

## Preliminary communication

## A facile access to CpCr(acac)Cl and related systems

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**Abstract**

CpCr(acac)Cl has been prepared by reacting CpCr(THF)Cl<sub>2</sub> with sodium acetylacetonate. Related Cr compounds containing the C<sub>5</sub>Me<sub>5</sub> group and ethylacetoacetate have also been studied. Catalysts active for the polymerization of ethylene are obtained by treating these compounds with aluminium alkyls while the title compound reacts with Et<sub>2</sub>AlCl or Et<sub>3</sub>Al to give [CpCr(μ-Cl)Et]<sub>2</sub>. © 1998 Elsevier Science S.A.

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30 years ago it was shown that CpCr(acac)Br in the presence of aluminium alkyls is active for the catalytic polymerization of ethylene [1]. As far as we are aware, this system has received no further attention – presumably because of the relative inaccessibility of the Cr compound, which is formed in low yield as a side product of the reaction between Cr(acac)<sub>3</sub> and CpMgBr [2,3], and because of the modest activity of the catalyst. As part of an investigation of the Cr-catalyzed oligomerization of alkenes [4], we were interested in preparing compounds of this type and report here a more facile synthesis and discuss the reaction with aluminium alkyls.

CpCr(acac)Cl (**1**) and Cp<sup>\*</sup>Cr(acac)Cl (**2**, Cp<sup>\*</sup> = C<sub>5</sub>Me<sub>5</sub>) may be prepared in excellent yield by reacting the appropriate dichloride with sodium acetylacetonate in THF. A related compound **3** is the product of the reaction with sodium ethylacetoacetate (Scheme 1).

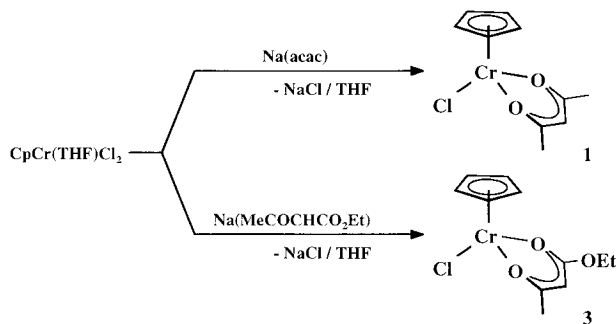
Typical experiment: CpCr(THF)Cl<sub>2</sub> (13.39 g, 51.5 mmol) was suspended in THF (200 ml) and cooled to –30 °C. Sodium acetylacetonate (6.26 g, 51.3 mmol), suspended in THF (100 ml), was added over 2 h and the reaction mixture then stirred at room temperature for 15 h. The reaction mixture was evaporated to dryness and the residue extracted with boiling acetone. The extract was concentrated to 200 ml and cooled to –70 °C

to give the compound as blue–green, metallic flakes which were isolated and dried under high vacuum. Crystals suitable for X-ray structural analysis were obtained from toluene. CpCr(acac)Cl (**1**) yield 9.05 g (70%). Satisfactory C, H, Cl and Cr analyses were found for this and the other compounds reported. MS (100 °C): *m/e* 251 (M<sup>+</sup>, 75%), 216 (M<sup>+</sup> – Cl, 100%), 186, 152. IR (KBr): *ν* 3100s, 1570s, 1520s, 1360s, 1350s, 1020s, 1005s, 935s, 835s. <sup>1</sup>H NMR (toluene-*d*<sub>8</sub>, 300 K): *δ* 41.5 (Cp), 30.6 (CH, acac), –32.0 (Me, acac). Magnetic susceptibility (μ<sub>eff</sub>, Evans method, toluene-*d*<sub>8</sub>, 300 K): 3.78 μ<sub>B</sub>. Crystal structure: see Fig. 1(a). Cp<sup>\*</sup>Cr(acac)Cl (**2**), blue rhombic crystals, yield 78%. From [Cp<sup>\*</sup>CrCl<sub>2</sub>]<sub>2</sub> and sodium acetylacetonate in THF. MS (70 °C): *m/e* 321 (M<sup>+</sup>, 73%), 285 (M<sup>+</sup> – Cl, 93%), 151, 135. IR (KBr): *ν* 2919s, 1570s, 1520s, 1360s, 935s, 805s. Magnetic susceptibility (μ<sub>eff</sub>, Evans method, toluene-*d*<sub>8</sub>, 300 K): 3.4 μ<sub>B</sub>. Crystal structure: see Fig. 1(b). CpCr(MeCOCHCO<sub>2</sub>Et)Cl (**3**), blue, metallic flakes, yield 30%. From CpCr(THF)Cl<sub>2</sub> and sodium ethylacetoacetate in THF. MS (75 °C): *m/e* 281 (M<sup>+</sup>, 43%), 246 (M<sup>+</sup> – Cl, 12%), 197, 161, 152. IR (KBr): *ν* 1591s, 1515s, 1286s, 1177s, 1064s, 1019s, 821m. Magnetic susceptibility (μ<sub>eff</sub>, Evans method, toluene-*d*<sub>8</sub>, 300 K): 3.68 μ<sub>B</sub>.

