Note

Chromium(III) complexes with terdentate 2,6-bis(azolylmethyl)pyridine ligands: Synthesis, structures and ethylene polymerization behavior

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ABSTRACT

Reactions of 2,6-bis(bromomethyl)pyridine with 3,5-dimethylpyrazole and 1H-indazole yield the terdentate ligands 2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine (**5**) and 2,6-bis(indazol-2-ylmethyl)pyridine (**6**). The molecular structure of the new compound **6** was determined by single-crystal X-ray diffraction. These ligands react with the $CrCl_3(THF)_3$ complex in THF to form neutral complexes of general formula [$CrCl_3$\{2,6-bis(azolylmethyl)pyridine-*N,N,N*\}] (**7**, **8**) which are isolated in high yields as stable green solids and characterized by means of elemental analysis, magnetic moments, IR, and mass spectroscopy. 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 in the polymerization of ethylene.

1. Introduction

Homogeneous olefin polymerization catalysts based on organometallic chromium complexes has received considerable attention in recent years. A large variety of complexes have been used in different polymerization studies, employing Cp-type ligands, non-Cp ligands that posses an heteroatomic donor set, and other mixed ligands [1]. The discovery of high activity catalysts based on iron and bis(imine)pyridyl ligands, reported separately by Brookhart et al. [2] and Gibson et al. [3], increased the interest in the design of new catalysts bearing this type of ligands and other related neutral terdentate N-donor ligands. Fig. 1 shows some selected examples of octahedral chromium complexes bearing these types of ligands.

For example, Köhn et al. [4] reported that *fac*-triazacyclohexene chromium(III) complexes (**1**) activated with methylaluminoxane (MAO) can polymerize ethylene and also show some trimetrization activity. *mer*-Bis(imino)pyridyl chromium(III) complexes (**2**) using different N-aryl substituents were recently described by Esteruelas et al. [5] and Small et al. [6], showing that the complexes are active in the polymerization and/or oligomerization of ethylene, after activation by MAO. Related chromium(III) complexes derived of ligands bis(benzimidazolyl) amine or pyridine have been reported by Gibson, which behave as exceptionally active catalysts in ethylene oligomerization [7]. Cartney described the synthesis of

bis(2-pyridylmethyl)amine chromium(III) complexes (**3**), reporting that the complexes' *fac* or *mer* coordination geometry depends on the substituents of the pyridyl ring [8]. These compound are moderately active in the polymerization of ethylene in the presence of MAO, showing that the *fac* derivatives are 30–40 times more active polymerization catalysts than their *mer* counterparts. Tosoh Corporation [9a] reported that *fac*-tris(pyrazolyl)methane chromium(III) complexes (**4**) are active and selective ethylene trimerisation catalysts in the presence on MAO under high ethylene pressure. Recently we reported that these types of complexes are active in the polymerization of ethylene at low pressure in the presence of MAO. The use of a substituent on the central carbon atom of the ligand has greater influence on polymerization activity than the pyrazole ring substituents [9b]. We had previously reported the synthesis and activity of the anionic complex [$CrCl_3$\{HB(Pz)$_3$\}]$^-$, which shows moderate activity and a wide molecular weight distribution associated with the presence of more than one active species [10].

Metal complexes containing related terdentate ligands derived from two pyrazolyl groups connected by a spacer atom to the central pyridine ring have been described [11]. Recently, the [2,6-(3,5-Me$_2$pzCH$_2$)py]VCl$_3$ complex has been described as an active precursor, in the presence of AlEtCl$_2$ as co-catalyst, for ethylene polymerization under relatively mild conditions [12].

