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New bis(azolylcarbonyl)pyridine chromium(III) complexes as initiators for ethylene polymerization

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ABSTRACT

Reaction of 2,6-pyridinedicarbonyl dichloride with 3,5-dimethylpyrazole and 1*H*-indazole, respectively, yield the tridentate ligands 2,6-bis(3,5-dimethylpyrazol-1-ylcarbonyl)pyridine (**1**) and 2,6-bis(indazol-1-ylcarbonyl)pyridine (**2**). The molecular structure of the new compound (**2**) was determined by single-crystal X-ray diffraction. These ligands react with $CrCl_3(THF)_3$ in THF to form neutral complexes of general formula [$CrCl_3${2,6-bis(azolylcarbonyl)pyridine-*N*,*N*,*N*}] (**3**, **4**) which were isolated in high yield as air stable green solids and characterized by elemental analysis, magnetic moment, IR, and mass spectroscopies. Theoretical calculations predict that the thermodynamically preferred structure of the complexes is the *fac* configuration. After reaction with methylaluminoxane (MAO) the chromium(III) complexes are active for the polymerization of ethylene.

1. Introduction

The chemistry of chromium(III) complexes has received much attention in recent years due to their potential applications as catalyst precursors in homogeneous olefin polymerization [1]. Two decades ago, the Brookhart [2] and Gibson [3] research groups reported the discovery of highly active iron and cobalt ethylene polymerization catalysts that incorporate bis(imino)pyridyl ligands. Following this discovery, the design, synthesis and catalytic behaviour of new chromium complexes bearing neutral tridentate N-donor ligands have undergone considerable development.

Bis(oxazolinyl)pyridine and bis(*N*-arylimino)pyridine chromium(III) complexes using different N-aryl substituents were described by Esteruelas et al. [4] and Small et al. [5], and showed that the complexes are active in the polymerization and/or oligomerization of ethylene, after activation by methylaluminoxane (MAO). Related chromium(III) complexes derived from bis(benzimidazolyl) amine or pyridine ligands have been reported by Gibson, which behave as exceptionally active catalysts for ethylene oligomerization [6]. Cartney described the synthesis of bis(2-pyridylmethyl)amine chromium(III) complexes, reporting that the coordination geometry of the complexes (*fac* or *mer*) depends on the substituents of the pyridyl ring [7]. These compound are moderately active in the polymerization of ethylene in the presence of MAO, with the *fac* derivatives being 30–40 times more active than their *mer* counterparts.

Furthermore, anionic and neutral chromium complexes containing sterically hindered tris(pyrazolyl)borate and tris(pyrazolyl)methane ligands have been reported as active species for the oligomerization and polymerization of ethylene [8,9]. Metal complexes containing related tridentate ligands derived from two pyrazolyl groups connected by a spacer atom to the central pyridine ring have also been described [10,11]. Recently Casagrande and co-workers reported the synthesis of a new chromium(III) complex with the tridentate ligand [2-(3-phenyl-1-pyrazolyl)ethyl]amine which possessed good activity and selectivity for the oligomerization of ethylene in the presence of MAO [12]. We have recently reported the synthesis and behaviour of the neutral complexes [$CrCl_3${2,6-bis(azolylmethyl)pyridine-*N*,*N*,*N*}], which upon activation with MAO, and under mild conditions produced high molecular weight polyethylene with a narrow molecular weight distribution [13].

As part of the continuation of the search for related new polymerization catalysts we now report the synthesis and characterization of neutral chromium(III) complexes supported by 2,6-bis(azolylcarbonyl)pyridine ligands. The molecular structure of the ligand 2,6-bis(indazol-1-ylcarbonyl)pyridine was determined by single-crystal X-ray diffraction. The chromium complexes, in the presence of methylaluminoxane (MAO), present higher activities than similar complexes in ethylene polymerization.

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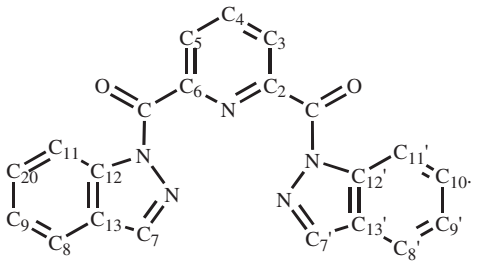
2. Experimental

2.1. General

All manipulations were performed in an inert atmosphere (nitrogen) using standard glovebox and Schlenk techniques. All reagent-grade solvents were dried, distilled, and stored under a nitrogen atmosphere. The starting compounds $CrCl_3(THF)_3$, 3,5-dimethylpyrazole, 1*H*-indazole and 2,6-pyridinedicarbonyl dichloride were purchased from Aldrich, and used as received. 2,6-Bis(3,5-dimethylpyrazol-1-ylcarbonyl)pyridine (**1**) was prepared according to published methods [11a]. Elemental analyses (C, H and N) were performed with a Fisons EA 1108 microanalyzer. FTIR spectra were recorded on a Bruker Vector-22 spectrophotometer using KBr discs. NMR spectra were recorded on a Bruker Avance-400 spectrometer. Chemical shifts are reported in ppm relative to $SiMe_4$ (^1H, $^{13}C\{^1H\}$), which was present as an internal standard. Mass spectra were obtained on a Micromass Quattro LC-Z electrospray mass spectrometer. Melting points were determined on an Electrothermal melting point apparatus in open capillary tubes and are uncorrected. Magnetic measurements were carried out at room temperature (293 K) on a Johnson Matthey MSB MK1 Magnetic Susceptibility Balance.