Compounds **1–3** are blue–green crystalline solids which are stable at room temperature and the crystal structures of both **1** and **2** have been established by X-ray diffraction (Fig. 1).

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Crystal data for  $\text{CpCr}(\text{acac})\text{Cl}$  (**1**):  $\text{C}_{10}\text{H}_{12}\text{ClCrO}_2$ , triclinic, space group  $P\bar{1}$ ,  $a = 6.592(1) \text{ \AA}$ ,  $b = 9.122(1) \text{ \AA}$ ,  $c = 9.673(1) \text{ \AA}$ ,  $\alpha = 108.03(1)^\circ$ ,  $\beta = 98.79(1)^\circ$ ,  $\gamma = 91.11(1)^\circ$ ,  $V = 545.3 \text{ \AA}^3$ ,  $Z = 2$ ,  $D_{\text{calc}} = 1.53 \text{ Mg m}^{-3}$ , 2633 measured reflections, 2483 unique reflections, 2228 reflections with  $I \geq 2\sigma(I)$  used in refinement, structure solved by direct methods,  $R = 0.031$ ,  $R_w = 0.041$  [ $w = 1/\sigma^2(F_o)$ ], EOF = 1.87, residual electron density  $0.27 \text{ e \AA}^{-3}$ . For  $\text{Cp}^*\text{Cr}(\text{acac})\text{Cl}$  (**2**):  $\text{C}_{15}\text{H}_{22}\text{ClCrO}_2$ , monoclinic, space group  $P2_1/a$ ,  $a = 14.069(2) \text{ \AA}$ ,  $b = 8.439(1) \text{ \AA}$ ,  $c = 14.195(2) \text{ \AA}$ ,  $\beta = 107.73(1)^\circ$ ,  $V = 1605.3 \text{ \AA}^3$ ,  $Z = 4$ ,  $D_{\text{calc}} = 1.33 \text{ Mg m}^{-3}$ , 9594 measured reflections, 5569 unique reflections, 4148 reflections with  $I \geq 2\sigma(I)$  used in refinement, structure solved by direct methods,  $R = 0.050$ ,  $R_w = 0.060$  [ $w = 1/\sigma^2(F_o)$ ], EOF = 2.34, residual electron density  $0.44 \text{ e \AA}^{-3}$ . The structures were solved by SHELX-86 and refined anisotropically for non-hydrogen atoms with H-atoms isotropic,  $\sum w(F_o - F_c)$  minimized. For the final refinement the program GFMLX was used.

The similarity between the two structures is surprising: presumably the larger size of the  $\text{Cp}^*$  group (compared to the Cp group) compensates for the stronger bond to the metal atom [5].

Nevertheless, the two compounds react differently with aluminium alkyls: **1** reacts with  $\text{Et}_2\text{AlCl}$  (or  $\text{Et}_3\text{Al}$ ) to give the dinuclear species  $[\text{CpCr}(\mu\text{-Cl})\text{Et}]_2$  (**4**) whereas **2** reacts with  $\text{Et}_2\text{AlCl}$  to give  $[\text{Cp}^*\text{Cr}(\mu\text{-Cl})\text{Cl}]_2$  [6].

