

Substituted cyclopentadienylchromium(III) complexes containing neutral donor ligands. Synthesis, crystal structures and reactivity in ethylene polymerization

René Rojas ^a, Mauricio Valderrama ^{a,*}, María Teresa Garland ^b

^a Departamento de Química Inorgánica, Facultad de Química, Pontificia Universidad Católica de Chile, Av. Vicuña Mackenna 4860, Casilla 306, Santiago 22, Chile

^b Departamento de Física, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Santiago, Chile

Abstract

Lithium derivatives of substituted cyclopentadiene ligands reacted with $\text{CrCl}_3(\text{THF})_3$ in THF solution to afford homodinuclear complexes of the type $[\{\eta^5\text{-RCp}\}\text{CrCl}(\mu\text{-Cl})\}_2]$ [$\text{R} = \text{SiMe}_3$ (**1**), $\text{CH}_2\text{C}(\text{Me})\text{CH}_2$ (**2**)]. Complex **1** reacts with pyrazole ($\text{C}_3\text{H}_4\text{N}_2$) to yield the mononuclear half-sandwich complex $[(\eta^5\text{-Me}_3\text{SiCp})\text{CrCl}_2(\text{pyrazole})]$ (**3**). The similar complex $[\text{Cp}^*\text{CrCl}_2(\text{pyrazole})]$ (**4**) was synthesised by reaction of $[\{\text{Cp}^*\text{CrCl}(\mu\text{-Cl})\}_2]$ with pyrazole. Complex **2** reacts with bidentate ligands to give binuclear complexes of the type $[\{\eta^5\text{-CH}_2\text{C}(\text{Me})\text{CH}_2\text{Cp}\}\text{CrCl}_2\}_2(\mu\text{-L-L})]$ [$\text{L-L} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ (**5**), *trans*- $\text{Ph}_2\text{P}(\text{O})\text{CH}=\text{CHP}(\text{O})\text{Ph}_2$ (**6**)]. All complexes were structurally characterised by X-ray diffraction. After reaction with methylaluminoxane these complexes are active in the polymerization of ethylene. At 25 °C and 4 bar of ethylene, complex **3** yields polyethylene with a bimodal molecular weight distribution centred at 155,000 and 2000 g/mol. Complex **4** shows similar activity, yielding only the low molecular weight fraction. On the other hand, the binuclear complexes **5** and **6** under the same conditions were three times more active than mononuclear complexes. The melting point of the polymers indicates the formation of linear polyethylene.

Keywords: Chromium complexes; Cyclopentadienyl ligands; Olefin polymerization; Polyethylene

1. Introduction

Homogeneous olefin polymerization catalysis based on organometallic chromium(III) complexes has attracted much attention in recent years [1]. Even though the potential of chromium(III) chemistry is limited due to the paramagnetic nature of the metal centre and the low stability of the resulting complexes, a large number of chromium complexes have been described. Commonly these organochromium complexes have been stabilised by halide or alkyl groups (R), σ -donor ligands (L), and a cyclopentadienyl group ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$, $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) as one of the ligands, forming a pseudo octahedral complex with a 15-electron configuration of the type $[\text{CpCrR}_3]^-$, $[\text{CpCr}(\text{L})\text{R}_2]$ and

$[\text{CpCr}(\text{L})_2\text{R}]^+$ [2]. These types of complexes behave as a catalyst in the polymerization of olefins.

In this relation, significant advances in Cp-based chromium catalyst systems have been made using complexes with the donor ligand, usually an N- or P-donor, bridged to the Cp. These types of complexes upon activation by methylaluminoxane (MAO) provide an excellent single-site catalyst for the polymerization of olefins [3]. Moreover, isoelectronic complexes containing boratobenzene instead of Cp^* , or Cp rings containing substituents that can interact with the metal centre or with the cocatalyst [MAO, $\text{B}(\text{C}_6\text{F}_5)_3$] must be considered as other possibilities to control some of the most important properties of the polymer, such as distribution and molecular weight [2e,4,5].

On the other hand, Lappert et al. [6] have shown that the Cp ligand can be modified by introducing substituents on the cyclopentadienyl ring (alkyl, allyl, silyl), and

*Corresponding author. Tel.: +5626864417; fax: +5626864744.
E-mail address: jmvalder@puc.cl (M. Valderrama).

can be used to stabilise complexes of unusual geometry or metal oxidation state. They also show that the steric bulk exerted by the electron-withdrawing SiMe₃ group has an important effect. Solubility in non-polar solvents and the crystallinity of their complexes is also enhanced. In short, the introduction of substituents into the cyclopentadienyl ring gives rise to a diverse chemistry, particularly with complexes that are used in polymerization reactions.

We now report the synthesis and structural characterisation of new mono- and bi-nuclear substituted cyclopentadienylchromium(III) complexes of formula [(η⁵-Me₃SiCp)CrCl₂(pyrazole)], [Cp*CrCl₂(pyrazole)] and [{"(η⁵-CH₂C(Me)CH₂Cp)CrCl₂}₂(μ-L-L)] [L-L = Ph₂PCH₂CH₂PPh₂, *trans*-Ph₂P(O)CH=CHP(O)Ph₂]. We also report the activity of the new organochromium(III) complexes in the ethylene polymerization reaction.

2. Experimental

2.1. General

All manipulations were routinely performed in an inert atmosphere (nitrogen or argon) using standard glove box and Schlenk-tube techniques. All reagent grade solvents (tetrahydrofuran, toluene, *n*-pentane, diethyl ether) were distilled over sodium/benzophenone ketyl. Dichloromethane was purified by distillation over P₂O₅.