2.2. Synthesis of 2,6-bis(indazol-1-ylcarbonyl)pyridine (*2*)

In a Schlenk tube equipped with a reflux condenser, 1*H*-indazole (2.260 g; 19.1 mmol), 2,6-pyridinedicarbonyl dichloride (1.960 g; 9.60 mmol), triethylamine (15 mL), and toluene (80 mL) were added and the mixture heated at reflux for 24 h. The resulting mixture was evaporated to dryness and the solid residue washed with water and extracted with chloroform. The organic layer was separated, dried with magnesium sulphate, filtered and evaporated to dryness. The solid residue was purified by crystallization from chloroform-diethyl ether to give a white solid. Yield 3.066 g (87%). M.p.: 251–252 °C. MS-ESI (*m*/*z*, ES^+): 367.36 $[M]^+$, 390.09 $[M+Na]^+$ *Anal.* Calc. for $C_{21}H_{13}N_5O_2$: C, 68.6; N, 19.1; H, 3.5. Found: C, 68.1; N, 19.0; H, 3.6%. FTIR (KBr, cm^{-1}): *ν* 1694s (C=O), 1573m, 1506m, 1431s, 1376s, 1346s, 1306m, 967s, 767s, 622m. Atom numbering for ligand **2** is as follows:



NMR ($CDCl_3$, 295 K): ^1H *δ* 7.43 (t, 2H, *J*(HH) = 7.6 Hz, H9,9′), 7.64 (t, 2H, *J*(HH) = 8.0 Hz, H10,10′), 7.77 (d, 2H, *J*(HH) = 8.0 Hz, H8,8′), 8.15–8.20 (m, 3H, H3,4,5-Py), 8.21 (s, 2H, H7,7′) and 8.57 (d, 2H, *J*(HH) = 8.4 Hz, H11,11′) ppm. $^{13}C\{^1H\}$: *δ* 116 (C11,11′), 121 (C8,8′), 125 (C9,9′), 126 (C2,C6), 127 (C3,C5), 130 (C10,10′), 137 (C4), 140 (C13,13′), 141 (C7,7′), 152 (C12,12′) and 166 (CO) ppm.

2.3. Synthesis of chromium(III) complexes

A solution of the 2,6-bis(azolylcarbonyl)pyridine ligand [2,6-bis(3,5-dimethylpyrazol-1-ylcarbonyl)pyridine (100 mg; 0.31 mmol) or 2,6-bis(indazol-1-ylcarbonyl)pyridine (104 mg; 0.3 mmol)] in THF (10 mL) was added via syringe to a solution of $CrCl_3(THF)_3$ (116 mg; 0.31 mmol) in THF (10 mL). The resulting solution was stirred at 70 °C for 8 h, giving a green suspension. The reaction volume was reduced, and diethyl ether added to afford a green solid, which was washed repeatedly with diethyl ether and dried under vacuum. The resulting compound was purified by dissolving in acetone, filtering and precipitating it through the addition of diethyl ether.

[$CrCl_3${2,6-Bis(3,5-dimethylpyrazol-1-ylcarbonyl)pyridine-*N*,*N*,*N*}] (**3**). Yield: 120 mg (87%). FTIR (KBr, cm^{-1}): *ν* 1719s (C=O), 1649s, 2428m, 1340s, 1047m, 991m, 957m, 749s, 688m, 348–358 (Cr–Cl) [25]. MS-ESI (*m*/*z*, ES^+): 481.70 $[M]^+$, 502.97 $[M+Na]^+$. *Anal.* Calc. for $C_{17}H_{17}N_5O_2Cl_3Cr$: C, 42.4; N, 15.5; H, 3.5. Found: C, 42.0; N, 15.1; H, 3.0%. $\mu_{eff} = 3.8\mu_B$.

[$CrCl_3${2,6-Bis(indazol-1-ylcarbonyl)pyridine-*N*,*N*,*N*}] (**4**). Yield: 117 mg (71%). FTIR (KBr, cm^{-1}): *ν* 1679s (C=O), 1612m, 1347s, 1434m, 1378s, 954s, 758s, 354s (Cr–Cl) [25–27]. MS-ESI (*m*/*z*, ES^+): 525.72 $[M]^+$, 548.94 $[M+Na]^+$. *Anal.* Calc. for $C_{21}H_{13}N_5O_2Cl_3Cr$: C, 48.0; N, 13.3; H, 2.5. Found: C, 47.0; N, 13.0; H, 3.3%. $\mu_{eff} = 4.0\mu_B$.