$[\text{CpCr}(\mu\text{-Cl})\text{Et}]_2$  (**4**).  $\text{CpCr}(\text{acac})\text{Cl}$  (0.81 g, 3.2 mmol) was suspended in toluene (50 ml) at  $-30^\circ\text{C}$  and treated dropwise with  $\text{Et}_2\text{AlCl}$  (2.3 ml of a 1.87 molar solution in toluene, 4.3 mmol). The reaction mixture was stirred for 15 h at room temperature. The resulting red solution was evaporated to dryness and the residue extracted with pentane. The combined extract was concentrated to 5 ml and cooled to  $-30^\circ\text{C}$  to give the compound as dark violet prisms which were recrystallized from pentane (5 ml) at  $-30^\circ\text{C}$  to remove a highly viscous impurity. Yield 0.26 g (45%). MS ( $40^\circ\text{C}$ ):  $m/e$  333 ( $\text{M}^+ - \text{C}_2\text{H}_4$ , 16%), 305, 182, 152, 117. Magnetic susceptibility ( $\mu_{\text{eff}}$ ):  $3.5 \mu_{\text{B}}$ . Crystal structure: see Fig. 2.

The same compound can be prepared (yield 41%) by reacting  $\text{CpCr}(\text{acac})\text{Cl}$  with  $\text{Et}_3\text{Al}$  in toluene at  $-30^\circ\text{C}$ .

$[\text{Cp}^*\text{Cr}(\mu\text{-Cl})\text{Cl}]_2$ .  $\text{Cp}^*\text{Cr}(\text{acac})\text{Cl}$  (1.99 g, 6.2 mmol) was reacted with  $\text{Et}_2\text{AlCl}$  (2.0 ml of a 0.68 molar solution in toluene, 13.6 mmol) in toluene at  $-30^\circ\text{C}$  to room temperature as described above to give the compound as a blue powder. Yield 1.55 g (97%) [6]. The crystal structure of **4** has been confirmed by X-ray diffraction (Fig. 2) and is related to that of  $[\text{CpCr}(\mu\text{-Cl})\text{Me}]_2$  which has been reported to be the product of