The starting compounds chlorotrimethylsilane, 3-bromo-2-methylpropene, 1,2-bis(diphenylphosphine)ethane (dppe), *trans*-1,2-bis(diphenylphosphine)ethylene (*trans*-dppethylene), pyrazole, Cp*Li, CpNa, CrCl₃ and CrCl₃(THF)₃, from Aldrich and Strem Chemical Inc., were used as received. *trans*-1,2-Bis(diphenylphosphineoxide)ethylene (*trans*-dppethyleneO₂) [7] and 1-trimethylsilylcyclopentadiene [8] were prepared according to literature procedures or modified literature procedures.

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. ¹H, ³¹P{¹H} and ¹³C{¹H} NMR spectra were recorded on a Bruker AC-200P and Avance-400 spectrometers. Chemical shifts are reported in ppm relative to SiMe₄ (¹H) and 85% H₃PO₄ (³¹P, positive shifts downfield) as internal and external standards, respectively.

2.2. Synthesis of 2-methylallylcyclopentadiene

The compound was prepared using the general method described for the synthesis of allylcyclopentadiene [9]. To a solution of sodium cyclopentadienide in

THF, prepared by reaction of sodium (3.3 g; 0.14 mol) with freshly cracked cyclopentadiene (10.0 g; 0.15 mol) in 150 ml of THF, 3-bromo-2-methylpropene (17.0 g; 0.14 mol) was added at -20 °C. After stirring at -20 °C for 8 h the mixture was filtered through Celite to give a completely clear slightly yellow solution. The solvent was carefully evaporated under reduced pressure, and vacuum distillation of the residue yielded 12.6 g (75%) of 2-methylallylcyclopentadiene isomers, b.p. 48–52 °C (10 mm). ¹H NMR (CDCl₃): δ 1.8 (s, 3H, CH₃), δ 2.9–3.2 (m, 4H, CH₂, C₅H₄; CH₂, allyl), δ 4.75 (s, 2H, CH₂, allyl) and δ 6.10–6.50 (s, 1H, CH, C₅H₄) [7].

2.3. Synthesis of [{"(η⁵-RCp)CrCl(μ-Cl)}₂] complexes

R = SiMe₃ (**1**). The compound was prepared by reacting a solution of CpSiMe₃ (200 mg; 1.44 mmol) in THF (30 ml) with a solution of *n*-butyllithium in hexane (0.95 ml of 1.6 M solution; 1.52 mmol) at -70 °C. The mixture was stirred at this temperature for 2 h, then warmed to room temperature (r.t.) and stirred for an additional 12 h. The resulting yellow solution was added to a THF suspension of CrCl₃(THF)₃ (542 mg; 1.40 mmol) at r.t. and the resulting dark blue solution was stirred for 12 h. Volatiles were removed in vacuum and the product was extracted with 20 ml of toluene. The solution was filtered through Celite and evaporated to dryness to give a dark-blue solid. The complex was crystallised from a toluene-*n*-pentane mixture. Yield: 290 mg, 77%. Anal. Found: C, 36.4; H, 5.2. C₁₆H₂₆Cl₄Cr₂Si₂ requires: C, 36.9; H, 5.0%.

R = CH₂C(Me)=CH₂ (**2**). The compound was prepared by reacting a solution of CpCH₂C(Me)=CH₂ (200 mg; 1.66 mmol) in THF (30 ml) with a solution of *n*-butyllithium in hexane (1.1 ml of a 1.6 M solution; 1.76 mmol) at -70 °C. The mixture was stirred at -70 °C for 2 h, warmed to r.t. and stirred for an additional 12 h. The resulting yellow solution was added to a THF suspension of CrCl₃(THF)₃ (623 mg; 1.60 mmol) at r.t., forming a dark green-blue solution which was stirred another 12 h. Volatiles were removed in vacuum and the product was extracted with 20 ml of toluene. The solution was filtered through Celite and evaporated to dryness to give a dark green-blue solid. Yield: 280 mg, 66%. Anal. Found: C, 47.0; H, 4.2. C₁₈H₂₂Cl₄Cr₂ requires: C, 46.7; H, 4.6%.

2.4. Synthesis of [(η⁵-Me₃SiCp)CrCl₂(pyrazole)] (**3**)

Freshly sublimed pyrazole (26 mg; 0.38 mmol) dissolved in 10 mL of THF was added at r.t. to a solution of **1** (100 mg; 0.19 mmol) in 30 ml of THF. During the addition the solution turned dark blue. After 12 h stirring at 10 °C, the solvent was removed under vacuum and the bright blue solid residue extracted with toluene (10 mL). The resulting solution was concentrated to a

small volume and the complex precipitated by addition of *n*-pentane. The product was filtered out, washed with *n*-pentane, and dried under vacuum. Yield: 60 mg, 48%. The complex was crystallised by diffusion of *n*-pentane into a toluene solution, yielding crystals as blue plates, which were washed with *n*-pentane and dried under vacuum. Anal. Found: C, 40.2; H, 5.3; N 8.4. C₁₁H₁₇N₂Cl₂CrSi requires: C, 40.3; H, 5.2; N, 8.5%. IR (KBr, cm⁻¹): ν(NH) 3303.

2.5. Synthesis of [Cp*CrCl₂(pyrazole)] (4)

A mixture of Cp*Li (200 mg; 1.407 mmol) and CrCl₃ (225 mg; 1.42 mmol) in THF (30 ml) was stirred overnight at r.t. A solution of freshly sublimed pyrazole (97 mg; 1.4 mmol) in THF (10 ml) was added and the mixture obtained was stirred at 70 °C for 24 h. The resultant solution was evaporated to dryness and the residue extracted with toluene. Removal of the solvent yielded a solid compound. Yield: 316 mg, 68%. The complex was crystallised by diffusion of *n*-pentane into a THF solution, yielding blue crystals, which were washed with *n*-pentane. Anal. Found: C, 47.8; H, 5.6; N 8.5. C₁₃H₁₉N₂Cl₂Cr requires: C, 47.9; H, 5.9; N, 8.6%. IR (KBr): ν(NH), 3396 cm⁻¹.

