

# Synthesis and characterization of chromium(I) bis( $\eta^6$ -toluene) derivatives containing sterically demanding anions

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## Abstract

The reaction of  $\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2$  with 1-benzoyl-6-hydroxy-6-phenyl fulvene, dbcpH, and with *pentakis*(methoxycarbonyl)cyclopentadiene, pcmcpH, proceeds with evolution of dihydrogen and the formation of the ionic derivatives  $[\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2][\text{X}]$  ( $[\text{X}]^- = 1,2\text{-dibenzoylcyclopentadienyl}$ ,  $[\text{dbcp}]^-$ , *pentakis*(methoxycarbonyl)cyclopentadienyl,  $[\text{pcmcp}]^-$ ), which have been characterized by IR and EPR spectroscopies, X-ray diffraction and electrochemical techniques. The sterically demanding anions do not affect the structural and electronic properties of the  $\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2^+$  cations in solution but strongly influence crystal packing. In fact, a rare *cis*-eclipsed conformation of the toluene rings is found for  $[\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2][\text{dbcp}] \cdot \text{THF}$ , whereas two independent complexes are observed in the unit cell of  $[\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2][\text{pcmcp}]$ , one with toluene rings in a *cis*-eclipsed conformation and the other in a staggered conformation (projections of methyl groups form an angle of  $151^\circ$ ).

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**Keywords:** Toluene derivatives; Chromium; X-ray; Fulvene; Oxidation

## 1. Introduction

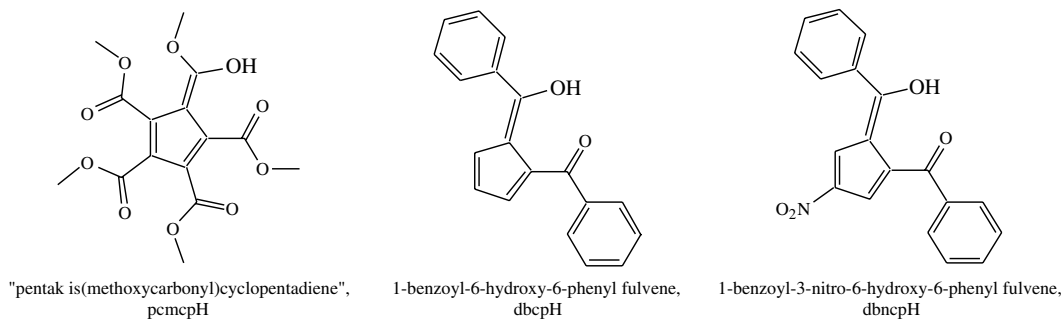
Recent contributions from our and other groups have reported on the use of complexes of transition metals in low oxidation states as precursors of organometallic, inorganic or coordination compounds [1,2]. As far as bis( $\eta^6$ -arene) derivatives are concerned, we have shown [2b,2c,2d,2e] that treatment of  $\text{V}(\eta^6\text{-1,3,5-Me}_3\text{C}_6\text{H}_3)_2$  with species containing active protons, such as  $\text{CF}_3\text{COOH}$  and hydrogen halides, or strong oxidizing agents, such as bromine or iodine in DME, proceeds with oxidation of the metal to II+ or III+ oxidation states and loss of arene ligands. On the other hand, monoelectronic oxidizing

agents such as ferricenium [3] or silver [4] cations react with  $\text{Ti}(\eta^6\text{-1,3,5-Pr}_3\text{C}_6\text{H}_3)_2$  or  $\text{V}(\eta^6\text{-arene})_2$  (arene = 1,3,5- $\text{Me}_3\text{C}_6\text{H}_3$ , 1,3,5- $\text{tBu}_3\text{C}_6\text{H}_3$ ) with the formation of  $[\text{M}(\eta^6\text{-arene})_2]^+$  cations. Similarly, the chemistry of  $\text{Nb}(\eta^6\text{-arene})_2$  compounds, affording  $[\text{Nb}(\eta^6\text{-arene})_2\text{L}]^+$  (L = CO, alkynes,  $\text{PMe}_3$ ) derivatives, has been widely investigated [5].

In the framework of our research projects, we recently decided to investigate the reactivity of  $[\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2]$  with the fulvene systems reported in Scheme 1 [6].

Our interest in these systems arises from the strong Brønsted acidity (the acidity of pcmcpH in water well compares to that of HCl [7]) of the hydroxyl proton, which is testified by the high chemical shift values found for this proton in  $^1\text{H}$  NMR experiments ( $\delta_{\text{H}} = 16.9, 18.2, 31.1$  ppm for dbcpH, dbncpH, pcmcpH in  $\text{CCl}_4$ , respectively) [7,8]. Moreover, once the hydroxyl proton is lost, these fulvene derivatives can rearrange to aromatic cyclopentadienyl

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Scheme 1.

systems stabilized by electron resonance. In view of these properties, we reckoned that these species could be used as oxidizing agents of  $\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2$ .