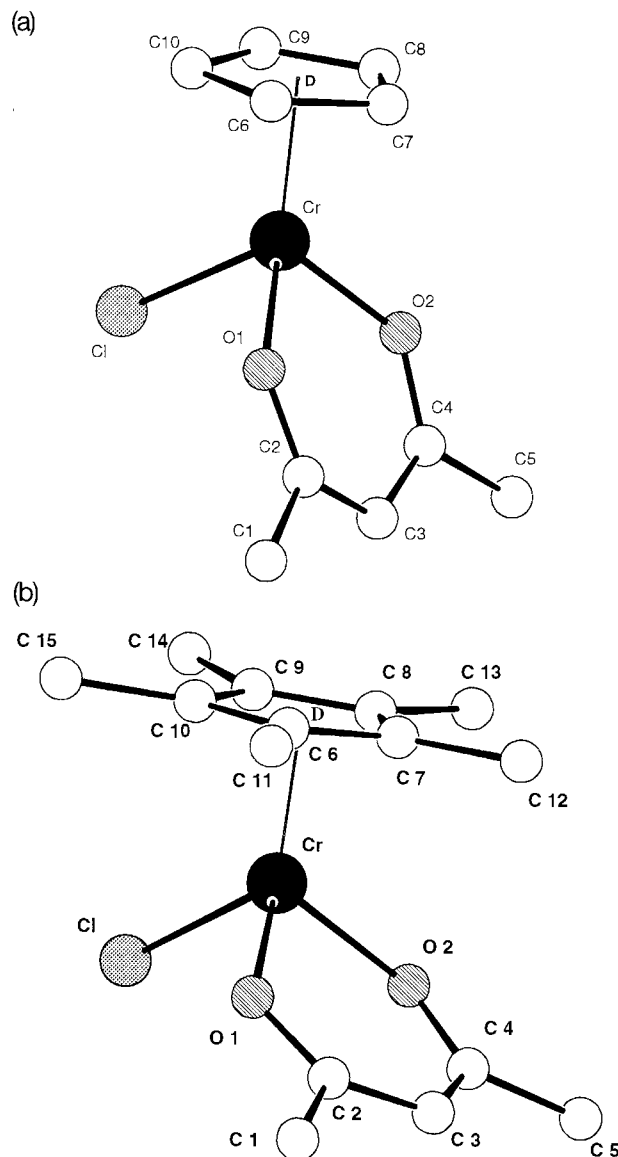


Fig. 1. The molecular structure of (a)  $\text{CpCr}(\text{acac})\text{Cl}$  (**1**) and (b)  $\text{Cp}^*\text{Cr}(\text{acac})\text{Cl}$  (**2**). Selected interatomic distances ( $\text{\AA}$ ) and angles ( $^\circ$ ): **1**, Cr–D 1.882, Cr–Cl 2.299(1), Cr–O(1) 1.944(1), O(1)–C(2) 1.278(2), C(1)–C(2) 1.502(3), C(2)–C(3) 1.391(3), D–Cr–Cl 123.2, D–Cr–O(1) 123.3, O(1)–Cr–O(2) 90.9(1), C(1)–C(2)–C(3) 119.9(2); **2**, Cr–D 1.885, Cr–Cl 2.307(1), Cr–O(1) 1.967(2), O(1)–C(2) 1.281(3), C(1)–C(2) 1.502(3), C(2)–C(3) 1.381(3), D–Cr–Cl 123.5, D–Cr–O(1) 120.3, O(1)–Cr–O(2) 90.0(1), C(1)–C(2)–C(3) 119.9(2).

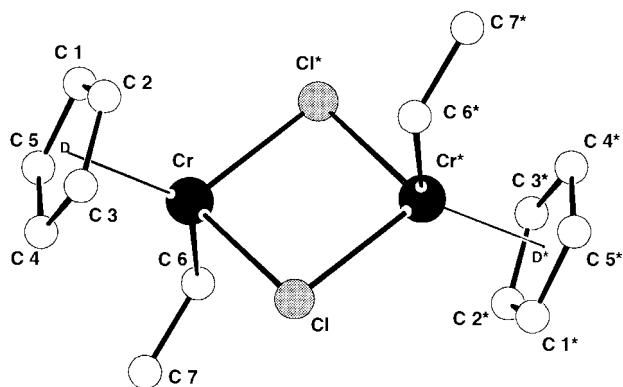


Fig. 2. The molecular structure of  $[\text{CpCr}(\mu\text{-Cl})\text{Et}]_2$  (**4**). Selected interatomic distances (Å) and angles ( $^\circ$ ): Cr–D 1.910, Cr–Cl 2.343(1), Cr\*–Cl 2.360(1), Cr–C(6) 2.082(7), C(6)–C(7) 1.44(1), D–Cr–Cl 124.9, D–Cr–Cl\* 123.6, Cl–Cr–Cl\* 91.5(1), Cr–Cl–Cr\* 88.5(1).

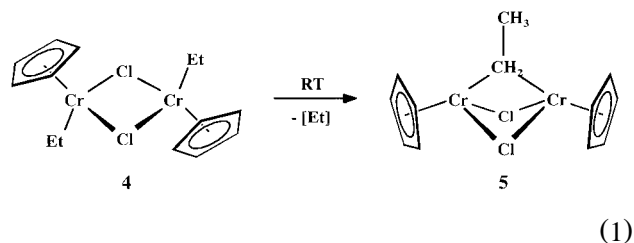
the reaction between  $\text{MeCr}(\text{THF})\text{Cl}_2$  and  $\text{TlCp}$  [7]. The Cr–Cr distance of 3.28 Å indicates that **4** does not contain a direct metal–metal bond and the magnetic susceptibility ( $\mu_{\text{eff}} = 3.5 \mu_{\text{B}}$ ) is characteristic of an antiferromagnetically coupled dimer.

Crystal data for  $[\text{CpCrEt}(\mu\text{-Cl})]_2$  (**4**):  $\text{C}_{14}\text{H}_{20}\text{Cl}_2\text{Cr}_2$ , monoclinic, space group  $C2/c$ ,  $a = 12.487(1)$  Å,  $b = 8.082(2)$  Å,  $c = 15.989(1)$  Å,  $\beta = 96.10(1)^\circ$ ,  $V = 1604.4$  Å<sup>3</sup>,  $Z = 4$ ,  $D_{\text{calc}} = 1.50$  Mg m<sup>-3</sup>, 2572 measured reflections, 2339 unique reflections, 1793 reflections with  $I \geq 2\sigma(I)$  used in refinement, structure solved by direct methods,  $R = 0.045$ ,  $R_w = 0.056$  [ $w = 1/\sigma^2(F_o)$ ], EOF = 2.15, residual electron density 0.58 e Å<sup>-3</sup>. The structures were solved by SHELX-86 and refined anisotropically for non-hydrogen atoms with H-atoms isotropic,  $\sum w(F_o - F_c)$  minimized. For the final refinement the program GFMLX was used.