2.4. X-ray crystal structure analysis for *2*

Formula $C_{21}H_{13}N_5O_2$, $M = 367.36$, colorless crystal $0.30 \times 0.10 \times 0.05$ mm, $a = 7.5103(2)$, $b = 10.5246(3)$, $c = 11.4631(3)$ Å, $\alpha = 85.214(2)$, $\beta = 80.140(2)$, $\gamma = 71.688(2)°$, $V = 2632.0(4)$ Å^3, $\rho_{calc} = 1.440$ g cm^{-3}, $\mu = 0.796$ mm^{-1}, empirical absorption correction (0.796 *T* 0.961), $Z = 2$, triclinic, space group $P\bar{1}$ (No. 2), $\lambda = 1.54178$ Å, $T = 223$ K, ω and φ scans, 8654 reflections collected (*h*, *k*, *l*), $[(\sin\theta)/\lambda] = 0.60$ Å^{-1}, 2943 independent ($R_{int} = 0.039$) and 2569 observed reflections [I 2(I)], 253 refined parameters, $R = 0.039$, $wR^2 = 0.097$, maximum residual electron density 0.16 (−0.20) e Å^{-3}, hydrogens calculated and refined as riding atoms.

Data set was collected with a Nonius Kappa CCD diffractometer. Programs used: data collection COLLECT [14a], data reduction Denzo-SMN [14b], absorption correction Denzo [14c], structure solution SHELXS-97 [14d], structure refinement SHELXL-97 [14e], graphics XP [14f].

2.5. Computational details

Density functional calculations were carried out using the ADF 2008.01 code[1] at the relativistic level incorporating scalar corrections via the ZORA Hamiltonian [15,16], in conjunction with all electron triple-ξ Slater type basis set plus polarization function (STO-TZP). Geometry optimizations were carried out via the analytical energy gradient method implemented by Verluis and Ziegler [17] under the unrestricted formalism.[2] Non-local exchange and correlations (XC) terms were incorporated via general gradient approximation (GGA), within the exchange functional proposed by Becke's 1988 [18] and the correlation by Perdew's 1986 (BP86) [19]. The symmetry was constrained to C_{2v} and C_s for *mer* and *fac* isomers, respectively.

2.6. Catalytic reactions

The polymerization reactions were carried out by charging a 100 mL Parr stainless steel autoclave (in a glovebox under an inert nitrogen atmosphere) with toluene (24 mL) and the desired amount of cocatalyst (MAO, 10 wt.% in toluene) and complex **3** (2.49 μmol) and **4** (2.28 μmol). The autoclave was sealed, brought out of the glovebox and connected to a mechanical stirrer, temperature controller and an ethylene line. The gas was fed continuously into the reactor to a pressure of 3.5 bar. After 20 min the ethylene was vented and the reaction ended by the addition of

[1] Amsterdam Density Functional (ADF) code, Release 2008, Vrije Universiteit, Amsterdam, The Netherlands.

[2] Unrestricted in the sense that we have different orbitals for different spin (α and β).

HCl–methanol (20% v/v). The polymer was isolated by filtration, washed with acetone and dried overnight at room temperature. The polymers were characterized by infrared spectroscopy (FTIR), gel permeation chromatography (GPC) and differential scanning calorimetry (DSC). GPC analysis was performed on a Polymer Laboratories high temperature GPC system; model PL 220, equipped with a refractive index detector. Samples were run at 150 °C in spectrophotometric grade 1,2,4-trichlorobenzene (TCB), stabilized with BHT (0.5 g BHT/4 L solvent). Molecular weights were calculated by using a universal calibration from narrow polystyrene standards in the molecular weight range of 580–7.5 million g/mol. Mark–Houwink parameters of $a = 0.7$ and $k = 47.7$ were utilized to correct for polyethylene. Polymer melting points (T_m) were determined by differential scanning calorimetry using a Mettler Toledo DSC 821 Calorimetry System with the heating scan at 10 °C/min from 25 to 200 °C. Reported results are those obtained in the second scan.

3. Results and discussion

2,6-Bis(3,5-dimethylpyrazol-1-ylcarbonyl)pyridine **(1)** was prepared according to reported synthetic methods [11a]. Following a similar protocol, the new tridentate N-donor ligand 2,6-bis(indazol-1-ylcarbonyl)pyridine **(2)** was prepared by reaction of 1*H*-indazole with 2,6-pyridinedicarbonyl dichloride in the presence of Et_3N, as shown in Scheme 1.

Compound **2** was isolated as white crystals in 87% yield by crystallization from chloroform-diethyl ether. In similar experimental conditions the reaction of 1*H*-indazole with 2,6-bis(bromomethyl)pyridine lead to the formation of a compound in which the indazolyl groups are bonded to the CH_2 spacer through the N2 [13]. However, in this case NMR spectroscopy confirmed the formation only of the isomer **2** where the indazole group are bonded to the C=O spacer to the N1 atom. The ^1H and ^{13}C chemical shifts were assigned with the aid of ^1H–^1H (COSY), DEPT, ^1H–^{13}C (HMQC), HMBC, and NOESY experiments.

In order to determine the molecular structure of **2**, an X-ray diffraction study was undertaken. Suitable crystals for structural determination were grown by slow diffusion of diethyl ether into a dichloromethane solution of compound **2**. A perspective view of the molecule is shown in Fig. 1.