In the search for related polymerization catalysts, in this paper we report the synthesis and characterization of new neutral chromium(III) complexes supported by 2,6-bis(azolylmethyl)

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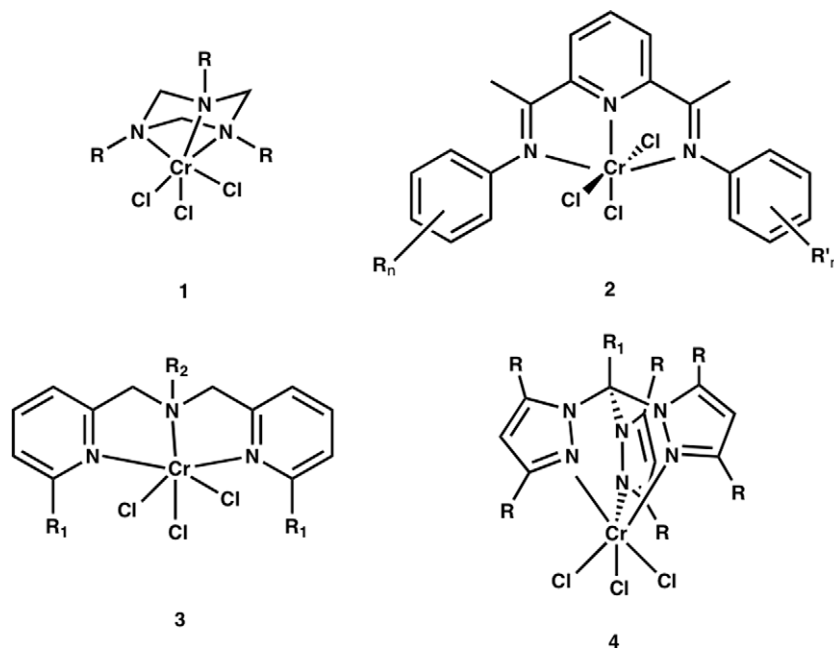 E-mail address: jmvalder@puc.cl (M. Valderrama).

Fig. 1. Selected chromium complexes with terdentate N-donor ligands.

pyridyl ligands. The molecular structure of the ligand 2,6-bis(indazol-2-ylmethyl)pyridine was determined by single-crystal X-ray diffraction. The chromium complexes in the presence of methylaluminoxane (MAO) catalyse the polymerization of ethylene with good activity.

2. Experimental

2.1. General

All manipulations were routinely performed in an inert atmosphere (nitrogen) using standard glove box and Schlenk-tube techniques. All reagent-grade solvents were dried, distilled, and stored under a nitrogen atmosphere. The starting compounds $CrCl_3(THF)_3$, 3,5-dimethylpyrazole, 1H-indazole, and 2,6-bis(bromomethyl)pyridine, from Aldrich, were used as received. Elemental analyses (C, H and N) were made with a Fisons EA 1108 microanalyzer. FTIR spectra were recorded on a Bruker Vector-22 spectrophotometer using KBr pellets. NMR spectra were recorded on a Bruker Avance-400 spectrometer. Chemical shifts are reported in ppm relative to $SiMe_4$ (^{1}H) as 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 ligands

2.2.1. Synthesis of 2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)-pyridine (**5**)

This ligand was prepared by modified literature procedures [11a]. In a Schlenk tube equipped with a reflux condenser, 3,5-dimethylpirazole (1.970 g, 20.5 mmol), potassium hydroxide (2.314 g; 41.2 mmol), tetrabutylammonium bromide (0.212 g; 0.63 mmol), and water (1 mL) were stirred at room temperature (r.t.) for 25 min, then 2,6-bis(bromomethyl)pyridine (2.55 g; 9.6 mmol) and toluene (25 mL) were added and the mixture was refluxed for 72 h. The resulting mixture was treated with water and the organic layer was separated and dried with magnesium sulphate. The

solution was evaporated to dryness to give a white solid, which was recrystallized from diethyl ether. Yield 1.858 g (66%). M.p.: 114–115 °C. IR (KBr, cm^{-1}): ν 1596m, 1580s, 1550s, 1481m, 1460s, 1419s, 1382s, 1356s, 1306m, 1257w, 1220w, 1153w, 1123w, 1091w, 1029m, 975w, 993w, 925w, 813w, 774s, 598w, 576w, 471w, 265m. NMR (CDCl$_3$, 295 K): ^{1}H δ 2.16 (s, 6H, Me$_5$-pz), 2.24 (s, 6H, Me3-pz), 5.87 (s, 2H, H4-pz), 5.30 (s, 4H, CH$_2$), 6.59 (d, 2H, J(HH) = 7.8 Hz, H3-py) and 7.50 (t, 1H, J(HH) = 7.8 Hz, H4-py) ppm. ^{13}C{^{1}H}: δ 11.21 (Me5), 13.67 (Me3), 54.4 (CH$_2$), 105.8 (C4, pz), 119.64 (C3,3′-py), 138.26 (C4-py), 139.91 (C5-pz), 147.82 (C3-pz) and 157.22 (C1-py) ppm. MS-ESI (m/z, ES$^+$): 296.2 [M+H]$^+$, 318.2 [M+Na]$^+$. Anal. Calc. for C$_{17}$H$_{21}$N$_5$: C, 69.1; N, 23.7; H, 7.2. Found: C, 69.1; N, 23.4; H, 7.5%.