2.6. Synthesis of [{ (η⁵-CH₂=(Me)CCH₂Cp)CrCl₂ }₂(μ-dppe)] (5)

To a solution of **2** (167 mg; 0.34 mmol) in 40 ml of THF, dppe (135 mg; 0.33 mmol) dissolved in THF (10 mL) was added at r.t. During the addition the solution turned dark blue. After 12 h stirring at 10 °C, the solvent was removed under vacuum and the bright blue residue extracted with toluene (10 mL). The solution obtained was concentrated and precipitated with *n*-pentane. The solid complex was filtered out, washed with *n*-pentane and dried under vacuum. Yield: 200 mg, 66%. The complex was crystallised by diffusion of *n*-pentane into a toluene solution, yielding blue needle-shaped crystals, which were washed with *n*-pentane and dried under vacuum. Anal. Found: C, 59.4; H, 5.3. C₄₄H₄₆Cl₄Cr₂P₂ requires: C, 59.9; H, 5.3%.

2.7. Synthesis of [{ (η⁵-CH₂=(Me)CCH₂Cp)CrCl₂ }₂(μ-trans-dppethyleneO₂)] (6)

trans-dppethyleneO₂ (167 mg; 0.38 mmol) dissolved in THF (10 ml) was added at r.t. to a solution of **2** (200 mg; 0.41 mmol) in 40 ml of THF. The solution turned dark blue. After 12 h stirring at 10 °C the solvent was removed in vacuum and the bright blue residue extracted with toluene (10 ml). The extract was concentrated and precipitated with *n*-pentane. The complex was filtered out, washed with *n*-pentane and dried under vacuum. Yield: 320 mg, 85%. The complex was crys-

tallised by diffusion of *n*-pentane into a toluene solution, yielding blue needle-shaped crystals, which were washed with *n*-pentane and dried under vacuum. Anal. Found: C, 58.2; H, 4.9. C₄₄H₄₄Cl₄Cr₂O₂P₂ requires: C, 57.9; H, 4.8%. IR (KBr, cm⁻¹): ν(PO) 1122.

2.8. Crystal structure determination of complexes 3–6

Suitable crystals for X-ray diffraction were grown by slow diffusion of *n*-pentane into toluene solutions of the complexes. Intensity data [λ(Mo Kα) = 0.71073 Å] were collected with a Bruker SMART APEX diffractometer, using 0.3° of separation between frames. Data integration was made using SAINT. The structures were solved using XS in SHELXTL by means of direct methods, and completed by Fourier difference synthesis. Refinement until convergence was achieved using XL SHELXTL [10]. Table 1 lists the crystallographic details.

2.9. Homopolymerization

Polymerization was carried out in a 600 ml Parr autoclave glass reactor. Toluene (200 ml) and MAO were introduced into the reactor under an inert nitrogen atmosphere. The reactor was partially evacuated and then purged with ethylene. Mechanical stirring was kept constant at 1000 rpm and the ethylene pressure was adjusted to 4 bar for 5 min before introducing the pre-catalyst, which was dissolved in toluene in the presence of MAO and pumped into the reactor to initiate the polymerization. Ethylene pressure and reactor temperature (25 or 60 °C) were monitored and kept constant throughout the polymerization. Consumption of ethylene was followed continuously using a mass flow controller connected to a computer.

Turning off the ethylene feed and relieving the pressure stopped the polymerization. The reaction mixture was poured into an HCl/methanol solution (5 vol%). The insoluble polymer product was recovered by filtration, and was washed with HCl/methanol solution and acetone.

2.10. Polymer characterisation

Gel permeation chromatography (GPC) was carried out on a Waters model 150 C instrument equipped with a refractive index detector and a set of three columns, Styragel HT type (HT3, HT4, HT6). 1,2,4-Trichlorobenzene was used as solvent. The analyses were performed at 140 °C and 1.0 ml/min. The columns were calibrated with molar mass distribution standards of polystyrene, polypropylene and polyethylene.

The calorimetric analyses were carried out on a Perkin–Elmer DSC7 calorimeter connected to a cooling system and calibrated with different standards. Sample mass ranged from 7 to 10 mg. Differential scanning

Table 1
Crystallographic data and structure refinement parameters for complexes 3–6