The pyridine and indazole rings are planar and the indazole and carbonyl groups are placed on different sides of the pyridine plane. All bond distances and bond angles fall within the expected ranges.

The reaction of $CrCl_3(THF)_3$ with the tridentate ligands (**1, 2**) in THF at 70 °C for 8 h leads to high yields of green solids characterized as neutral octahedral complexes of the type [$CrCl_3${2,6-bis(azolylcarbonyl)pyridine-*N*,*N*,*N*}] [azol = 3,5-dimethylpyrazol (**3**), 1*H*-indazol (**4**)], Scheme 2.

The chromium complexes are air stable at room temperature and show a very low solubility in organic solvents. Elemental analysis, FTIR, and mass spectroscopy were used to characterize the isolated complexes. The FTIR spectra shows strong absorption bands at 1689–1719 and 348–358 cm^{-1} range which are assigned to ν(C=O) and ν(Cr–Cl), respectively [11,20,21]. The spin state of

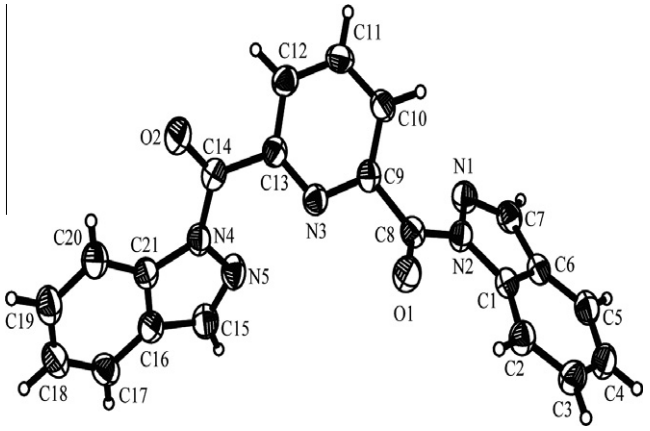
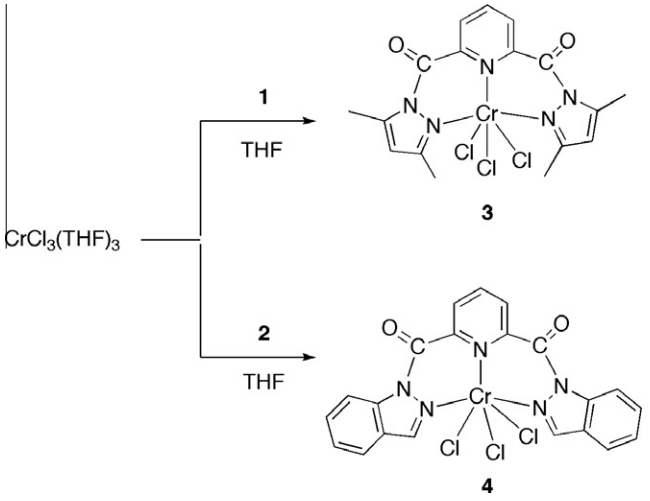


Fig. 1. ORTEP plot of compound **2**. Thermal ellipsoids are shown at the 50% probability level (H atoms omitted for clarity). The numbering is arbitrary and different from that used in the ^{13}C NMR spectrum. Select bond distances (Å) and bond angles (°): N(1)–N(2), 1.3926(18); N(2)–C(1), 1.395(2); N(1)–C(7), 1.304(2); N(2)–C(8), 1.388(2); N(3)–C(9), 1.338(2); N(3)–C(13),1.334(2); C(1)–C(6), 1.397(2); C(1)–C(2), 1.391(2); C(2)–C(3), 1.376(2); C(3)–C(4), 1.398(3); C(4)–C(5), 1.369(3); C(5)–C(6), 1.395(2); C(6)–C(7), 1.431(2); N(1)–N(2)–C(8), 122.14(13); C(8)–N(2)–C(1), 126.76(13); N(1)–N(2)–C(7), 105.77(13); N(2)–C(8)–C(9), 117.93(13); N(3)–C(9)–C(8), 113.15(14).

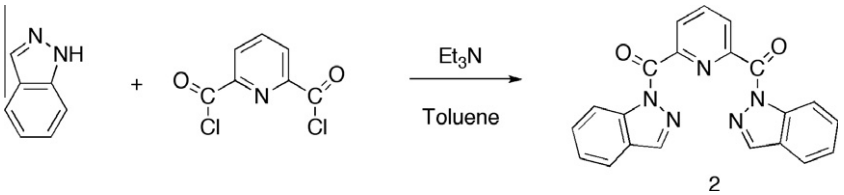


Scheme 2.

the complexes was confirmed by magnetic susceptibility measurements ($\mu_{eff} = 3.8–4.0\mu_B$), which indicate the presence of three unpaired electrons on the chromium center.

Due to the low solubility of the complexes in common solvents, all attempts to obtain single crystals appropriate for X-ray diffraction were unsuccessful. However, the spectroscopy, analytical data and theoretical calculations are consistent with the proposed formulation.