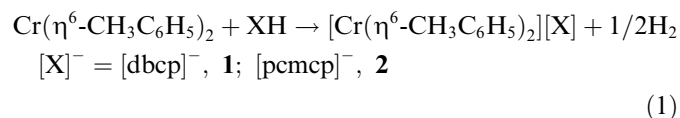
This hypothesis has been recently confirmed showing that  $[\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2][\text{dbncp}]$  and  $\text{H}_2$  are formed in the reaction of  $\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2$  with dbncpH [9], the cation  $[\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2]^+$  representing the first example of bis-toluene chromium complex with a *cis*-eclipsed conformation of toluene rings in the crystalline state. However, due to the difficulties encountered in crystal growing, the structure of  $[\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2][\text{dbncp}]$  could not be determined to an high degree of accuracy. Therefore, we looked for other examples of these compounds and the present paper reports on the oxidation of  $\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2$  by dbcpH and pcmcph, which once again proceeds with dihydrogen evolution and the formation of  $[\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2][\text{X}]$  ( $[\text{X}]^- = [\text{dbcp}]^-$  (**1**) and  $[\text{pcmcph}]^-$  (**2**), respectively) derivatives. We will show that the conformation of the  $\eta^6$ -bonded toluene rings in the solid state is governed by the anion, whereas no influence of the anion on the structure and the redox behaviour of the  $[\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2]^+$  cation has been observed in solution.

It must be noticed that, as far as we know, no other examples are reported in the literature concerning the use of pcmcph and dbcpH as oxidising agents. In fact, the sandwich compound  $\text{Ru}(\text{Cp}^*)(\eta^5\text{-dbcp})$  [10], representing to date the only transition metal complex of the  $[\text{dbcp}]^-$  anion, was obtained from 1-benzoyl-6-hydroxy-6-phenyl fulvene [11] by deprotonation with TIOEt followed by the reaction of the thallos salt with  $[\text{Ru}(\mu_3\text{-Cl})\text{Cp}^*]_4$ . On the other hand, pcmcph, which has a fulvenoid structure in the solid state and undergoes ionization in polar solvents with the formation of the  $[\text{C}_5(\text{COOMe})_5]^-$  anion [7], has been widely used in coordination chemistry [12]. Owing to its high stability, resulting from charge delocalization on the five ester groups, the uncoordinated  $[\text{pcmcph}]^-$  anion is reported in rhodium(I) [13], rhodium(III) [14], iridium(I) [13], copper(I) [15], gold(I) [16], and tin(IV) [17] derivatives. Moreover, compounds in which the  $[\text{C}_5(\text{COOMe})_5]^-$  anion is coordinated through oxygen atoms are known for the first-row transition metals in their II+ or III+ oxidation states [12]. Nevertheless, all these compounds were obtained by metathetical- and not by redox reactions.

## 2. Results and discussion

### 2.1. Synthesis and properties of the complexes

$\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2$  reacts with dbcpH and pcmcph with the formation of dihydrogen (identified by gas chromatography) and chromium(I) derivatives of general formula  $[\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2][\text{X}]$  ( $[\text{X}]^- = [\text{dbcp}]^-$ ,  $[\text{pcmcph}]^-$ ),



In the case of pcmcph, the reaction is fast, occurring while  $\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2$  is added to the fulvene solution, whereas heating at the reflux temperature of the mixture for some hours is required to obtain an appreciable quantity of product in the case of dbcpH. This difference can be attributed to the higher acidity of pcmcph with respect to dbcpH [7]. Compounds **1** and **2** have been obtained from THF as red and yellow crystals, which analyze as  $[\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2][\text{dbcp}] \cdot \text{THF}$  and  $[\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2][\text{pcmcph}]$ , respectively.

The IR spectrum of **1** is characterized by a strong absorption at  $1556\text{ cm}^{-1}$  assigned to the C=O stretching vibration, the same vibration occurring at  $1631\text{ cm}^{-1}$  in the parent fulvene and at  $1620\text{ cm}^{-1}$  in  $\text{Ru}(\text{Cp}^*)(\eta^5\text{-dbcp})$  [10]. Analogously, the IR spectrum of **2** shows two strong bands at  $1715$  and  $1688\text{ cm}^{-1}$ , to be compared with the more complicated pattern found in  $\text{RuCp}(\eta^5\text{-pcmcph})$  ( $1758\text{s}$ ,  $1734\text{vs}$  and  $1723\text{vs}\text{ cm}^{-1}$ ) [18] and in  $\text{Rh}(\text{COD})(\eta^5\text{-pcmcph})$  ( $1742\text{s}$ ,  $1736\text{s}$  and  $1727\text{s}\text{ cm}^{-1}$ ) [13]. The shifts towards higher wavenumbers observed for  $[\text{dbcp}]^-$  and  $[\text{pcmcph}]^-$  anions in ruthenium and rhodium complexes with respect to the chromium compounds can be ascribed to the different charge distribution resulting from the pentahapto coordination to the metal.

