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Note

Trimethylsilylcyclopentadienylchromium(III) complexes with diphenyl-2-pyridylphosphine: synthesis, structural characterisation and catalytic behaviour of $[(C_6H_5)_2PC_5H_4NH][(\eta^5\text{-}Me_3SiCp)CrCl_3]$ ☆

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Abstract

Reaction of $CrCl_3$ with $LiCpSiMe_3$ in THF leads to the formation of a solvated intermediate, $[(\eta^5\text{-}Me_3SiCp)CrCl_2(THF)]$, which in turn reacts with diphenyl-2-pyridylphosphine to yield the complex $[(C_6H_5)_2PC_5H_4NH][(\eta^5\text{-}Me_3SiCp)CrCl_3]$ (**1**) in 66% yield. As a secondary product was isolated the neutral complex $[(\eta^5\text{-}Me_3SiCp)CrCl_2\{(C_6H_5)_2PC_5H_4N\}]$ (**2**) in 5% yield. The structure of complex **1** has been determined by single crystal X-ray diffraction. In the anion the metal centre shows a pseudo-octahedral geometry with the centroid of the trimethylsilylcyclopentadienyl ligand occupying the centre of three octahedral sites, and three chloride atoms completing the co-ordination sphere. Complex **1** in the presence of MAO leads to the formation of an active catalyst for the polymerization of ethylene.

Keywords: Chromium complexes; Cyclopentadienyl complexes; Diphenyl-2-pyridylphosphine complexes; Crystal structure; Ethylene polymerization

1. Introduction

The chemistry of organometallic chromium(III) complexes containing cyclopentadienyl ligands ($Cp = C_5H_5$, $Cp^* = C_5Me_5$) has attracted considerable attention during the last years. Halide or alkyl groups (R) and a donor ligand (L) have stabilised the majority of these compounds forming distorted octahedral complexes with a 15-electron configuration [1–5]. The halide type complexes ($[CpCr(L)Cl_2]$ or $[CpCr(L)_2Cl]^+$), in the presence of methylaluminoxane (MAO), behave as catalysts in the ethylene polymerization reaction. Significant advances have been made using as precatalyst a complex with the ancillary donor ligand bridged to the Cp unit [6].

Recently we reported the synthesis, structural characterisation and activity in the ethylene polymerization reaction of new mono- and binuclear complexes with substituted cyclopentadienylchromium(III) complexes of formula $[(\eta^5\text{-}Me_3SiCp)CrCl_2(N\text{-pyrazole})]$, $[Cp^*CrCl_2(N\text{-pyrazole})]$ and $[\{\eta^5\text{-}CH_2C(Me)CH_2Cp)CrCl_2\}_2(\mu\text{-dppe})]$ ($dppe = Ph_2PCH_2CH_2PPh_2$) [7].

In this communication we describe the synthesis of new half-sandwich trimethylsilylcyclopentadienylchromium(III) complexes containing diphenyl-2-pyridylphosphine $[(C_6H_5)_2PC_5H_4N]$, either in its protonated form as counter-ion or as a monodentate neutral donor ligand. The molecular structure of the complex $[(C_6H_5)_2PC_5H_4NH][(\eta^5\text{-}Me_3SiCp)CrCl_3]$, determined by single crystal X-ray diffraction is reported. We also describe the activity of the anionic complex in the ethylene polymerization reaction.

2. Experimental

2.1. General

All manipulations were routinely performed in an inert atmosphere (nitrogen or argon) using standard

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glove box and Schlenk-tube techniques. All reagent-grade solvents (tetrahydrofuran, toluene, and *n*-pentane) were distilled over sodium/benzophenone ketyl. The starting compounds chlorotrimethylsilane, *n*-butyllithium 1.6 M/hexane, diphenyl-2-pyridylphosphine, $CrCl_3(THF)_3$ and $CrCl_3$, from Aldrich and Alfa Aesar, 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. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on Bruker AC-200P and Avance-400 spectrometers. Chemical shifts are reported in ppm relative to $SiMe_4$ (^1H) and 85% H_3PO_4 (^{31}P, positive shifts to higher frequency) as internal and external standards, respectively. Magnetic measurements were carried out at room temperature (293 K) on a Johnson Matthey Magnetic Susceptibility Balance MSB MK1. Conductivity was measured in ca. 5×10^{-4} M acetone solutions, using a WTW LF-521 conductimeter.