In the octahedral environment of the chromium atom the bis(azolyl)piridine ligand is tridentate and acquires a *mer* or *fac*



Scheme 1.

configuration. Some examples of *mer* configuration have been described in homoleptic complexes of the type [M(2,6-bis(pyrazol-1-ylmethyl)pyridine-*N*,*N*,*N*)$_2$]A$_2$ (M = Ni, Cd; A = ClO_4, BF_4) [10a,b] and [CuX_2(2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine-*N*,*N*,*N*)] (X = Cl^-, Br^- or NO_3^-) [10c,22]. However, the flexibility of the six-membered chelate rings allows the ligand to acquire a *fac* configuration, as reported for complex [BiI_3(2,6-bis(pyrazol-1-ylmethyl)pyridine)] [10b].

We proposed to distinguish the stability and the electronic states of both d^3 chromium complexes (**3** and **4**) since both complexes can acquire a *mer* or *fac* configuration, each with two possible electronic states (quadruplet and doublet). Density Functional (DFT) calculations were carried out with the aim to clarify the preferred ground state. In Table 1, the calculated relative binding energies of the studied systems are shown.

It is clearly observed that the *fac* isomer in the quadruplet ground state is at the lowest energy, and therefore, the thermodynamically preferred structure. This is in agreement with the interpretation of the experimental magnetic susceptibility data. Also we have tested another geometrical structure for these complexes, in which the ligand has an ONO coordination mode through the C=O moieties, resulting that the structures with this coordination are 2 eV higher in energy when compared with the already described proposed structures. Hence, we focus our discussion on the *fac* 4F complexes, with NNN coordination mode.

A comparison of some selected distances and angles, with previously reported compounds [$CrCl_3${2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine-*N*,*N*,*N*}] (**5**) and [$CrCl_3${2,6-bis(indazol-2-ylmethyl)pyridine-*N*,*N*,*N*}] (**6**) [13], are presented in Table 2. It can be seen that the presence of the C=O moiety in place of a CH_2 group, produces a change in the hybridization of the carbon atom from sp^3 to sp^2, which induces a shortening of the chromium coordinative bonds, i.e. Cr–Cl and Cr–N bonds. At the same time, there is an increase in the distance between the rings that compose the tridentate ligand structure, which is evaluated by measuring the centroid to centroid distance on each ring, see Table 2, concomitantly there is a dihedral angle increase, when taking into account the dihedral angle formed by the planes of the rings in the ligand.

Some selected frontier molecular orbitals (FMO), are presented in Fig. 2. The three orbitals in which the three unpaired electrons are located, belong the "t_{2g}" block, in analogy to a d^3 metal in an octahedral arrangement, denoting a high participation of the $(n-1)d_{xy}$, $(n-1)d_{xz}$ and $(n-1)d_{yz}$ metallic orbitals and the *np* orbitals of the chloride nucleus, with an almost negligible participation of the tridentate ligand (<3%). The next lowest occupied orbitals can be referred to the "t_{1u}" block, mainly composed of the n*p* orbitals of the chloride ligands, similarly to the results obtained for **5** and **6** [13]. However, the unoccupied "e_g" orbitals in the titled complexes are located in LUMO+2 and LUMO+3, i.e. in higher unoccupied orbitals than **5** and **6** [13], where the LUMO and LUMO+1 in the present case corresponds to a ligand centred orbitals (Fig. 2), in contrast with **5** and **6**, where the "e_g" block is located at LUMO and LUMO+1 [13].

Table 1
Relative binding energies (eV).

	Relative binding energies (eV)
Indazol	
fac ^{4}F	0.00
fac ^{2}P	0.76
mer ^{4}F	0.05
mer ^{2}P	0.88
Pirazol	
fac ^{4}F	0.00
fac ^{2}P	0.83
mer ^{4}F	0.77
mer ^{2}P	1.58

Table 2
Selected bond distances (Å) and angles (°).

	Indazol	**6**[a]	Pyrazol	**5**[a]
d Cr–Cl[b]	2.299	2.313	2.285	2.313
d Cr–N[c]	2.122	2.350	2.108	2.303
d Cr–N[d]	2.134	2.241	2.145	2.294
d $Centroid_{py}$–$Centroid_L$[e]	4.854	4.534	4.758	4.637
d $Centroid_L$–$Centroid_L$[f]	5.231	4.826	5.664	5.536
L–L angle[g]	132.9	98.3	139.8	120.3
Py-L angle[h]	153.1	122.4	151.2	133.4

[a] Data from reference [13].
[b] Average values.
[c] Referred as the distance between the chromium and the nitrogen of the pyridine fragment of the ligand.
[d] Referred as the distance between the chromium and the nitrogen of the indazol or pyrazol fragment of the ligand respectively.
[e] The distance between the centroid of the pyridine ring and the centroid of the indazol or pyrazol ring.
[f] The distance between the centroids of both indazol or pyrazol rings.
[g] The dihedral formed by both planes of the indazol or pyrazol rings.
[h] The dihedral formed by the planes of the pyridine ring and the indazol or pyrazol rings.