In  $\text{CH}_3\text{CN}$  solution, compounds **1** and **2** display a one-electron  $\text{Cr}(\text{I})/\text{Cr}(\text{0})$  reduction process possessing features of chemical reversibility on the cyclo-voltammetric time scale; half-wave potentials ( $-0.90$  and  $-0.91\text{ V}$  vs. SCE for **1** and **2**, respectively) and peak-to-peak separations ( $65\text{ mV}$  for both compounds) are similar to those of other  $\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2^+$  cations reported in the literature [19].

Both **1** and **2** exhibit an irreversible oxidation ( $E_p = 0.94$  V vs. SCE) assigned to a Cr(I)/Cr(II) passage followed by fast decomposition; for complex **1** an irreversible oxidation ( $E_p = 0.48$  V vs. SCE) is also observed which can be ascribed to an electron removal from the [dbcp]<sup>−</sup> anion.

X-band EPR spectra of **1** and **2** were recorded both in fluid and frozen THF and MeCN solution and in the solid state; representative spectra are shown in Figures EPR1 and EPR2 given as Supplementary Material. Spectra characteristic of the  $[\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2]^+$  cation [20] are observed in isotropic solution at room temperature; nine of the eleven lines resulting from the hyperfine coupling of the unpaired electron with 10 equivalent protons ( $I = 1/2$ ) on the toluene rings are observed, whereas coupling with methyl protons is not resolved being small with respect to the spectral line-width (about 1.9 G). In fact, values of the hyperfine coupling constants determined by DFT calculations (spin density surfaces are shown in Figure EPR3 of Supplementary Material) are of 3.24, 3.45, and 3.37 G for *para*, *meta*, and *ortho* protons on the toluene rings, respectively. A hyperfine coupling constant of  $-0.52$  G is obtained for toluene methyl protons, in agreement with previous MO calculations performed on chromium(I) bis(arene) cations [20d,20f,20h–22]. The EPR isotropic parameters for both **1** and **2** ( $g_{\text{iso}} = 1.9865$ ,  $a_{\text{H}} = 3.51$  G and  $a_{53\text{Cr}} = 17.7$  G) are in agreement with those reported for other  $[\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2]^+$  salts [20]. In frozen solution and in the solid state, both **1** and **2** show axial EPR spectra; the parallel and perpendicular components of the  $g$  tensor determined by spectra simulation (Table 1) are similar to those reported for  $[\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2]\text{I}$  in frozen solution [20e]. No resolution of the hyperfine structure is observed in the powder spectra, as found for several methyl substituted chromium(I) bis(arene) cations [20e,20f,20g].

## 2.2. X-ray crystallography

The crystal structure of **1**·THF consists of separated  $[\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2]^+$  cations and [dbcp]<sup>−</sup> anions, no classi-

cal hydrogen bonds occurring in the solid. The shortest interionic interactions amount to 2.3 Å and they occur between the benzylic oxygen atoms of the anion and the hydrogen atoms of the toluene ligand of the cation. In the crystal, six cations and six anions form the walls of a channel parallel to the crystallographic axis  $c$ , a view of the crystal structure along  $c$  being reported in Fig. 1. The ions are arranged in an alternating way; hydrogen atoms of the coordinated toluene in the cations point towards the centre of gravity of the neighbouring anions. The resulting channel has a radius of ca. 5 Å and contains six molecules of THF per repeating unit along  $c$ . An ORTEP plot of the cation and the anion is shown in Fig. 2 and selected bond lengths and angles are reported in Table 2.

The striking feature of this structure is the arrangement of the toluene rings in the cationic moiety with an almost *cis*-eclipsed conformation with respect to the methyl groups, the angle between the projections of the two methyl groups on a common plane being 6.5°. In fact, most of the  $\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2$  derivatives known to date [23] invariably adopt a *trans*-eclipsed conformation [24], which is the conformation minimizing the steric repulsions between the methyl substituents. It has to be noted that in crystalline

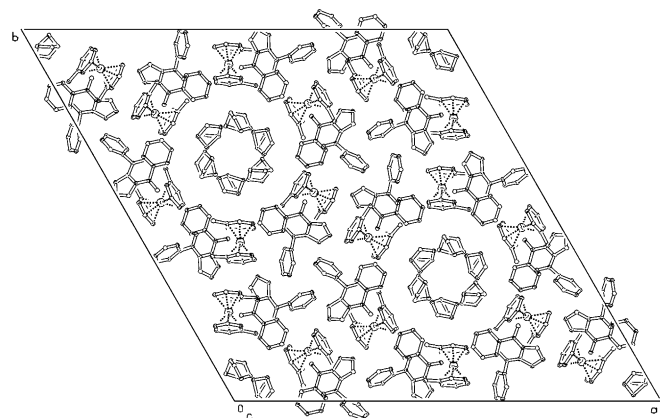


Fig. 1. View of the crystal structure of  $[\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2][\text{dbcp}]\cdot\text{THF}$  (**1**·THF) along the crystallographic axis  $c$ .