2.2.2. Synthesis of 2,6-bis(indazol-2-ylmethyl)pyridine (**6**)

In a Schlenk tube equipped with a reflux condenser, 1H-indazole (0.567 g; 4.8 mmol), 2,6-bis(bromomethyl)pyridine (0.637 g; 2.4 mmol), triethylamine (1 mL), and toluene (50 mL) were added and the mixture was refluxed for 72 h. The resulting mixture was evaporated to dryness and the solid residue was treated with water and extracted with CHCl$_3$. The organic layer was separated, dried with magnesium sulphate, and evaporated to dryness. The solid residue was crystallized from dichloromethane-diethyl ether to give a white solid. Yield 324 mg (40%). M.p.: 178–180 °C. FTIR (KBr, cm^{-1}): ν 1626m, 1590s, 1512m, 1467m, 1435m, 1416w, 1388m, 1372w, 1162w, 1147m, 1138s, 1136m, 1007w, 991w, 975w, 811s, 792s, 755s, 731m, 689w, 646m, 552w, 324w. Atom numbering for compound **1** is as follows:
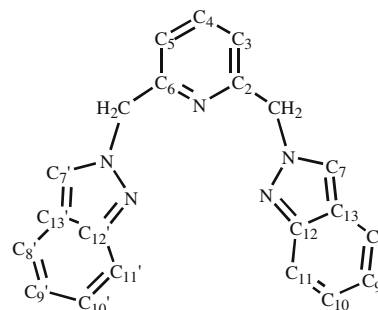
NMR (CDCl$_3$, 295 K): ^{1}H δ 5.71 (s, 4H, CH$_2$), 6.95 (d, 2H, J(HH) = 7.8 Hz, H3,5), 7.10 (t, 1H, J(HH) = 7.6 Hz, H9,9′), 7.32 (t, 2H,1H, J = 7.6 Hz, H10.10′), 7.54 (t, 2H, J(HH) = 7,8 Hz, J(HH) = 9 Hz, H4), 7.65 (d, 2H, J(HH) = 8.4 Hz, H8,8′), 7.73 (d, 2H, J(HH) = 8.7 Hz, H11,11′) and 8.04 (s, 2H, H7,7′) ppm. ^{13}C{^{1}H}: δ 59 (CH$_2$), 117.8 (C11,11′), 120.5 (C3,C5), 121.4 (C8,8′), 122.1 (C9,9′), 122.4 (C13,13′), 123.9 (C7,7′), 126.4 (C10,10′), 138.5 (C4), 149.4 (C2,C6) and 155.9 (C12,12′) ppm. MS-ESI (m/z, ES$^+$): 340.2 [M+H]$^+$, 362.1 [M+Na]$^+$. Anal. Calc. for C$_{21}$H$_{17}$N$_5$: C, 74.3; N, 20.6; H, 5.0. Found: C, 74.5; N, 20.6; H, 4.8%.

2.3. Synthesis of complexes

A solution of the 2,6-bis(azolylmethyl)pyridine ligand [2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine (118.2 mg; 0.4 mmol) and 2,6-bis(indazol-2-ylmethyl)pyridine (136.4 mg; 0.4 mmol)] in THF (15 mL) was added via syringe to a solution of CrCl$_3$(THF)$_3$ (150 mg; 0.4 mmol) in THF (15 mL). The resulting mixture was stirred at 50 °C for 8 h. The green solid formed was filtered off, washed with THF and diethyl ether, and dried under vacuum. The complex formed was purified by dissolving in N,N-dimethylformamide, filtered, and precipitated by adding diethyl ether.

