirring at 500 rpm. The complex, dissolved in 25 mL of toluene, was introduced using another sample vessel, using a slight overpressure of nitrogen. Monomer uptake was monitored by calibrated mass flow meters. Polymerizations were quenched by venting the monomer and quenching with a small volume of MeOH. The polymers were isolated by filtration, washed with MeOH, de-ashed with a solution of 4 M HCl in MeOH, washed with MeOH, and then dried in vacuo at 60 °C prior to GPC analysis (1,2,4-trichlorobenzene at 145 °C using both narrow MWD polystyrene and broad MWD PE standards for calibration).

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