2.2. Preparation of complexes

Synthesis of $[(C_6H_5)_2PC_5H_4NH][(\eta^5\text{-}Me_3SiCp)CrCl_3]$ (**1**). A suspension of $Me_3SiCpLi$ (303 mg; 2.1 mmol) in *n*-pentane (prepared by reacting a stoichiometric amount of Me_3SiCpH in *n*-pentane (20 ml) with a solution of *n*-butyllithium in hexane at –70 °C), was added via syringe to a suspension of $CrCl_3$ (374 mg; 2.1 mmol) in THF. After stirring the deep blue solution formed, for 12 h at room temperature, a solution of diphenyl-2-pyridylphosphine (555 mg; 2.1 mmol) in THF (10 ml) was added. The mixture was stirred for 4 h, evaporated to dryness and the solid residue extracted with toluene. The addition of *n*-pentane causes the precipitation of a blue–green solid, which was filtered off and washed with pentane. The complex was crystallised from toluene–pentane. Yield: 766 mg (66%). Anal. Found: C, 53.7; H, 4.9; N, 2.5%. $C_{25}H_{28}Cl_3CrNPSi$ requires: C, 53.6; H, 5.0; N, 2.5%. IR (KBr, cm^{-1}): ν 3424 s, br, 1437 m, 1194 m, 1120 m, 840 m, 737 m, 724 m, 684 m, 547 s. ^1H NMR (C_6D_6, 298 K): δ 7.8 (m, 2H), 7.93 (m, 10H), 8.28 (m, 1H), 8.94 (m, 1H). ^{31}P NMR (C_6D_6, 298 K): δ 18.7 (s, br). $\mu_{eff} = 3.8\ \mu_B$, $\Lambda_M = 101\ ohm^{-1}\ cm^2\ mol^{-1}$.

The mother liquor was evaporated to dryness and the blue oil residue was triturated with *n*-pentane. The obtained solid was dissolved in the minimal amount of toluene and precipitated by adding pentane. The complex was filtered, washed with *n*-pentane and dried under vacuum. The blue solid was characterised as the neutral compound $[(\eta^5\text{-}Me_3SiCp)CrCl_2(N\text{-}(C_6H_5)_2PC_5H_4N)]$ (**2**). Yield 57 mg (5%). Anal. Found: C, 56.8; H, 5.0; N, 2.6%. $C_{25}H_{27}Cl_2CrNPSi$ requires: C, 57.4; H, 5.2; N, 2.7%. IR (KBr, cm^{-1}): ν 1571 m, 1435 m, 1250 m, 899 m, 836 s, 751 m, 694 s, 522 m, $\mu_{eff} = 3.7\ \mu_B$.

2.3. X-ray crystallography of $[(\eta^5\text{-}Me_3SiCp)CrCl_3][(C_6H_5)_2PC_5H_4NH]$

$C_{25}H_{28}Cl_3CrNPSi$, $M = 559.89$, blue crystal of $0.40 \times 0.16 \times 0.08$ mm in size, triclinic, space group $P\bar{1}$, $a = 13.762(3)$ Å, $b = 15.457(3)$ Å, $c = 15.688(3)$ Å, $\alpha = 116.707(3)°$, $\beta = 90.457(3)°$, $\gamma = 111.013(3)°$, $V = 2725.1$ Å^3, $Z = 4$, $D_c = 1.365$ Mg m^{-3}, μ(Mo, Kα) = 0.831 mm^{-1}, $F(000) = 1156$. Intensity data were collected on a Bruker Smart CCD diffractometer in $\theta/2\theta$ scan method at 150 K, using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). $1.48 < 2\theta < 25.00°$, $-16 \leqslant h \leqslant 16$, $-18 \leqslant k \leqslant 18$, $-18 \leqslant l \leqslant 18$, 24923 reflections of which 9600 were independent ($R_{int} = 0.0314$) are used in all calculations. 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 [8]. H atoms were placed at geometrically idealised positions and refined using a riding model. Final $R(F) = 0.0326$ for 9600 reflections $[I > 2\sigma(I)]$; $wR(F^2) = 0.0810$ for all data; 583 parameters; goodness of fit = 0.894. Maximum peak and hole in final Fourier difference map +0.480 and −0.312 e Å^{-3}, respectively.