In order to obtain more information about the electronic reorganization due to the differences in the multidentade ligand, calculations of the electrostatic potential surface were performed. As can be observed in Fig. 3, there non-exist significant variations when the CH_2 is replaced by a C=O moiety, compare **6** to **4** or **5** to **3**, however the presence of the C=O group produce a small increase in the electrostatic potential over the carbon atom in the tridentate ligand. These results suggest that the catalytic activity can be increased in complexes which contain the C=O moiety, due to a deshielding effect caused by a diminishing of the steric hindrance (Fig. 3), and hence, allows a more effective interaction with the MAO.

Considering that the most probable structure of the complexes is a *fac* configuration, the behaviour of complexes **3** and **4** as initiators for ethylene polymerization under mild reaction conditions was studied, in order to compare these activities with those recently described for related bis(azolylmethyl)pyridine chromium(III) complexes [13].

The catalytic behaviour of the complexes in the presence of methylaluminoxane (MAO) and the properties of the polymers are summarized in Table 3. It is noteworthy that we did not observe the presence of waxes after filtration of the solid polymer and evaporation the toluene solutions. However we did not analyze the solutions by GC, and we cannot confirm that small quantities of oligomers are possibly formed.

Analysis of the data shows that complex **4** has a higher activity than complex **3**, indicating that the more extended conjugation of the indazole rings makes the metal center more electron deficient, increasing the reactivity of the coordinated ethylene.

The new compound **4** presents higher activity than those shown by the bis(indazolylmethyl)pyridine chromium(III) complex under similar conditions (152 kg PE mol Cr^{-1} bar^{-1} h^{-1}) [13]. This is likely due to the presence of the carbonyl moiety as spacer group, which interacts with MAO through Lewis acid-base interaction that decreases the electronic density at the metal center. This type of interaction was observed in palladium complexes containing bis(1,3-R_2pyrazolylcarbonyl)benzene where the presence of a carbonyl group reduced the σ-donor ability of the nitrogen donor atoms [23]. Recently the catalytic behaviour of nickel complexes bearing α-keto-β-diimine ligands was described and it was concluded that the increase in reactivity is a result of the attachment

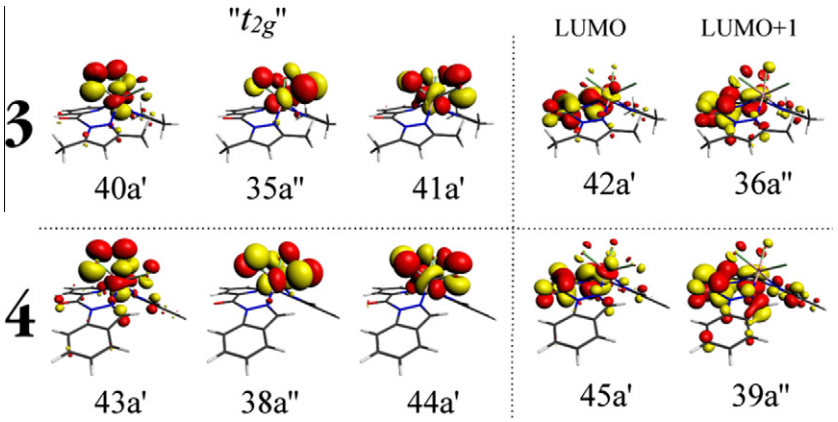


Fig. 2. Selected frontier molecular orbitals of compounds **3** and **4**.

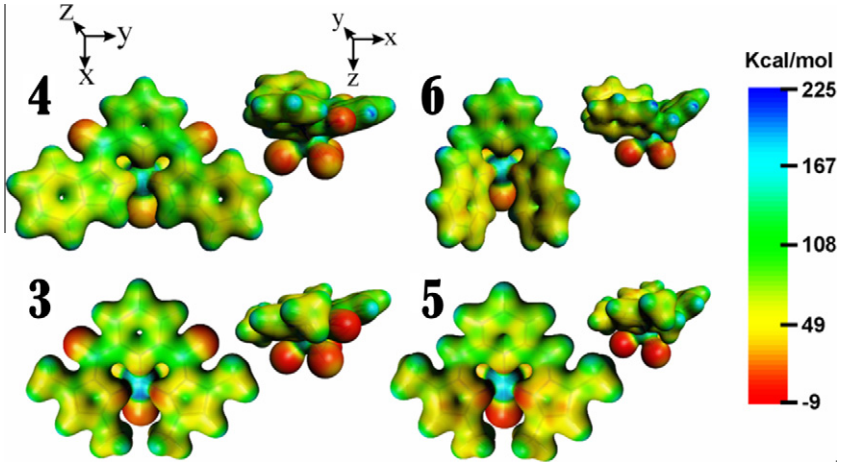


Fig. 3. Electrostatic potential surface in Kcal/mol. [$CrCl_3${2,6-bis(indazol-1-ylcarbonyl)pyridine-*N*,*N*,*N*}] (**4**), [$CrCl_3${2,6-bis(indazol-2-ylmethyl)pyridine-*N*,*N*,*N*}] [13] (**6**), [$CrCl_3${2,6-bis(3,5-dimethylpyrazol-1-ylcarbonyl)pyridine-*N*,*N*,*N*}] (**3**) and [$CrCl_3${2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine-*N*,*N*,*N*}] (**5**) [13].