(**7**) [CrCl$_3${2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine-N,N,N}] (**2**). Yield: 162 mg (86%). FTIR (KBr, cm^{-1}): ν 1607m, 1534w, 1519s, 1497m, 1471s, 1424s, 1394m, 1362s, 1291m, 1263m, 1210w, 1163w, 1128w, 1048m, 795m, 676w, 417w, 339s, 294s. MS-ESI (m/z, ES$^+$): 477.0 [M+Na]$^+$. Anal. Calc. for C$_{17}$H$_{21}$N$_5$CrCl$_3$: C, 45.0; N, 15.4; H, 4.7%. Found C, 44.5; N, 15.1; H, 4.8%. $\mu_{eff.}$ = 3.9 μ_B.

(**8**) [CrCl$_3${2,6-bis(indazol-2-ylmethyl)pyridine-N,N,N}] (**3**). Yield: 186 mg (94%). FTIR (KBr, cm^{-1}): ν 1630s, 1611m, 1578m, 1523s, 1468m, 1426s, 1362w, 1251w, 1311s, 1180m, 1164m, 1151m, 1036m, 990m, 938w, 916w, 806s, 755s, 736m, 636m, 618w, 500w, 437w, 407m, 360s, 336s, 305s. Anal. Calc. for C$_{21}$H$_{17}$N$_5$CrCl$_3$: C, 50.7; N, 14.1; H, 3.4. Found C, 50.3; N, 13.2; H, 3.5%. $\mu_{eff.}$ = 3.8 μ_B.

2.4. Crystal structure of 2,6-bis(indazol-2-ylmethyl)pyridine (**6**)

C$_{21}$H$_{17}$N$_5$, M = 339.40, colorless needles 0.30 × 0.08 × 0.06 mm in size, orthorhombic, space group Pna2(1), a = 8.2171(15), b = 6.2393(11), c = 32.072(6) Å, V = 1644.3(5) Å^3, Z = 4, D$_c$ = 1.371 Mg m^{-3}, μ (Mo Kα) = 0.085 mm^{-1}, F(0 0 0) = 712. Intensity data were collected on a Bruker Smart CCD diffractometer in $\theta/2\theta$ scan method at 150(2) K, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). 3.33 < 2θ < 26.64°, $-10 \leqslant h \leqslant 10$, $-7 \leqslant k \leqslant 7$, $-38 \leqslant l \leqslant 40$, 12 207 reflections of which 3315 were independent (R$_{int}$ = 0.0902) and were used in all calculations. The SMART program package was used for data collection [13a]. The raw frame data were processed using SAINT [13b] and SADABS [13c]. Subsequent calculations were carried out using the SHELXL-97 program [13d]. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters on non-all hydrogen atoms. H atoms were placed at geometrically idealized positions and refined using a riding model. Final R(F) = 0.1252 for 3315 reflections [I > 2σ(I)]; wR(F^2) = 0.1629 for all data; 235 parameters; goodness of fit = 1.041. Maximum peak and hole in final Fourier difference map = +0.323 and -0.243 eÅ^{-3}, respectively.

2.5. Computational details

All the calculations were carried out using the ADF 2007.01 code [14] at the relativistic level incorporating scalar corrections via the ZORA Hamiltonian [15,16]. For the calculations all electron triple-ζ Slater basis set plus polarization function (STO-TZP) were employed. Geometry optimizations were carried out via the analytical energy gradient method implemented by Verluis and Ziegler [17]. Exchange and correlations (XC) corrections 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 polymerizations were carried out by charging a 500 mL Parr autoclave reactor with toluene (100 mL), the desired amount of cocatalyst (methylaluminoxane, MAO) and catalysts **7** and **8** under nitrogen. The reactor was attached to an ethylene line, and the gas was fed continuously into the reactor at a specific pressure. The pressurized reaction mixture was stirred at a temperature (60 °C) controlled by the reactor heater. Ethylene consumption was monitored by a mass flow meter controlled inline with the ethylene feed. At the end of the reaction the ethylene feed was removed, the vessel vented, and the reaction quenched with HCl–methanol (20% V/V). The polymers produced were isolated by filtration, washed several times with acetone, and dried overnight under vacuum, and the polymerization activity was calculated from the mass of product obtained. The polymers were characterized by infrared spectroscopy (FTIR), gel permeation chromatography (GPC), and differential scanning chromatography (DSC). Molar mass distribution was obtained with a Waters (Alliance GPC 2000) high-temperature GPC instrument equipped with three Styragel HT type columns (HT3, HT5 and HT6E). 1,2,4-Trichlorobenzene was used as solvent at a flow rate of 1 mL/min and a temperature of 135 °C. The columns were calibrated with polystyrene standards. Polymer melting points (T$_m$) were determined by differential scanning calorimetry using TA Instruments DSC 2920 equipment. Heating scans at 10 °C/min from -10 °C to 170 °C. Reported results are those obtained in the second scan.