2.4. Catalytic reactions

The polymerizations were carried out by charging a Parr autoclave reactor with toluene and the desired amount of cocatalyst (MAO) and catalyst **1**, in a glovebox under an inert atmosphere. The reaction vessel would then be sealed, brought out of the glovebox, and placed in an ice-water bath for temperature control. Ethylene gas was introduced to the reaction, and the consumption of monomers was monitored by a mass flow controlled inline with the ethylene feed. At the end of the reaction (30 min) the ethylene feed was removed, the vessel vented, and the reaction quenched with HCl–Methanol (10% V/V). The polymers produced were isolated by filtration and washed several times with acetone. The polymers were dried overnight under vacuum, and the polymerization activities were calculated from the mass of product obtained. The polymers were characterised by GPC (in a high temperature chromatograph, Pl-GPC 200). The melting point of the polymers were measured on a differential scanning calorimeter instrument, model DSC 2920, at a rate of 10 °C/min for three cycles using a temperature range of 50–200 °C.

3. Results and discussion

Recently, we have described the preparation of the binuclear complex $[\{(\eta^5\text{-}Me_3SiCp)CrCl(\mu\text{-}Cl)\}_2]$ by reaction of the lithium derivative $LiCpSiMe_3$ (obtained by reaction of Me_3SiCpH with buthyllithium in THF at –70 °C) with $CrCl_3(THF)_3$. This preparation involves the formation of a solvated intermediate [(η^5-Me_3SiCp)$CrCl_2$(THF)], in which THF can easily be removed to form the binuclear compound [7].

The formation of this type of intermediate has been demonstrated in the synthesis of similar complexes with Cp [9]. On the other hand, the addition of bidentate donor ligands (L_2) to THF solutions of the mononuclear complex [$CpCrCl_2$(THF)], in 1:1 and 1:2 molar ratio, led to the formation of complexes of the types [$CpCrCl_2$(η^1-L_2)] and [{$CpCrCl_2$}2(μ-L_2)], respectively [9].

On the basis of these results, we carried out the reaction of the intermediate compound [(η^5-Me_3SiCp)$CrCl_2$(THF)] in THF solution with the bidentate ligand diphenyl-2-pyridylphosphine [$(C_6H_5)_2PC_5H_4N$] in 1:1 molar ratio. The deep blue solution was evaporated to dryness, extracted with toluene and the addition of *n*-pentane gave a room temperature-stable blue compound.

The complex is stable in air and is soluble in toluene, benzene, acetone and chloroform. As expected of a paramagnetic material, the ^1H NMR spectrum in C_6D_6 shows only broad multiple signals in the region δ 7.8–8.94 ppm, assigned to the ligand protons. The ^{31}P NMR spectrum exhibits a broad single resonance at δ 18.7 ppm, indicating that the phosphorus atom is not in the proximity of the paramagnetic chromium centre [free ligand, ^{31}P NMR ($CDCl_3$): δ −4.8 (s)]. The spin state of the complex was confirmed by magnetic susceptibility ($\mu_{eff} = 3.8\ \mu_B$) and conductivity measurements which show that the complex behaves as a 1:1 electrolyte in acetone solution.

In order to obtain an unambiguous characterisation of complex **1**, an X-ray diffraction study was undertaken. Suitable crystals for structural determination were obtained from a slow diffusion of *n*-pentane into a toluene solution of the complex. There are two independent molecules in the unit cell and their molecular structures are shown in Fig. 1. The structure consists of discrete $[(C_6H_5)_2PC_5H_4NH]^+$ and [(η^5-Me_3SiCp)$CrCl_3$]$^-$ ions and a detailed view of a molecule with the atom numbering is given in Fig. 2. The bonding parameters of the second independent molecule are in most cases within the range of the standard deviation of the first molecule.