Table 3
Polymerization experiments.[a]

Precatalyst	Precatalyst (μmol)	Al/Cr	Yield (g)	Activity[b]	T_m (°C)	Mw (g/mol)	Mn (g/mol)	Mw/Mn
3	2.49	1500	0.14	48.3	143	293 000	85 000	3.5
4	2.28	1500	0.68	256.7	133	273 000	81 000	3.4
3	2.49	500	0.08	28.5	137	113 000	51 000	2.2
4	2.28	500	0.20	76.3	134	168 000	54 000	3.1

[a] Reaction conditions: solvent, toluene (24 mL); polymerization time, 20 min; stirrer rate, 600 rpm; reaction temperature, 60 °C; pressure, 3.5 bar.
[b] kg polymer/(mol precat.) (h)(bar).

of a Lewis acid to the exocyclic oxygen site, increasing the cationic character of the metal center [24].

The new complexes show good activity compared to values generally reported for non-metallocene chromium catalysts [1c]; however, their activities are lower than those shown by the related chromium(III) complexes containing tridentate N-donor ligands. Complexes bearing bis(imino)pyridine for example, are very active catalysts for ethylene polymerization, showing activities of up to 4140 kg PE mol Cr^{-1} bar^{-1} h^{-1} [4]. Some chromium derivatives containing bis(benzimidazolyl)methyl amine, upon activation with MAO (ratio Al/Cr ca. 8000), afford highly active catalysts for the linear oligomerization of ethylene (ca. 5000 kg PE mol Cr^{-1} bar^{-1} h^{-1}) [6a].

It must be considered that the different activities found depend in all cases on the conditions used in the polymerization reaction (ratio Al/Cr, pressure, temperature). The polymers obtained in the polymerization were characterized using GPC, DSC and FTIR. GPC analysis of the resulting polymers shows high molecular weights (Mw) and molecular weight distributions (PDI) with values varying between 2.2 and 3.5, higher than which corresponds to single site catalysts. As to the thermal properties, DSC analysis showed melting points in the 133–134 °C range, indicating the absence of branching in the polymer chain, as confirmed by the FTIR spectra, which show the typical linear polyethylene signals; ν(CH), 2918 and 2850 cm^{-1}; δ(CH), 1473 and 719 cm^{-1} [25].

4. Conclusions

In summary, we have synthesized and fully characterized new air-stable octahedral chromium(III) complexes bearing the tridentate ligands 2,6-bis(3,5-dimethylpyrazol-1-ylcarbonyl)pyridine

and 2,6-bis(indazol-1-ylcarbonyl)pyridine. Theoretical studies and magnetic experimental data show that the thermodynamically preferred structures are the *fac* rather than the *mer* isomers, allowing a more effective interaction with of the methylaluminoxane (MAO). As direct consequence, the chromium complexes with the *fac* conformation in the presence of MAO, catalyse the polymerization of ethylene with good activity, producing high molecular weight linear polyethylene. In addition these catalysts show high activity for ethylene polymerization when compared with known chromium systems.

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Appendix A. Supplementary material

CCDC 798250 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.08.065.