Table 1  
EPR parameters for  $[\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2][\text{dbcp}]$  (**1**) and  $[\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2][\text{pcmc}]$  (**2**) in different experimental conditions

System	$T$ (K)	$g_{\parallel}^a$	$g_{\perp}^a$	$\langle g \rangle^b$	$g_{\text{iso}}^c$	$a_{\text{H}} \text{ (G)}^c$
<b>1</b> in THF	298				1.9865	3.51
<b>1</b> in MeCN	298				1.989	3.50
<b>1</b> in MeCN	105	2.004	1.983	1.990		
Solid <b>1</b>	298	1.998	1.989	1.992		
Solid <b>1</b>	105	2.004	1.983	1.990		
<b>2</b> in THF	298				1.9865	3.51
<b>2</b> in MeCN	105	2.007	1.984	1.992		
Solid <b>2</b>	298	2.006	1.982	1.990		
Solid <b>2</b>	105	2.006	1.982	1.990		
$[\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2]^{\text{d}}$						3.24 ( <i>para</i> ), 3.45 ( <i>meta</i> ), 3.37 ( <i>ortho</i> ), $-0.52$ (methyl)

<sup>a</sup> Errors are of 8 units on the last digit.

<sup>b</sup>  $\langle g \rangle = (g_{\parallel} + 2g_{\perp})/3$ .

<sup>c</sup> Errors are of 5 units on the last digit.

<sup>d</sup> From DFT calculation.

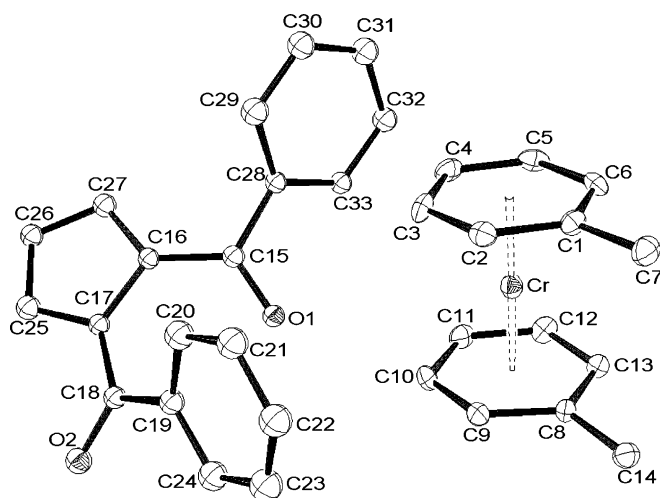


Fig. 2. ORTEP plot of the cation and anion in  $[\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2][\text{dbcnp}] \cdot \text{THF}$  ( $1 \cdot \text{THF}$ ). Displacement ellipsoids are with 50% probability; hydrogen atoms and a molecule of clathrated THF have been omitted for clarity.

Table 2  
Bond lengths (Å) and angles (°) for  $[\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2][\text{dbcnp}] \cdot \text{THF}$  ( $1 \cdot \text{THF}$ )

Cr–C3	2.129(5)	Cr–C11	2.130(5)
Cr–C5	2.131(5)	Cr–C12	2.132(5)
Cr–C2	2.142(5)	Cr–C9	2.143(5)
Cr–C4	2.148(5)	Cr–C10	2.149(5)
Cr–C13	2.153(5)	Cr–C6	2.157(5)
Cr–C1	2.166(5)	Cr–C8	2.179(5)
O1–C15	1.245(5)	O2–C18	1.260(5)
C15–C16	1.460(6)	C15–C28	1.492(6)
C16–C27	1.414(6)	C16–C17	1.438(6)
C17–C25	1.388(6)	C17–C18	1.446(6)
C18–C19	1.513(6)	C26–C27	1.391(6)
O1–C15–C16	122.4(5)	O1–C15–C28	116.9(5)
C16–C15–C28	120.7(5)	O2–C18–C17	121.4(5)
O2–C18–C19	116.2(5)	C17–C18–C19	122.2(5)

$[\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2][7,7,8,8\text{-tetracyanoquinonedimethane}]$  [24b] and  $[\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2][1,3\text{-cyclohexanedione}]_2$  [24c] the cation is disordered due to two different conformations (A and B) adopted by the aromatic rings: in conformation A the methyl groups are at  $120^\circ$  in projection and in conformation B are *trans* in projection with respect to the chromium atom. As far as we know, an almost *cis*-eclipsed disposition of the toluene ligands was observed for the first time in crystalline  $[\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2][\text{dbcnp}]$  [9]; in that case the angle between the two projections of the methyl groups onto a common plane is  $3.6(3)^\circ$ .

The *cis* conformation observed for  $[\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2][\text{dbcnp}]$  and for the compounds reported in this paper is due to favourable packing; intramolecular energy differences between the alternative conformations are negligible with respect to intermolecular interactions, see below.