3. Results and discussion

The ligand 2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine (**5**) was prepared by a phase-transfer catalyzed reaction of 2,6-bis(bromomethyl)pyridine with 3,5-dimethylpyrazole, modifying a previously reported method [11a]. When the reaction was carried out starting from 1H-indazole, the initial deprotonation reaction with KOH gave a mixture of two regioisomers in low yield (10%), corresponding to the N1-(**6′**) and N2-(**6**) disubstituted indazoles (Scheme 1).
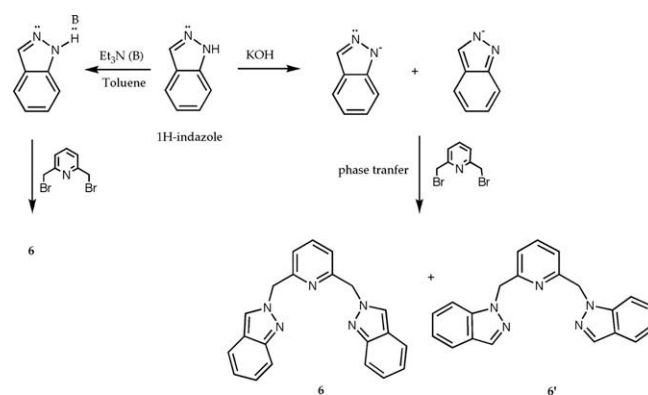

Scheme 1.

When the synthesis was carried out in refluxing toluene in the presence of noncoordinating bases such as Et$_3$N, the reaction was directed towards isomer **6**, since the electron pair located at N2 becomes more reactive than the corresponding one at N1 [20]. Compound **6** was isolated as white crystals in 40% yield by crystallization from dichloromethane-diethyl ether. NMR spectroscopy confirmed the formation of isomer **6**. The ^{1}H and ^{13}C chemical shifts were assigned with the aid of ^{1}H–^{1}H^1 (COSY), DEPT, ^{1}H–^{13}C (HMQC), HMBC, and NOESY experiments (see Section 2).

In order to obtain an unambiguous characterization of isomer **6**, 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 **6**. A perspective view of the molecule is shown in Fig. 2,

The pyridine and indazole rings are each planar and the indazole groups connected to the methylene spacers are placed on opposite side of the pyridine plane. The structure has two-fold crystallographic symmetry (C_2) and all bond distances and bond angles fall within the expected ranges.