Crystal parameters	3	4	5	6
Chemical formula	C ₁₁ H ₁₇ N ₂ SiCrCl ₂	C ₁₃ H ₁₉ N ₂ Cl ₂ Cr	C ₄₄ H ₄₆ P ₂ Cr ₂ Cl ₄	C ₄₄ H ₄₄ P ₂ O ₂ Cr ₂ Cl ₄
Formula weight	328.3	326.2	882.6	912.6
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group (no.)	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> -1
<i>Z</i>	4	4	4	2
<i>a</i> (Å)	10.783(1)	13.899(3)	13.178(3)	9.286(3)
<i>b</i> (Å)	10.340(1)	8.0906(15)	17.516(4)	10.921(3)
<i>c</i> (Å)	13.897(2)	14.131(3)	9.958(2)	12.228(4)
α (deg)	90.00	90.00	90.00	74.671(5)
β (deg)	94.024(2)	105.544(3)	109.80(3)	84.965(5)
γ (deg)	90.00	90.00	90.00	65.352(5)
Volume (Å ³)	1545.8(3)	1530.9(5)	2162.7(7)	1086.6(5)
$\rho_{\text{cal.}}$ (mg m ⁻³)	1.411	1.415	1.355	1.394
Cryst. Dimens. (mm)	0.45 × 0.15 × 0.05	0.20 × 0.20 × 0.10	0.26 × 0.20 × 0.10	0.18 × 0.14 × 0.12
Temperature (K)	293	150	293	293
θ range for data collection (°)	3.78–55.96	1.83–24.99	1.64–23.29	1.73–28.06
Index ranges	–13 ≤ <i>h</i> ≤ 14; –13 ≤ <i>k</i> ≤ 13; –9 ≤ <i>l</i> ≤ 18	–16 ≤ <i>h</i> ≤ 16; –7 ≤ <i>k</i> ≤ 9; –14 ≤ <i>l</i> ≤ 16	–14 ≤ <i>h</i> ≤ 14; –19 ≤ <i>k</i> ≤ 14; –11 ≤ <i>l</i> ≤ 10	–12 ≤ <i>h</i> ≤ 4; –14 ≤ <i>k</i> ≤ 10; –15 ≤ <i>l</i> ≤ 15
Reflections collected	3423	7780	3105	4561
Independent reflections	2372	2694	1544	1075
Refinement method	Full-matrix least-squares on <i>F</i> ²			
Data/restraints/parameters	2372/0/157	2694/0/168	1544/1/226	1075/49/235
Goodness-of-fit on <i>F</i> ²	1.0300	1.070	0.885	0.718
Final <i>R</i> indices	<i>R</i> (<i>F</i>) = 0.0426 <i>wR</i> (<i>F</i> ²) = 0.1012	<i>R</i> (<i>F</i>) = 0.0323 <i>wR</i> (<i>F</i> ²) = 0.0929	<i>R</i> (<i>F</i>) = 0.0671 <i>wR</i> (<i>F</i> ²) = 0.116	<i>R</i> (<i>F</i>) = 0.0790 <i>wR</i> (<i>F</i> ²) = 0.1952
<i>R</i> indices (all data)	<i>R</i> (<i>F</i>) = 0.0696 <i>wR</i> (<i>F</i> ²) = 0.1126	<i>R</i> (<i>F</i>) = 0.0369 <i>wR</i> (<i>F</i> ²) = 0.0959	<i>R</i> (<i>F</i>) = 0.1157 <i>wR</i> (<i>F</i> ²) = 0.1956	<i>R</i> (<i>F</i>) = 0.2567 <i>wR</i> (<i>F</i> ²) = 0.2346
Largest diff. peak and hole (e Å ⁻³)	0.386 and –0.205	0.386 and –0.344	0.686 and –0.394	0.482 and –0.392

calorimetry (DSC) melting curves were recorded at a rate of 10 °C/min. The melting temperature (*T*_m) values reported were obtained from the second heating curve.

3. Results and discussion

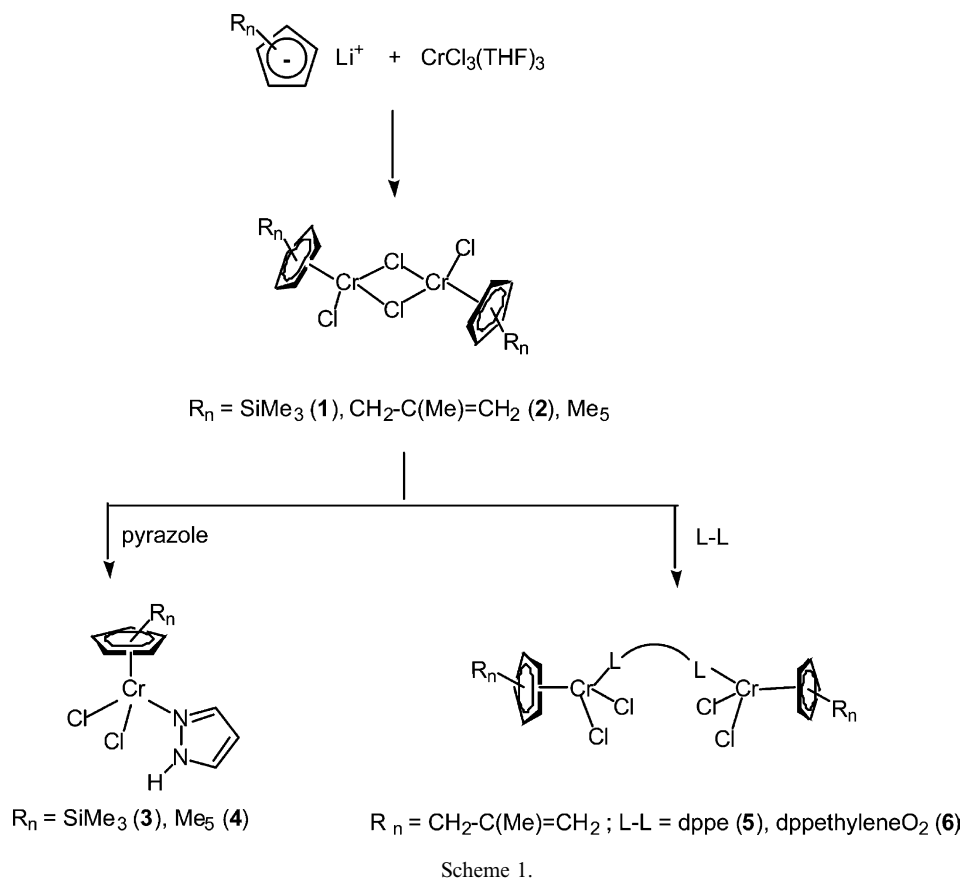
Substituted cyclopentadiene derivatives of the type RC₅H₅ (R = SiMe₃, CH₂C(Me)CH₂) have been prepared using a standard procedure that involves the reaction of trimethylsilyl chloride or methylallyl bromide with sodium cyclopentadiene. The methylallylcyclopentadienide derivative was isolated by vacuum distillation as a mixture of isomers and characterised by ¹H NMR spectroscopy. The spectrum shows various signals associated with the presence of four types of protons at δ 1,8 (s, Me), 2,9–3,2 (m, CH₂), 4,75 (s, CH₂), 6,1–6,5 (m, C₅H₄). This spectrum is in agreement with those reported by Parker and Werner [11], who obtained the methylallyl derivative by decomposition of the complex [(η^3 -methylallyl)Pd(η^5 -C₅H₅)] in the presence of a Lewis base.