The centroid–Cr–centroid angle is  $178.6^\circ$ , but the two arene rings are not coplanar, the angle between the least-squares planes being  $3.0(3)^\circ$ ; the average Cr–centroid dis-

tance ( $1.620(3)$  Å) and the average C–C distance within the toluene rings ( $1.408(6)$  Å) are close to those reported in the literature for other  $[\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2]^+$  cations [24].

Due to the fact that the structural parameters of the  $[\text{dbcnp}]^-$  anion are reported here for the first time, reference will be made to  $\text{Ru}(\text{Cp}^*)(\eta^5\text{-dbcnp})$  [10], where  $[\text{dbcnp}]^-$  is  $\eta^5$ -bonded to Ru(II), and to similar substituted fulvenes, i.e., 1-*p*-toluoyl-6-hydroxy-6-*p*-tolylfulvene [25] and  $[\text{dbncp}]^-$ . The five-membered ring of  $[\text{dbcnp}]^-$  shows C–C bond distances comprised between  $1.388(6)$  and  $1.438(6)$  Å, similar to those observed in the *p*-tolyl-substituted protonated species [ $1.390(2)$  and  $1.413(2)$  Å] [25] and in the nitro-substituted  $[\text{dbncp}]^-$  anion [ $1.36(1)$  and  $1.40(1)$  Å] [9]. The C16–C17 bond distance is shorter [ $1.438(6)$  Å] than the corresponding one in 1-*p*-toluoyl-6-hydroxy-6-*p*-tolylfulvene [ $1.464(2)$  Å] [25] or  $[\text{dbncp}]^-$  [ $1.46(1)$  Å] [9]. However, the main differences between the protonated and the anionic species are observed for the C=O and the  $\text{C}_{\text{carbonyl}}\text{--C}_{\text{Cp}}$  ring bond distances: in  $[\text{dbcnp}]^-$ , the C15–O1 [ $1.245(5)$  Å], C18–O2 [ $1.260(5)$  Å], C15–C16 [ $1.460(6)$  Å], and C17–C18 [ $1.446(6)$  Å] bond lengths (see Table 1) are similar to those found for the corresponding bonds in  $[\text{dbncp}]^-$  [ $1.24(1)$ ,  $1.21(1)$ ,  $1.47(1)$ ,  $1.45(1)$  Å] [9], but significantly different from those determined for 1-*p*-toluoyl-6-hydroxy-6-*p*-tolylfulvene [ $1.2762(18)$ ,  $1.2881(18)$ ,  $1.415(2)$ ,  $1.408(2)$  Å] [25]. Short C–O and long C–C distances are observed in 1,2-aryloxy substituted aromatics such as 1,2-dimesitylbenzene (C=O:  $1.214$ ,  $1.213$  Å;  $\text{C}_{\text{aromatic}}\text{--C}_{\text{carbonyl}}$ :  $1.502$ ,  $1.501$  Å) [26] and 4,5,12,13-tetrabenzoyl[2,2]paracyclophane [C=O:  $1.218(3)$  av. Å;  $\text{C}_{\text{aromatic}}\text{--C}_{\text{carbonyl}}$ :  $1.500(3)$  av. Å] [27]. The shorter C–O and the longer C–C distances observed in  $[\text{dbcnp}]^-$  suggest that the electron delocalization, which involves the five-membered ring and the proton located in between the two carbonyl oxygen atoms in the fulvene species, is confined to the ring upon deprotonation.

Compound **2** crystallizes in the monoclinic space group  $P2_1/c$  with two independent cation–anion pairs *per* unit cell. No classical hydrogen bonds occur in the solid, the shortest contacts involving interactions between the carbonyl oxygen atoms of the anion and the hydrogen atoms of toluene. A plot of the ORTEP structure of **2** is reported in Fig. 3; bond distances and angles are listed in Table 3. The two independent molecules (A and B) differ in the conformation of the methyl substituents on the toluene ligands, which are almost *cis*-eclipsed in A and form an angle of  $151.1^\circ$  in B. The presence of both conformers in the same solid is an experimental proof for the low rotational barrier of the  $\eta^6$ -toluene ligands.

The different conformations of toluene ligands observed in  $[\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2][\text{pcmcp}]$  with respect to  $[\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2][\text{dbcnp}] \cdot \text{THF}$  and  $[\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2][\text{dbncp}]$  can be ascribed to crystal packing effects related to the different steric demand of the different anions. Cation–anion interactions within the  $[\text{pcmcp}]^-$  salt are still important enough to induce the cation to assume two different configurations, both with toluene methyl groups in sterically hampered positions. Given that toluene ligands in the