In the anionic complex the metal centre shows a pseudo-octahedral geometry, commonly described as a "three-legged piano stool" configuration, with the centroid of the trimethylsilylcyclopentadienyl ligand occupying the centre of three octahedral sites and three chloride atoms completing the co-ordination sphere. The Cr(1)–G1 ($Me_3SiC_5H_4$ centred) distance of 1.885 Å [individual Cr–C bond distances range from 2.224(2) to 2.240(2) Å] compares well with those found in other trimethylsilylcyclopentadienyl chromium(III) complexes [7]. The Cr–Cl bond distances [2.3111(8), 2.3134(8) and 2.3497(7) Å] are comparable with the corresponding values observed in the related complexes Li[$CpCrCl_3$] [Cr–Cl range: 2.211(18)–2.322(18) Å] [10] and [Cp^*_2Cr][Cp^*CrCl_3](Cr–Cl range: 2.3195(14)–2.3308(14) Å) [11]. However the Cl–Cr–Cl bonds angles [96.73(3), 98.45(3), 93.75(3)°] are similar to those observed in the complex [Cp^*_2Cr][Cp^*CrCl_3] [Cl–Cr–Cl range: 95.02(6)–98.34(6)°][11], but slightly larger than those found in complex Li[$CpCrCl_3$] [Cl–Cr–Cl range: 91.3(2)–95.7(2)°] [10]. This difference is probably due to the fact that in the complex Li[$CpCrCl_3$] the lithium atom directly interacts with the three chloride atoms, reducing the Cl–Cr–Cl angles. In complex **1** and in complex [Cp^*_2Cr][Cp^*CrCl_3], the corresponding cation is not involved in any particularly strong interaction with any part of the anion, and the Cl–Cr–Cl angles are only restricted by the steric demands of the ring substituents.

In the cation, the angles involving the *P* atoms reflect a slightly distorted tetrahedral geometry (C–P–C average = 101.21°). The proton bonded to the nitrogen atom is not observed in the ^1H NMR (C_6D_6, $CDCl_3$) spectrum of complex **1**. However, the ^1H NMR pattern is

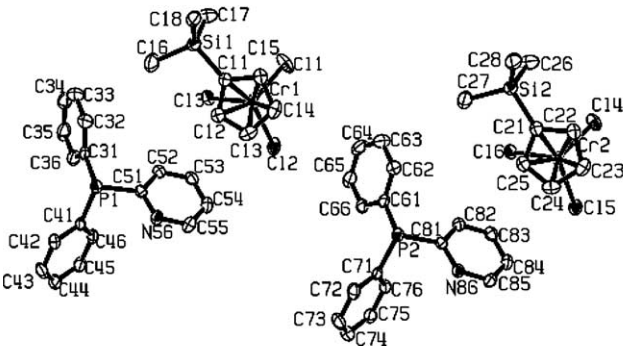

Fig. 1. View of the structure of the two independent molecules of [$(C_6H_5)_2PC_5H_4NH$][(η^5-Me_3SiCp)$CrCl_3$] (thermal ellipsoids at 50% probability level).

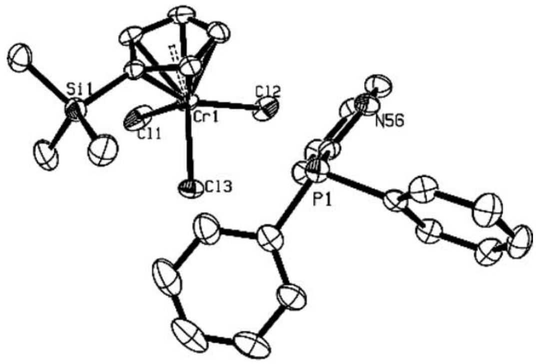

Fig. 2. Molecular structure of complex **1**. Selected bond distances (Å) and angles (°): G1(centroid)–Cr(1), 1.885; Cr(1)–Cl(1), 2.3111(8); Cr(1)–Cl(2), 2.3134(8); Cr(1)–Cl(3), 2.3497(7); C(11)–Si(1), 1.883(2); G1–Cr(1)–Cl(1), 120.5; G1–Cr(1)–Cl(2), 121.5; G1–Cr(1)–Cl(3), 120.0; Cl(1)–Cr(1)–Cl(2), 96.73(3); Cl(1)–Cr(1)–Cl(3), 98.45(3); Cl(2)–Cr(1)–Cl(3), 93.75(3).