The reaction of RC₅H₅ derivatives with *n*-butyllithium in THF at –70 °C leads to the formation of the corresponding lithium salts (white solids), which in turn react with CrCl₃(THF)₃ in THF at room temperature to

yield dark-blue or dark-green bimetallic complexes of formula [(η^5 -RCp)CrCl(μ -Cl)]₂ [R = SiMe₃ (**1**), CH₂C(Me)CH₂ (**2**)] (Scheme 1). The complexes are thermally stable at room temperature but decompose rapidly in the presence of air. They are excellent precursors for the preparation of half-sandwich complexes by cleavage of the chloride bridges upon reaction with donor ligands.

Thus, complex **1** reacts in THF with pyrazole (C₃H₄N₂) in a 1:2 molar ratio to yield the mononuclear complex [(η^5 -Me₃SiCp)CrCl₂(pyrazole)] (**3**) as blue crystals in 60% yield. The related compound [Cp*CrCl₂(pyrazole)] (**4**) can be prepared by a similar reaction of the previously described dimer complex [(Cp*CrCl(μ -Cl))₂] [12] with pyrazole in THF. On the other hand, complex **2** reacts in THF with the bidentate ligands Ph₂PCH₂CH₂PPh₂ (dppe) and with trans-Ph₂P(O)CH=CHP(O)Ph₂ (*trans*-dppethyleneO₂) in a 1:1 molar ratio to give the binuclear complexes [(η^5 -CH₂C(Me)CH₂Cp)CrCl₂]₂(μ -L-L)] [L-L = dppe (**5**), *trans*-dppO₂ethylene (**6**)] as deep blue solids in good yields.

Complexes **3–6** are stable at room temperature and can even be handled briefly in air. All the complexes are fairly soluble in dichloromethane, THF and toluene, and were crystallised from toluene–*n*-pentane. Elemental



analysis, FTIR and X-ray diffraction methods were used to fully characterise the isolated complexes. The solid state IR spectra of complexes **3** and **4** in KBr pellets show a strong absorption band at 3303 and 3396 cm^{-1} , respectively, corresponding to the $\nu(\text{NH})$. As expected, the $\nu(\text{P}=\text{O})$ stretching of complex **6**, a broad band centred at 1122 cm^{-1} , is shifted to lower frequencies relative to those observed in the free ligand [$\nu(\text{P}=\text{O})$, 1186 cm^{-1}], most likely as a consequence of the decrease in bond order upon co-ordination.

Suitable crystals of complexes **3** and **4** for X-ray structure determination were grown by slow diffusion of *n*-pentane into THF or a toluene solution, respectively. A perspective view of the structure of the complexes is shown in Figs. 1 and 2. Relevant bond distances and bond angles are given in Table 2. In the complex the chromium atom shows a “three-legged piano stool configuration”, with the cyclopentadienyl ligand formally occupying three octahedral sites; the pyrazole ligand bonded to the metal centre through the nitrogen-donor atom, and two chlorine atoms complete the co-ordination sphere. The structure of complex **3** shows that the pyrazole ligand has the same spatial orientation as the SiMe_3 substituent of the cyclopentadienyl ring and presents an intramolecular hydrogen contact between the NH group and one of the chloride ligands,

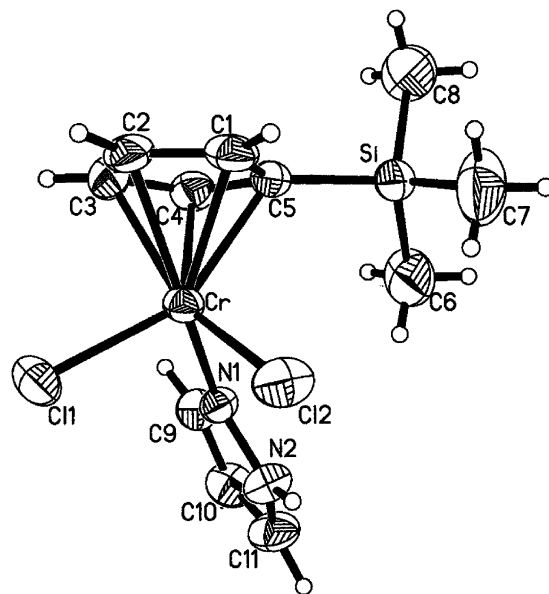


Fig. 1. Molecular structure of $[(\text{Me}_3\text{SiCp})\text{CrCl}_2(\text{pyrazole})]$ (**3**). Thermal ellipsoids are shown at the 40% probability level.

$\text{H}(2\text{A})\text{-Cl}(2) = 2.576 \text{ \AA}$. The normal axis of the ring plane coincides with its gravity centre.

The Cr-G ($\text{Me}_3\text{SiC}_5\text{H}_4$ or Cp^* centroids) distances are 1.881 and 1.884 \AA , respectively [individual Cr-C bond

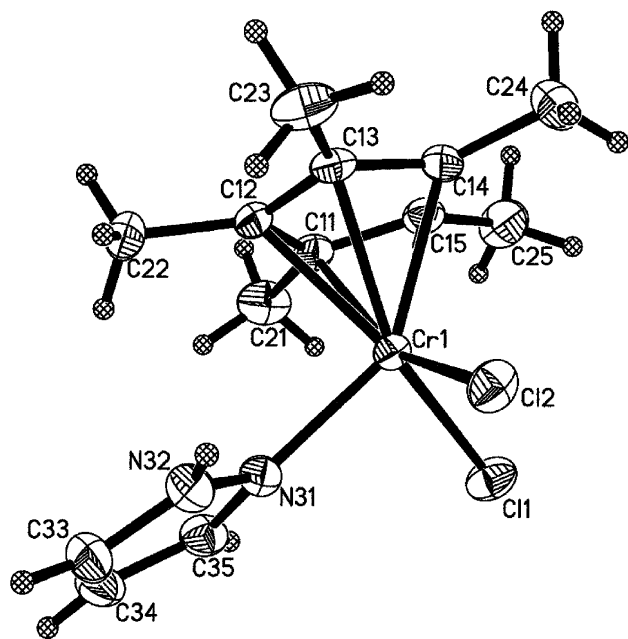


Fig. 2. Molecular structure of $[\text{Cp}^*\text{CrCl}_2(\text{pyrazole})]$ (**4**). Thermal ellipsoids are shown at the 50% probability level.