The reaction of CrCl$_3$(THF)$_3$ with the terdentate ligands (**5**, **6**) in tetrahydrofuran at 50 °C leads to high yields of green solids characterized as neutral octahedral complexes of the type [CrCl$_3${2,6-bis(azolylmethyl)pyridine-*N,N,N*}]   [azolyl = 3,5-dimethylpyrazol-1-yl (**7**), indazol-2-yl (**8**)], Scheme 2.
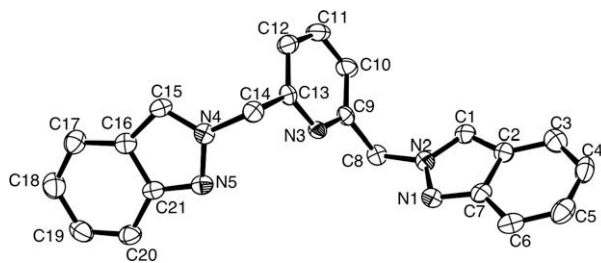
Fig. 2. ORTEP plot of ligand **6**. Thermal ellipsoids are shown at the 50% probability level (H atoms omitted for clarity). The numbering is arbitrary and different from that used in the ^{13}C NMR spectrum. Select bond distances (Å) and bond angles (°): N(1)–N(2), 1.356(5); N(2)–C(1), 1.334(5); N(1)–C(7), 1.339(5); N(2)–C(8), 1.458(5); N(3)–C(9), 1.330(5); N(3)–C(13),1.337(5); C(1)–C(2), 1.385(6); C(2)–C(3), 1.402(6); C(2)–C(7), 1.422(6); C(3)–C(4), 1.358(6); C(4)–C(5), 1.399(7); C(5)–C(6), 1.369(6); C(6)–C(7), 1.411(6); N(1)–N(2)–C(8), 119.2(3); C(8)–N(2)–C(1),126.8(3); N(1)–N(2)–C(1), 114.0(3); N(2)–C(8)–C(9), 112.5(3); N(3)–C(9)–C(8), 116.1.
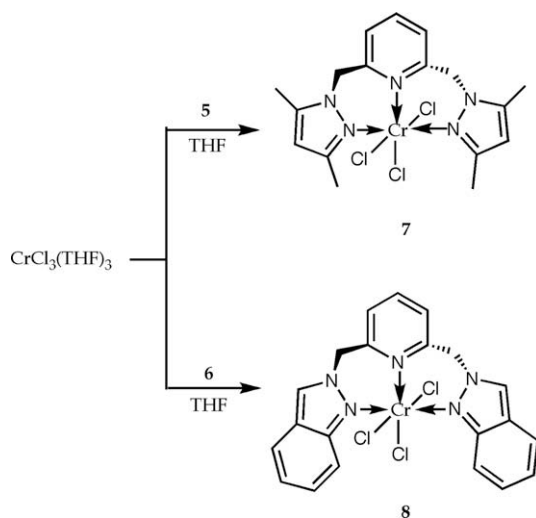
Scheme 2.

Table 1
Relative binding energies (eV) and main distances (Å) for the calculated compounds.

	Relative binding energies (eV)	d Cr–Cl[a]	d Cr–N[b]	d Cr–N[c]
7				
fac ^{4}F	0.00	2.313	2.303	2.294
fac ^{2}P	0.93	2.308	2.298	2.290
mer ^{4}F	1.04	2.307	2.243	2.230
mer ^{2}P	1.92	2.303	2.232	2.226
8				
fac ^{4}F	0.00	2.313	2.350	2.241
fac ^{2}P	0.90	2.301	2.330	2.241
mer ^{4}F	1.20	2.315	2.241	2.232
mer ^{2}P	2.06	2.300	2.217	2.231

[a] Average values.
[b] Referred as the distance between the chromium and the nitrogen of the pyridine fragment.
[c] Distance of the chromium and the nitrogen of the indazol or pyrazol fragments.

The chromium complexes are stable in air at room temperature and show very low solubility in organic solvents. Elemental analysis, FTIR, and mass spectroscopy were used to characterize the isolated complexes. The solid state FTIR spectra in KBr pellets show strong absorption bands in the 1519–1523 and 294–360 cm^{-1} ranges, assigned to *v*(C–N) and *v*(Cr–Cl), respectively [21,22]. The spin state of the complexes was confirmed by magnetic susceptibility measurements ($\mu_{eff.} \approx 3.8$–3.9 μ_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 ligand is acting in its tridentate form. The molecular structure of ligand **6** shows that the disposition of the donor nitrogen atoms is probably the most appropriate to form a *mer* configuration. Some examples of this type of 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$_4$) [11a,b] and [CuCl$_2$(2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine-*N,N,N*)] (X = Cl, N$_3$) [23]. However, the flexibility of the six-membered chelate rings formed, allows the ligands to acquire a *fac* configuration, as reported for complex [BiI$_3$(2,6-bis(pyrazol-1-ylmethyl)pyridine)] [11b].