Whereas solutions of  $[\text{CpCr}(\mu\text{-Cl})\text{Et}]_2$  in toluene react further at 60 °C to give  $\text{Cp}_2\text{Cr}$  and  $[\text{CpCrCl}_2]_2$ , in the solid a slow rearrangement occurs at room temperature to give a red–violet dinuclear species, which is provisionally (we are still attempting to grow crystals adequate for a structure determination) identified as  $\text{Cp}_2\text{Cr}_2(\mu\text{-Cl})_2(\mu\text{-Et})$  (**5**) (Eq. (1)) from the mass spectral data and a comparison of the IR spectroscopic data with those for  $[\text{Cp}^*\text{Cr}(\mu\text{-Et})]_2$  whose structure has been established by X-ray diffraction [8].

$(\text{CpCr})_2(\mu\text{-Cl})_2(\mu\text{-Et})$  (**5**):  $[\text{CpCr}(\mu\text{-Cl})\text{Et}]_2$  (0.18 g, 0.5 mmol) was stored under argon for 2 months at room temperature during which time the crystals changed color from violet to blue. The solid was dissolved in pentane to give a blue solution which was filtered and cooled to –30 °C to give the compound as red–violet plates which were washed with pentane at –78 °C and dried under high vacuum. Yield 0.13 g (79%). MS (40 °C):  $m/e$  332 ( $\text{M}^+ - \text{H}$ , 9%), 304 ( $\text{M}^+ - \text{Et}$ , 18%), 182, 152, 117. IR (KBr):  $\nu$  3101m, 2919m, 2851m,

2822m, 1437m, 1418m, 1385w, 1356w, 1262w, 1115w, 1016m, 1003s, 802s.



This behavior should be compared with that of  $[\text{CpCr}(\mu\text{-Cl})\text{Me}]_2$  which has been shown to react further in toluene at 60 °C to give the trinuclear species  $[\text{CpCrCl}]_3(\mu\text{-CH})$  [7].

Treatment of **1** and **2** with aluminium alkyls ( $\text{Et}_3\text{Al}$ ,  $\text{Et}_2\text{AlCl}$ , MAO) gives catalysts for the polymerization of ethylene which are considerably more active than  $\text{CpCr}(\text{acac})\text{Br}$  [1]. The most active system is  $\text{Cp}^*\text{Cr}(\text{acac})\text{Cl}/\text{Et}_3\text{Al}$  (Cr:Al 1:300) and in toluene at 33 °C with an initial ethylene pressure of 50 bar this system has an activity of  $4.2 \times 10^4$  mol PE mol Cr<sup>-1</sup> h<sup>-1</sup>. [The polymerization reactions were carried out in a 200 ml steel autoclave containing a solution of 0.0035 mmol of the chromium compound and 100 to 300 equiv. of the aluminium alkyl in 20 ml toluene with an initial pressure of 50 bar of ethylene at RT. After 1 h the polymerization was quenched with 200 ml ethanol and the polymer was filtered off, washed with ethanol and dried under vacuum.] Interestingly,  $\text{CpCr}(\text{acac})\text{Cl}$  (**1**)/ $\text{Et}_2\text{AlCl}$  (Cr:Al 1:300) and  $[\text{CpCr}(\mu\text{-Cl})\text{Et}]_2$  (**4**)/ $\text{Et}_2\text{AlCl}$  (Cr:Al 1:300) show comparable activity ( $5 \times 10^3$  mol PE mol Cr<sup>-1</sup> h<sup>-1</sup>) and the far-reaching suggestion that dinuclear species play a role is being explored further. The product of the polymerization is in all cases linear polyethylene (crystallinity 65–70%) having a melting point of ca. 130 °C.

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