distances range from 2.223(3) to 2.234(3) Å in **3** and 2.221(2) to 2.249(2) Å in **4**], which compare well with those found in other cyclopentadienyl chromium(III) complexes [2a,2d,3a,3d,13]. The Cr–Cl bond distances [**3**: 2.295(1) and 2.299(1) Å and **4**: 2.3036(7) and 2.3302(6) Å] are comparable with the corresponding values observed in similar neutral amino-substituted cyclopentadienyl-

chromium dichloride complexes $[(\text{Me}_2\text{NC}_2\text{H}_4\text{C}_5\text{Me}_4)\text{CrCl}_2]$ [Cr–Cl = average 2.297(1) Å] and $[(1,3\text{-cyclo-C}_4\text{H}_8\text{NC}_2\text{H}_4(\text{Me}_3\text{Si})\text{C}_5\text{H}_3\text{CrCl}_2)]$ [Cr–Cl = average 2.285(1) Å] [3d]. However, the Cr–N bond distances [**3**: 2.061(2); **4**: 2.0723(17) Å] are smaller than those found in the above mentioned complexes [Cr–N = 2.175(2) and 2.125(3) Å, respectively], but are similar to the distances found in the related pyridine complexes, $[\text{Cp}^*\text{Cr}(\text{py})_2\text{Et}]\text{PF}_6$ [Cr–N = 2.085(9) Å] [14] and $[(\text{C}_5\text{H}_5\text{B})\text{CrMe}_2(\text{py})]$ [Cr–N = 2.078(3) Å] [15].

Crystals of complexes **5** and **6** suitable for X-ray diffraction work were grown by slow diffusion of *n*-pentane into a dichloromethane solution of the complexes. Figs. 3 and 4 display the molecular representation of complexes **5** and **6**, respectively. Table 3 shows selected bond distances and angles for both structures. The complexes are homodinuclear, with the two chromium centres connected by the phosphorus or oxygen atoms of the bidentate ligands. A substituted η^5 -coordinated cyclopentadienyl ligand and two chlorine atoms complete the distorted pseudooctahedral environments of the two chromium centres.

In the complexes the Cp ring is slightly slip distorted, with the exocyclic methylallyl substituent pushed away from the chromium atoms. The Cr–G (Cp centroid) and Cr–Cl distances in the complexes [**5**: Cr–G = 1.879 Å, Cr–Cl = average 2.314(2) Å; **6**: Cr–G = 1.848 Å, Cr–Cl = average 2.296(3) Å] compare quite well with those reported in the literature for similar binuclear complexes, such as $[\text{CpCrCl}_2]_2(\mu\text{-dmpe})$ [Cr–G = 1.884(3) Å,

Table 2
Selected bond distances and angles for $[(\text{Me}_3\text{SiCp})\text{CrCl}_2(\text{pyrazole})]$ (**3**) and $[\text{Cp}^*\text{CrCl}_2(\text{pyrazole})]$ (**4**)

Complex 3		Complex 4	
<i>Bond distances (Å)</i>			
Cr–G ^a	1.881	Cr–G	1.884
Cr–C(1)	2.228(3)	Cr–C(11)	2.221(2)
Cr–C(2)	2.223(3)	Cr–C(12)	2.249(2)
Cr–C(3)	2.229(3)	Cr–C(13)	2.240(2)
Cr–C(4)	2.228(3)	Cr–C(14)	2.242(2)
Cr–C(5)	2.234(3)	Cr–C(15)	2.244(2)
Cr–Cl(1)	2.295(1)	Cr–Cl(1)	2.3036(7)
Cr–Cl(2)	2.299(1)	Cr–Cl(2)	2.3302(6)
Cr–N(1)	2.061(2)	Cr–N(31)	2.0723(17)
N(1)–N(2)	1.343(3)	N(31)–N(32)	1.351(2)
N(1)–C(9)	1.238(3)	N(31)–C(35)	1.352(3)
N(2)–C(11)	1.327(4)	N(32)–C(33)	1.349(3)
Si–C(5)	1.873(3)		
<i>Bond angles (deg)</i>			
Cl(1)–Cr–Cl(2)	97.23(4)	Cl(1)–Cr–Cl(2)	98.54(3)
Cl(1)–Cr–G	120.2	Cl(1)–Cr–G	122.7
Cl(2)–Cr–G	123.4	Cl(2)–Cr–G	122.7
N(1)–Cr–G	123.7	N(31)–Cr–G	120.0
Cl(1)–Cr–N(1)	93.76(7)	Cl(1)–Cr–N(31)	92.54(5)
Cl(2)–Cr–N(1)	91.00(6)	Cl(2)–Cr–N(31)	92.79(5)
Cr–N(1)–N(2)	124.1(2)	Cr–N(1)–N(2)	124.71(12)

^a G = represent the centroid of the Me_3SiCp and Cp^* ligands.