As stated before, two isomers, namely *fac* and *mer*, can exist, and also two possible electronic states, quadruplet and Kramer's doublet. Due to these facts, we investigated theoretically which of those isomers and electronic states would be preferred.

Table 1 shows the relative energies and selected distances of the systems studied. It is seen that the thermodynamically preferred structures are the *fac* isomers rather than the *mer* isomers, and also the quadruplet ground state is thermodynamically preferred compared to the doublet in all cases. Table 1 also shows the variation of the chromium-ligand distances in the compounds. The chromium-chloride distance remains almost unchanged, compared to the chromium–nitrogen distances in the *fac* and *mer* isomers. The chromium–nitrogen distances from the pyridine and indazol or pyrazol fragments, respectively, are longer in the *fac* than in the *mer* isomers due to the steric repulsion exerted by the methyl groups in **7** or the six-member ring in **8**.

Fig. 3 shows the MO Diagram of the two quadruplet *fac* isomers of systems **7** and **8** under the unrestricted DFT formalism.[1] It must

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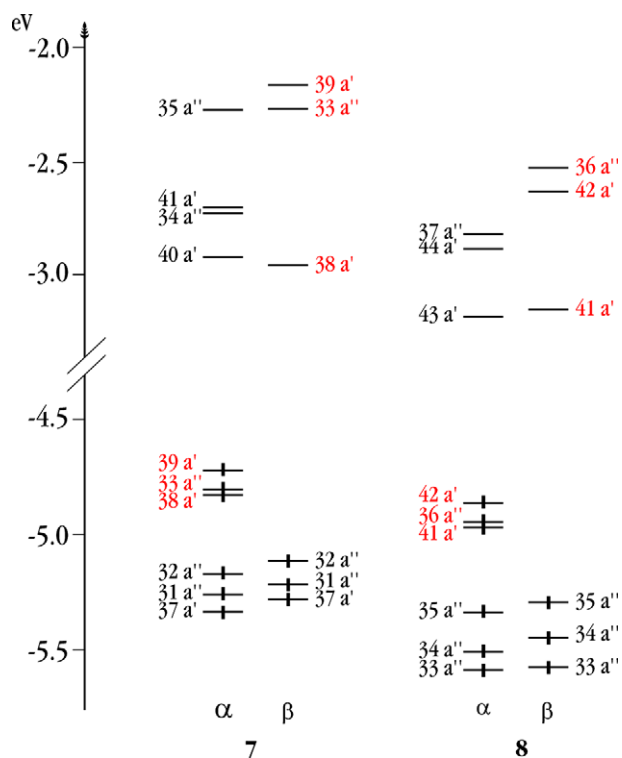[1] Unrestricted in the sense that we have different orbitals for different spin (α and β).

Fig. 3. MO Diagram of the quadruplet *fac* isomers of **7** and **8** complexes.

Table 2
Results of the ethylene polymerization experiments.[a]

Precatalysts	[Precat.] (mol 10)	Yield (g)	Activity[b]	T_m (°C)	M_w (g/mol)	M_n (g/mol)	M_w/M_n
7	8.15	3.8	115	133	78 196	45 039	1.74
8	8.00	4.9	152	135	126 929	59 120	2.15

[a] Reaction conditions: solvent, toluene (100 mL); MAO/toluene 10% (15 mL); Al/Cr ratio ~3000; polymerization time, 1 h; stirrer rate, 1000 rpm; reaction temperature, 60 °C; pressure, 4 bar.
[b] kg polymer/(mol precat.)(h)(bar).

derivatives [9b]. The catalytic behavior of the complexes in the presence of methylaluminoxane (MAO) and the properties of the polymers are summarized in Table 2.

Analysis of the data show that complex **8** have higher activity than complex **7**, indicating that the more extended conjugation of the indazole rings makes the metal centre more electron deficient, increasing the reactivity of the coordinated ethylene. The new compounds present activities lower than those shown by the *fac*-tris(pyrazolyl)methane chromium(III) complexes under similar conditions (320 kg PE mol Cr^{-1} bar^{-1} h^{-1}), probably due to the lower constrained effect produced by the bis(azolylmethyl)pyridine ligands [9b,21].