Table 1
Ethylene polymerization data

Reaction conditions[a]				Polymer properties				
Entry	Al/Cr	[Cr] mol × 10^6	Pressure (psi)	Activity[b]	T_m °C	$M_w \times 10^3$	M_n	M_w/M_n
1	500	3.8	100	104	132.0	220	2000	120
2	500	3.8	200	118	131.0	145	1316	109
3	1,000	1.0	100	260	132.0	257	1588	162
4	1,000	1.0	200	247	131.6	162	1530	106

[a] Solvent, toluene; polymerization time, 30 min; stirrer rate, 1000 rpm; reaction temperature, 20 °C.

[b] kg polymer/(molCr)(h)(bar).

similar to those shown by the compound $[(C_6H_5)_2PC_5H_4NH]BF_4$ (prepared by reaction of the ligand with HBF_4 in diethyl ether), which also exhibits a broad signal centred at δ 13.2 ppm ($CDCl_3$) assigned to the NH proton.

The unexpected formation of complex **1** (66% yield) can be discussed on the basis of the formation of the following equilibrium in THF solution:

$$(\eta^5\text{-}Me_3SiCp)CrCl_2(THF) + LiCl \rightleftharpoons Li[(\eta^5\text{-}Me_3SiCp)CrCl_3] + THF$$

The addition of the ligand diphenyl-2-pyridylphosphine does not displace the THF ligand, probably due to steric reasons, and the ligand is protonated in the solution by traces of water or by decomposition of the solvent. Thus, the addition of a non-polar solvent such as *n*-pentane causes the precipitation of the ionic compound. This result is analogous to that described by Poli et al [9], who also demonstrate that the reaction of $[CpCrCl_2(THF)]$ with $[Ph_3PNPh_3]Cl$ yield the compound $[Ph_3PNPh_3][CpCrCl_3]$.

On the other hand, the evaporation of mother liquor of complex **1** yields a blue residue, which by treatment with *n*-pentane gives a deep blue solid in low yield (5%). This compound was purified by precipitation from a mixture of toluene-*n*-pentane. The elemental analysis indicates that the isolated complex corresponds to the neutral mononuclear compound $[(\eta^5\text{-}Me_3SiCp)CrCl_2\{(C_6H_5)_2PC_5H_4N\}]$ (**2**), with the ligand probably bonded through the nitrogen atom. As expected, its effective magnetic moment ($\mu_{eff} = 3.7\ \mu_B$) indicates the presence of three unpaired electrons in the chromium centre. No ^{31}P NMR resonance is observed for this compound probably due to the proximity of the phosphorus nucleus to the paramagnetic centre. Unfortunately, no suitable crystals were obtained to carry out an X-ray diffraction study.

Reactivity Profile of Catalyst 1/MAO. The reactivity toward ethylene of compound **1**, activated using MAO, was carried out under mild reaction conditions. Table 1 shows the results for two concentrations of **1** and two Al/Cr ratios at 100 and 200 psi of ethylene pressure. Their evaluation showed an increase in the catalytic activity at lower concentrations of Cr and consequently higher Al/Cr ratio in the reactor. Also, the catalytic behaviour is independent of the ethylene pressure in the reactor.

The products obtained by this catalyst were characterised by GPC analysis and revealed a molecular weight (M_w) over 200,000 for polymers obtained at 100 psi and a very broad polydispersity. The molecular weight decreased at 200 psi and also its molecular weight distribution. DSC performed on this sample showed a melting peak at 132 °C, typical of a linear polyethylene.

The large molecular weight distribution can be associated with the presence of three terminal chloride atoms, which can be substituted by methyl in the reaction with MAO. This process probably generates intermediate complexes such as the co-ordinatively unsaturated $[(\eta^5\text{-}Me_3SiCp)CrMe_2]$ and $[(\eta^5\text{-}Me_3SiCp)CrMeCl]$, and the co-ordinatively saturated trialkyl and dialkylchloride complexes $[(\eta^5\text{-}Me_3SiCp)CrMe_3]$ and $[(\eta^5\text{-}Me_3SiCp)CrMe_2Cl]$ [1,2]. In all these cases the conformation is not restricted to only one site catalyst, as occurs in complexes of the types $CpMCl_2$ (M = Ti, Zr) or $(\eta^5,\eta^1\text{-}RCp)CrCl_2$. It is probable that these kinds of intermediates are responsible for the broad molecular weight distribution and also for the change of the molecular weight at higher pressures.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 226442 for complex **1**. Copies of this information may be obtained free of the charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1 EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccd.cam.ac.uk).

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