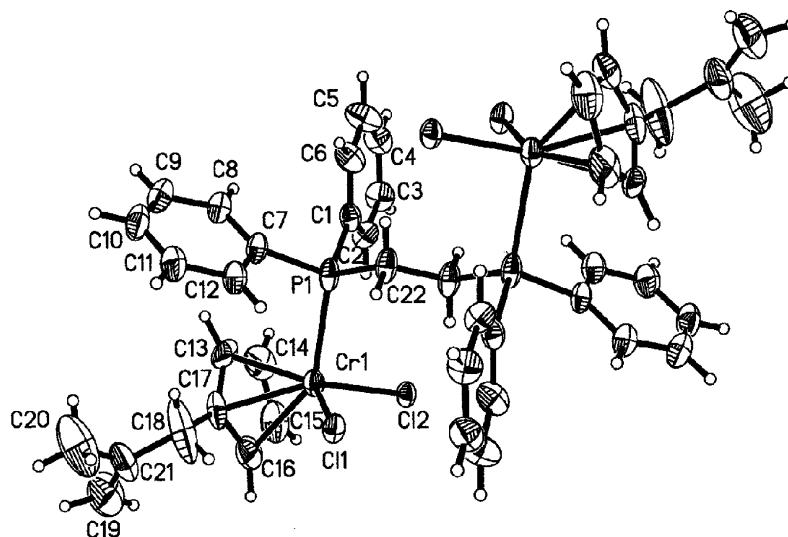


Fig. 3. Molecular structure of $[\{(\text{CH}_2=\text{C}(\text{Me})\text{CH}_2\text{Cp})\text{CrCl}_2\}_2(\mu\text{-dppe})]$ (**5**). Thermal ellipsoids are shown at the 20% probability level.

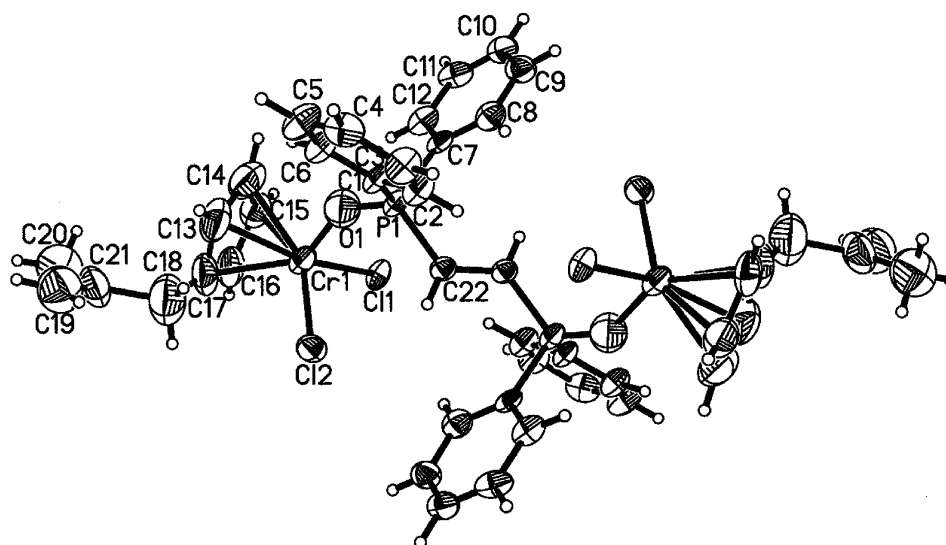


Fig. 4. Molecular structure of $[\{(\text{CH}_2=\text{C}(\text{Me})\text{CH}_2\text{Cp})\text{CrCl}_2\}_2(\mu\text{-dppethyleneO}_2)]$ (**6**). Thermal ellipsoids are shown at the 20% probability level.

Cr–Cl = average 2.291(2) Å and $[\text{CpCrCl}_2]_2(\mu\text{-dmmpm})$ [Cr–G = 1.882(7) Å, Cr–Cl = average 2.288(2) Å] [2d].

In complex **5**, the Cr–P distance [2.581(3) Å] is slightly longer than those found in the above mentioned similar complexes $[\text{CpCrCl}_2]_2(\mu\text{-dmpe})$ [Cr–P = 2.414(2) Å] and $[\text{CpCrCl}_2]_2(\mu\text{-dmmpm})$ [Cr–P = 2.414(2) Å] [2d], and in the related compounds $[\text{Cp}^*\text{CrMe}_2(\text{PMe}_3)]$ [Cr–P = 2.426(2) Å] [12] and $[(\text{C}_5\text{H}_5\text{B-Me})\text{CrCl}_2(\text{PMe}_3)]$ [Cr–P = average 2.4126(13) Å] [15]. The lengthening of the Cr–P bond may be associated with the increase of the steric requirements due to the Ph substituent on the phosphorus atoms.

On the other hand, complex **6** shows the expected *trans* conformation with a crystallographic inversion centre in the middle of the C=C bond. The Cr–O dis-

tance [1.824(9) Å] is smaller compared with the distances found in the related complex containing THF or diethyl ether ligands bound to the chromium(III) centre, $[\text{Cp}^*\text{Cr}(\text{THF})(\text{CH}_2\text{SiMe}_3)_2]$ [Cr–O = 2.122(3) Å] [2a] and $[\text{Cp}^*\text{Cr}(\text{OEt}_2)_2\text{CH}_2\text{SiMe}_3][\text{B}\{\text{C}_6\text{H}_3(\text{CF}_3)_2\}_4]$ [Cr–O = average 2.02(2) Å] [16]. This decrease is probably a result of the σ , π donor character of the P=O moiety.

In complex **6** the chromium atoms show fewer steric requirements than their homologous compound **5**, confirmed by the increased Cl–Cr–Cl angle of 98.82(11)° compared with the similar angle in **4**, 96.97(8)°. Moreover, the O(1)–Cr(1)–G angle (113.7°) is smaller than the P(1)–Cr(1)–G (119.8°) angle, probably as a consequence of repulsion between the phenyl groups of the phosphine and the substituted cyclopentadienyl ring.