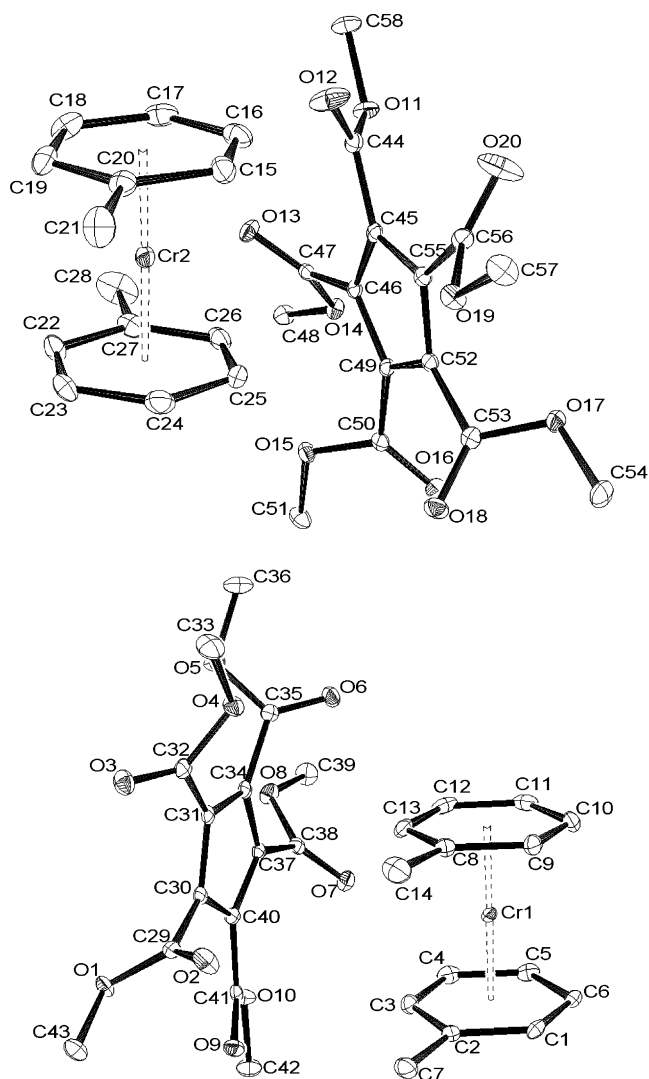


Fig. 3. ORTEP plot of the two independent cations and anions in  $[\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2][\text{pcmcP}]$  (**2**). Displacement ellipsoids are drawn with 50% probability; hydrogen atoms have been omitted for clarity.

isolated cation are essentially free to rotate (an energy difference of 0.09 kcal/mol is found between the *trans*- and *cis*-eclipsed conformations by DFT calculations), these ligands are easily locked in place in the solid state by the surrounding ions, due to the presence of the protruding methyl groups [28]. The rotameric conformations adopted are therefore determined by the optimization of intermolecular interactions of peripheral atoms [29,30]. The mean C–C distance within the toluene rings [1.414(2) Å] is in agreement with the usually observed C–C bond distances in  $\eta^6$ -coordinated chromium arene derivatives [31], and the angle centroid–Cr–centroid is very close to 180°, being 179.08(10)° and 178.15(10)° for molecule A and molecule B, respectively. No distortion along the axis connecting the *para* and the *ipso* carbon atoms of the toluene rings is observed.

As far as the anion is concerned, the average values of the C–C, C=O and C–O bond distances [1.411(3), 1.211(3),

Table 3  
Bond lengths (Å) and angles (°) for  $[\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2][\text{pcmcP}]$  (**2**)

Cr1–C13	2.132(2)	Cr1–C12	2.133(3)
Cr1–C11	2.135(3)	Cr1–C5	2.138(2)
Cr1–C4	2.139(2)	Cr1–C6	2.140(2)
Cr1–C1	2.141(2)	Cr1–C10	2.146(3)
Cr1–C3	2.150(2)	Cr1–C9	2.158(3)
Cr1–C8	2.179(2)	Cr1–C2	2.179(2)
Cr2–C24	2.138(3)	Cr2–C25	2.140(3)
Cr2–C22	2.143(3)	Cr2–C16	2.144(3)
Cr2–C23	2.146(3)	Cr2–C26	2.146(3)
Cr2–C15	2.147(3)	Cr2–C19	2.149(3)
Cr2–C18	2.159(3)	Cr2–C17	2.163(3)
Cr2–C20	2.166(3)	Cr2–C27	2.170(3)
C29–O1–C43	114.75(19)	C32–O4–C33	115.7(2)
C35–O5–C36	115.0(2)	C38–O8–C39	117.3(2)
C41–O10–C42	115.06(19)	O2–C29–O1	123.6(2)
O2–C29–C30	123.6(2)	O1–C29–C30	112.87(19)
O3–C32–O4	123.0(2)	O3–C32–C31	125.5(2)
O4–C32–C31	111.5(2)	O6–C35–O5	123.4(2)
O6–C35–C34	125.0(2)	O5–C35–C34	111.6(2)
C40–C37–C38	128.9(2)	O7–C38–O8	123.6(2)
O7–C38–C37	126.4(2)	O8–C38–C37	110.0(2)
O9–C41–O10	122.7(2)	O9–C41–C40	123.8(2)
O10–C41–C40	113.5(2)	C44–O11–C58	115.60(19)
C47–O14–C48	115.62(18)	C50–O15–C51	115.01(19)
C53–O17–C54	114.00(19)	C56–O19–C57	116.02(19)
O12–C44–O11	122.2(2)	O12–C44–C45	125.8(2)
O11–C44–C45	112.1(2)	C46–C45–C55	107.9(2)
C49–C46–C47	125.4(2)	O13–C47–O14	122.5(2)
O13–C47–C46	125.7(2)	O14–C47–C46	111.8(2)
O16–C50–C49	124.4(2)	O15–C50–C49	112.9(2)
C55–C52–C53	127.3(2)	O18–C53–O17	123.3(2)
O18–C53–C52	124.9(2)	O17–C53–C52	111.7(2)
O20–C56–O19	122.2(2)	O20–C56–C55	126.7(2)
O19–C56–C55	111.1(2)		