References

[1] (a) K.H. Theopold, Eur. J. Inorg. Chem. (1988) 15;
(b) G.J.P. Bristovsek, V.C. Gibson, D.F. Wass, Angew. Chem., Int. Ed. Engl. 38 (1999) 429;
(c) V.C. Gibson, S.K. Spitzmesser, Chem. Rev. 103 (2003) 283.
[2] (a) B.L. Small, M. Brookhart, A.M.A. Bennett, J. Am. Chem. Soc. 120 (1998) 4049;
(b) B.L. Small, M. Brookhart, J. Am. Chem. Soc. 120 (1998) 7143;
(c) B.L. Small, M. Brookhart, Macromolecules 32 (1999) 2120.
[3] (a) G.J.P. Bristovsek, M. Bruce, V.C. Gibson, B.S. Kimberley, P.J. Maddox, S. Mastroianni, S.J. Mc Tavish, C. Redshaw, G.A. Solan, S. Strömberg, A.J.P. White, D.J.J. Williams, J. Am. Chem. Soc. 121 (1999) 8728;
(b) G.J.P. Bristovsek, S. Mastroianni, G.A. Solan, S.P.D. Baugh, C. Redshaw, V.C. Gibson, A.J.P. White, D.J.J. Williams, M.R.J. Elsegood, Chem. Eur. J. 6 (2000) 2221;
(c) G.J.P. Bristovsek, V.C. Gibson, B.S. Kimberley, S. Mastroianni, C. Redshaw, G.A. Solan, A.J.P. White, D.J.J. Williams, J. Chem. Soc., Dalton Trans. (2001) 1639;
(d) G.J.P. Bristovsek, V.C. Gibson, S. Mastroianni, D.C. Oakes, C. Redshaw, G.A. Solan, A.J.P. White, D.J.J. Williams, Eur. J. Inorg. Chem. (2001) 431;
(e) G.J.P. Bristovsek, V.C. Gibson, S.K. Spitzmesser, K.P. Telmann, A.J.P. White, D.J. Williams, J. Chem. Soc., Dalton Trans. (2002) 1159.
[4] (a) M.A. Esteruelas, A.M. López, L. Méndez, M. Oliván, E. Oñate, New J. Chem. 26 (2002) 1542;
(b) M.A. Esteruelas, A.M. López, L. Méndez, M. Oliván, E. Oñate, Organometallics 22 (2003) 395.
[5] B.L. Small, M.J. Cartney, D.H. Holman, C.E. O'Rourke, J.A. Halfen, Macromolecules 37 (2004) 4375.
[6] (a) A.K. Tomov, J.J. Chirinos, R.J. Long, V.C. Gibson, M.R.J. Elsegood, J. Am. Chem. Soc. 128 (2006) 7704;
(b) V.C. Gibson, A.K. Tomov, To BP Chemical Ltd., WO 2004/083263.;
(c) A.K. Tomov, J.J. Chirinos, D.J. Jones, R.J. Long, V.C. Gibson, J. Am. Chem. Soc. 127 (2005) 10166.
[7] M.J. Cartney, N.J. Robertson, J.A. Halfen, L.N. Zakharov, A.L. Rheingold, Organometallics 23 (2004) 6184.
[8] R. Rojas, M. Valderrama, G. Wu, Inorg. Chem. Commun. 7 (2004) 1295.
[9] (a) T. Yoshida, T. Yamamoto, H. Okada, H. Murakita, US2002/0035029 (Tosoh Corporation), January 16, 2001;
(b) I. García-Orozco, R. Quijada, K. Vera, M. Valderrama, J. Mol. Catal. A: Chem. 260 (2006) 70.
[10] (a) A.W. Watson, D.A. House, P.J. Steel, Inorg. Chim. Acta 130 (1987) 167;
(b) D.L. Reger, R.F. Semeniuc, M.D. Smith, Cryst. Growth Des. 5 (2005) 1181;
(c) P. Manikandan, K.R.J. Thomas, P.T. Manoharan, J. Chem. Soc., Dalton Trans. (2000) 2779;
(d) S. Mahapatra, N. Gupta, R. Mukherjee, J. Chem. Soc., Dalton Trans. (1991) 2911.
[11] (a) M.S. Mohlala, I.A. Guzei, J. Darkwa, S.F. Mapolie, J. Mol. Catal. A: Chem. 241 (2005) 93;
(b) H.S. Abbo, S.F. Mapolie, J. Darkwa, S.J.J. Titinchi, J. Organomet. Chem. 692 (2007) 5327.
[12] L.L. de Oliveira, R.R. Campedelli, A.L. Bergamo, A.H.D. dos Santos, O.L. Casagrande, J. Braz. Chem. Soc. 21 (2010) 1318.
[13] J. Hurtado, D. Mac-Leod Carey, A. Muñoz-Castro, R. Arratia-Pérez, R. Quijada, G. Wu, R. Rojas, M. Valderrama, J. Organomet. Chem. 694 (2009) 2636.
[14] (a) B.V. Nonius (1998).;
(b) Z. Otwinowski, W. Minor, Methods Enzymol. 276 (1997) 307;
(c) Z. Otwinowski, D. Borek, W. Majewski, W. Minor, Acta Crystsallogr., Sect. A 59 (2003) 228;
(d) G.M. Sheldrick, Acta Crystsallogr., Sect. A 46 (1990) 467;
(e) G.M. Sheldrick, Acta Crystsallogr., Sect. A 64 (2008) 112;
(f) Bruker AXS (2000).
[15] E. Van Lenthe, E.J. Baerends, J.G. Snijders, J. Chem. Phys. 101 (1994) 9783.
[16] E. Van Lenthe, E.J. Baerends, J.G. Snijders, J. Chem. Phys. 99 (1993) 4597.
[17] L. Verluis, T. Ziegler, J. Chem. Phys. 88 (1988) 322.
[18] A.D. Becke, Phys. Rev. A 38 (1988) 3098.
[19] J.P. Perdew, Phys. Rev. B 33 (1986) 8822.
[20] A. Sánchez-Méndez, G.F. Silvestri, E. de Jesús, F.J. de la Mata, J.C. Flores, R. Gómez, P. Gómez-Sal, Eur. J. Inorg. Chem. (2004) 3287.
[21] M.J. Abrams, R. Faggiani, C.J.L. Lock, Inorg. Chim. Acta 106 (1985) 69.
[22] R. Gupta, R. Mukherjee, Polyhedron 20 (2001) 2545.
[23] I.A. Guzei, K. Li, G.A. Bikzhanova, J. Darkwa, S.F. Mapolie, J. Chem. Soc., Dalton Trans. (2003) 715.
[24] J.D. Azoulay, R.S. Rojas, A.V. Serrano, H. Ohtaki, G.B. Galland, G. Wu, G.C. Bazan, Angew. Chem., Int. Ed. 48 (2009) 1089.
[25] A.M. Dominguez, A. Zárate, R. Quijada, T. López, J. Mol. Catal. A: Chem. 207 (2004) 155.