Table 3

Selected bond distances and angles for complexes $[\{(Meallyl)Cp)CrCl_2\}_2(\mu\text{-dppe})]$ (**5**) and $[\{(CH_2C(Me)CH_2Cp)CrCl_2\}_2(\mu\text{-dppO}_2\text{ethylene})]$ (**6**)

Complex 5		Complex 6	
<i>Bond distances (Å)</i>			
Cr(1)–G ^a	1.879	Cr(1)–G ^a	1.848
Cr(1)–C(11)	2.312(2)	Cr(1)–C(11)	2.303(3)
Cr(1)–C(12)	2.316(2)	Cr(1)–C(12)	2.290(3)
Cr(1)–C(13)	2.209(7)	Cr(1)–C(13)	2.182(9)
Cr(1)–C(14)	2.209(7)	Cr(1)–C(14)	2.195(9)
Cr(1)–C(15)	2.243(7)	Cr(1)–C(15)	2.225(8)
Cr(1)–C(16)	2.264(7)	Cr(1)–C(16)	2.239(8)
Cr(1)–C(17)	2.243(7)	Cr(1)–C(17)	2.205(9)
Cr(1)–P(1)	2.581(3)	Cr(1)–O(1)	1.824(9)
		P(1)–O(1)	1.354(9)
<i>Bond angles (deg)</i>			
Cl(1)–Cr(1)–G	122.0	Cl(1)–Cr(1)–G	120.5
Cl(2)–Cr(1)–G	122.7	Cl(2)–Cr(1)–G	123.5
P(1)–Cr(1)–G	119.8	O(1)–Cr(1)–G	113.7
P(1)–Cr(1)–Cl(1)	90.55(8)	O(1)–Cr(1)–Cl(1)	97.5(3)
P(1)–Cr(1)–Cl(2)	97.61(8)	O(1)–Cr(1)–Cl(2)	97.7(3)
Cl(1)–Cr(1)–Cl(2)	96.97(8)	Cl(1)–Cr(2)–Cl(2)	98.82(11)
		O(1)–P(1)–C(22)	119.7(5)
		O(1)–P(1)–C(1)	107.0(5)
		O(1)–P(1)–C(7)	109.0(6)
		Cr(1)–O(1)–P(1)	141.6(6)

^aG = represent the centroid of the CH₂C(Me)CH₂Cp ligand.

Reactivity profile of individual catalysts. The reactivities toward ethylene of compounds **3** and **4** in the presence of methylaluminoxane (MAO), are shown in Table 4 (entries 1–2). These results show no important changes in reactivity with respect to the different ligands bonded to the chromium centre. However, there are noticeable differences if the results obtained with the dinuclear complexes (entries 3–6) are compared. These compounds under the same polymerization conditions showed activities three orders of magnitude greater. Also, when the bimetallic compounds are compared, it is seen that **6** shows increased activity with increasing temperature, in contrast with its homolog **5**, whose activity decreases. This behaviour is probably due to the greater thermal stability of complex **6** and to the decrease in the steric hindrance on the chromium centre (where the interaction with MAO to form active species

occurs) due to the greater distance of the phosphorus phenyl groups from the metal centre.

Molecular weight distribution. The systems that include a monometallic complex (3/MAO/C₂H₄), produced a polymer which is characterised by a bimodal molecular weight distribution. The high molecular weight fraction is centred at 155,000 g/mol, while that of low molecular weight is centred at 2000 g/mol. On the other hand, in the polymer obtained with precatalyst **4** the high molecular weight fraction is very small, while the prevalent fraction (that of low molecular weight) had a polydispersity index of 1.4, centred at 1000 g/mol. The presence of two molecular weight fractions can be probably associated with the existence of two sites having different reactivity: (i) the metal centre by direct interaction with the cocatalyst (MAO) is alkylated and generates the vacancy for the co-ordination of the olefin,

Table 4

Olefin polymerization data^a

Entry	Precatalysts	[Precat.] Mol × 10 ⁶	Temperature °C	Activity ^b	T _m ^c °C
1	3	4.3	25	44	133
2	4	4.3	25	37	133
3	5	4.3	25	142	130
4	5	4.3	60	85	–
5	6	11.0	25	140	133
6	6	5.8	60	172	–

^a Reaction conditions: solvent, toluene; Al/Precat. = 1000; polymerization time, 30 min; stirrer rate, 1000 rpm; pressure, 4 bar.^b kg polymer/[(mol Precatalyst)(h)(bar)].^c Melting point determined by DSC.

and (ii) the NH group of the co-ordinated pyrazole can react with MAO which in turn alkylates the metal centre and generates the co-ordination vacancy. Reports on similar half-sandwich systems containing a cyclopentadienyl ring functionalized with amines as ligand have shown the production of polymer fractions with different molecular weights, and have been associated with the presence of more than one catalytic site in the complex [2e,5].

At present a very detailed study is being made of the effect of cocatalyst concentration and reaction temperature on reactivity and mainly on the properties of the polymers obtained with these systems, with the purpose of understanding better the origin of polymer fractions having different molecular weights.

Thermal properties. Differential scanning calorimetry (DSC) analysis shows (Table 4, entries 1–2) that the products obtained from different systems have different thermal properties. In polymers obtained with 3/MAO/C₂H₄ one peak clearly defined at 133 °C and a broad shoulder towards low temperature were present. In contrast, the polymers from 4/MAO/C₂H₄ (Table 4, entry 2) show only a single transition, consistent with a more homogeneous product structure. Thus, the thermal properties are consistent with gel-permeation chromatography (GPC) data. On the other hand, the polymers obtained with the bimetallic complexes (5/MAO/C₂H₄ and 6/MAO/C₂H₄), (Table 4, entries 3–6), are not characterised by GPC. However, DSC analysis shows only a single transition close to 132 °C, characteristic of linear polyethylene.

4. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC reference numbers: 216615 (3); 216616 (4); 216735 (5); 216736 (6). Copies of this information may be obtained free of the charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>.)

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