The new complexes show good activity compared to general values reported for non-metallocene chromium [1c]; however, their activities are lower than those shown by the related chromium(III) complexes containing terdentate N-donor ligands. As example, complexes bearing bis(imino)pyridine are very active catalysts for ethylene polymerization, showing activities up to 4140 kg PE mol Cr^{-1} bar^{-1} h^{-1} [5]. 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}) [7]. 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).

GPC, DSC and FTIR techniques characterized the polymers obtained in the polymerization. GPC analysis of the resulting polymers shows high molecular weights (M_w), with a monomodal molecular weight distribution (M_w/M_n) that correspond to a single-site catalyst. As to the thermal properties, DSC analysis showed melting points in the 133–135 °C range, indicating the absence of branching in the polymer chain, as confirmed by the FTIR spectra, which show the typical linear polyethylene signals; v(CH), 2918 and 2850 cm^{-1}; δ(CH), 1473 and 719 cm^{-1} [24].

4. Conclusions

In summary, we have synthesized and fully characterized new air-stable octahedral chromium(III) complexes bearing the terdentate ligands 2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyri-
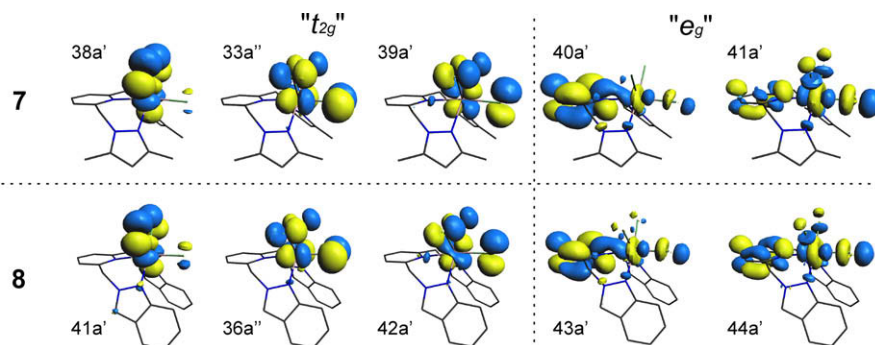
be noted the high energy separation between the occupied and unoccupied orbitals (Gap > 1.5 eV) indicates the high stability of these systems compared to the other isomers in which this separation is lower (see MO Diagrams in Supplementary material).

The three orbitals in which the three unpaired electrons are located belong to the so-called "t_{2g}" block, as can be expected for a d^3 metal in an octahedral arrangement, with a high participation of the d_{xy}, d_{xz} and d_{yz} metallic orbitals and the p orbitals of the chlorine nucleus, as can be seen in Fig. 4.

The next lowest orbitals correspond to "t_{1u}", proceeding from the p orbitals of the chloride ligands. The LUMO and LUMO + 1 correspond to those "e_g", presented in Fig. 4, one of which corresponds to the mixing of p orbitals from two chloride atoms and the $dx^2 - y^2$ metallic orbital, and the other corresponds to the dz^2 orbital of chromium and the LUMO + 1 of the pyridine fragment of the pincer ligand.

Considering that the most probably structure of the complexes is a *fac* configuration, we studied the behavior of complexes **7** and **8** as initiators for ethylene polymerization under mild reaction conditions, in order to compare these activities with those recently described for related *fac*-tris(pyrazolyl)methane chromium(III)

Fig. 4. The "t_{2g}" and "e_g" blocks of the quadruplet *fac* isomers for **7** and **8** complexes.

dine and 2,6-bis(indazol-2-ylmethyl)pyridine. The molecular structure of the 2,6-bis(indazol-2-ylmethyl)pyridine ligand shows that the disposition of the donor nitrogen atoms is appropriate to form a *mer* configuration; however, theoretical studies show that the thermodinamically preferred structures are the *fac* isomers rather than the *mer* configuration. Upon activation with MAO, under mild conditions the chromium(III) complexes produced high molecular weight polyethylene with narrow molecular weight distribution that corresponds to single-site catalysts.

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Appendix A. Supplementary material

CCDC 711856 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.jorganchem.2009.04.014.

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