1.349(3) Å, respectively] are similar to those observed in  $[\text{NMe}_4][\text{pcmcP}]$  [1.406(5), 1.200(4), 1.338(5) Å] [32]. On the other hand, a significant lengthening of the C<sub>5</sub> ring C–C bond distances occurs on coordination as observed in  $\text{RuCp}(\eta^5\text{-pcmcP})$  [18] [1.438(2) Å] and in  $\text{Rh}(\text{COD})(\eta^5\text{-pcmcP})$  [13] [1.426(3) Å], the C=O and C–O bonds remaining equal within the experimental error [1.197(3), 1.331(2) and 1.193(3), 1.327(3) Å in the ruthenium and rhodium compounds, respectively]. Planarity of the C<sub>5</sub> rings in the anion of both A and B is demonstrated by the average internal angle, which is invariably 108°, as expected for a regular planar pentagonal polygon.

### 3. Conclusions

The reactivity of  $\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2$  with fulvene precursors of substituted cyclopentadienyl rings has been studied and compounds of general formula  $[\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2][\text{X}]$  ( $[\text{X}]^- = [\text{dbcp}]^-$  (**1**),  $[\text{pcmcP}]^-$ , (**2**)), have been prepared. The results of the present paper represent a confirmation of the data recently reported by some of us on  $[\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2][1,2\text{-dibenzoyl-4-nitro-cyclopentadienyl}]$  [9]. As a matter of fact, compounds **1** and **2** and  $[\text{Cr}(\eta^6\text{-CH}_3\text{-C}_6\text{H}_5)_2][1,2\text{-dibenzoyl-4-nitro-cyclopentadienyl}]$  represent

rare examples of chromium bis(toluene) cations showing a *cis*-eclipsed conformation of the arene ligands, which can be ascribed to packing effects associated to the anions. In fact, the energy gap between the *cis*- and the *trans*-eclipsed conformations in vacuo is very small (0.09 kcal/mol from DFT calculation) and EPR data in isotropic solution show equivalence of the ring protons, indicating that the toluene rings are essentially free to rotate. In the solid state, the aromatic ligands are locked in place by the surrounding anions and the cation adopts the conformation dictated by the energetics of the lattice formation: on going from [dbcpr]<sup>−</sup> to the less sterically demanding [pcmcp]<sup>−</sup> the cation adopts both the *cis*- and a *pseudo trans*-disposition of the methyl groups.

Finally, the results reported in this paper have to be considered complementary to those obtained with the bis(arene) derivatives of titanium(0), vanadium(0) and niobium(0) which react with the fulvene species of Scheme 1 with oxidation of the metal and loss of the aromatic ligands to give *O,O'*-coordination compounds of vanadium(II) or titanium(III) and niobium(III) [33]. This trend is probably related to both the higher aptitude to oxidation with consequent loss of the  $\pi$ -acid arene ligands (the Cr(0)  $\rightarrow$  Cr(I) oxidation leaves one electron in an orbital which still has a weak metal–ligand bonding character, while the oxidation by two- or the three electrons of Group 4 and 5 metals remove completely the electrons from metal arene bonding orbitals) and the high oxygen affinity peculiar to the elements of Groups 4 and 5.

## 4. Experimental

### 4.1. General procedures

Unless otherwise noted, all operations were carried out under an inert atmosphere (argon); before use, all the glassware was oven-dried, evacuated (0.01 Torr) and filled with argon. Infrared spectra were recorded on a FT-IR Perkin–Elmer mod.1725X spectrometer on nujol mulls prepared under rigorous exclusion of air. X-band EPR spectra of **1** and **2** in fluid and frozen THF solution were recorded on a Varian E112 spectrometer equipped with a Varian E257 unit for temperature control. The spectrometer was interfaced to an IPC 610/P566C industrial grade Avantech computer by means of a data acquisition system [34] and a software package [35] specially designed for EPR experiments. Sample solutions (25–20  $\mu$ L) were enclosed under argon atmosphere in quartz tubes fitted with a quartz–Pyrex joint and a Bibby Quickfit Rotaflo PTFE tap (DISA, Milan). Simulations of EPR spectra were performed using the WINSIM 32 program [36]. EPR spectra of **1** and **2** in fluid and frozen MeCN solution and in the solid state were recorded on a BRUKER ER 200-SRDD spectrometer operating at X-band ( $\nu = 9.7874$  GHz). The operational microwave frequency (Bruker Microwave bridge ER 401 MR) was tested with an XL Microwave Frequency Coun-

ter 3120 and the external magnetic field  $H_0$  was calibrated by using a dpph powder sample ( $g_{\text{dpph}} = 2.0036$ ). The temperature was controlled with a Bruker ER 4111 VT device (accuracy of  $\pm 1$  °C). Computer simulation of the EPR spectra was carried out by using the SIM14 A program. Cyclic voltammetry was performed in a three-electrode cell having a platinum disk working electrode (1.5 mm in diameter) surrounded by a platinum-spiral counter electrode and the aqueous saturated calomel reference electrode (SCE) mounted with a Luggin capillary. Either a BAS 100A electrochemical analyzer or a multipurpose Amel instrument (a Model 566 analog function generator and a Model 552 potentiostat) were used as polarizing units. DFT geometry optimization and calculation of the electron spin density distribution of the  $[\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2]^+$  cations were performed using the Linux version of the Spartan'02 software [37]. We adopted the BP86 scheme, that uses the functional proposed by Becke [38] and Perdew [39], and the 6-31G\*\* basis set that is appropriate for calculations of split-valence-plus-polarization quality. The following compounds were prepared as reported in the literature:  $\text{Cr}(\eta^6\text{-MeC}_6\text{H}_5)_2$  [40], pcmcpH [41], dbcprH [11].

### 4.2. Preparation of $[\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2][\text{dbcpr}] \cdot \text{THF}$ (**1** · THF)

$\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2$  (0.437 g, 1.8 mmol) was added to a solution of dbcprH (0.507 g, 1.8 mmol) in THF (120 ml) and the resulting solution was stirred under reflux for 5 h. The reaction vessel was slowly cooled first to room temperature and then down to ca. 243 K:  $[\text{Cr}(\eta^6\text{-CH}_3\text{-C}_6\text{H}_5)_2][\text{dbcpr}] \cdot \text{THF}$  was obtained (0.489 g, 46% yield) as yellow crystals suitable for an X-ray diffraction analysis. Anal. Calc. for  $\text{C}_{37}\text{H}_{37}\text{CrO}_3$ : C, 75.1; H, 8.0. Found: C, 75.3; H, 8.3%. IR (Nujol):  $\tilde{\nu}/\text{cm}^{-1}$  3050w, 1587m, 1556s, 1432m, 1341s, 1313w, 1125m, 1055m, 1020m, 854s, 723s, 667s. The compound loses THF in high vacuum at room temperature with formation of a yellow microcrystalline solid.

### 4.3. Preparation of $[\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2][\text{pcmcp}]$ (**2**)

$\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2$  (0.407 g, 1.7 mmol) was added to a solution of pcmcpH (0.606 g, 1.7 mmol) in THF (100 ml); immediate reaction took place, as demonstrated by the sudden change of colour of the solution, which became bright yellow. After 24 h of stirring, THF was removed in vacuo; as soon as the solution concentrated, a yellow solid separated out.  $[\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2][\text{pcmcp}]$  was recovered by filtration and vacuum dried (0.588 g, 57% yield). A part (0.176 g) of this compound was suspended in THF (20 ml) and the mixture heated to reflux, filtered while hot, and slowly cooled down to ca. 277 K, yielding the compound as long yellow needles suitable for an X-ray diffraction analysis. Anal. Calc. for  $\text{C}_{29}\text{H}_{31}\text{CrO}_{10}$ : C, 58.9; H,

5.2. Found: C, 58.1; H, 5.9%. IR (Nujol):  $\tilde{\nu}/\text{cm}^{-1}$  3061w, 1715s, 1688vs, 1273m, 1212vs, 1065m, 1010m, 838w, 722w.

#### 4.4. X-ray structure determination of $[\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2][\text{dbcp}] \cdot \text{THF}$ (**1** · THF)

Crystal data and parameters of data collection and structure refinement of a solvate of composition  $[\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2][\text{dbcp}] \cdot \text{THF}$  are compiled in Table 4.

Data were collected with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) on a Bruker Smart Apex CCD area detector on a D8 goniometer at 110(2) K on a prismatic yellow crystal of approximate dimensions  $0.30 \times 0.05 \times 0.05 \text{ mm}$ . A set of 49,238 reflections with indices  $-49 \leq h \leq 49$ ,  $-48 \leq k \leq 49$ ,  $-10 \leq l \leq 10$  were collected with the  $\omega$  scan method in the range  $2.3^\circ \leq \theta \leq 25.1^\circ$ . An empirical absorption correction (min. trans. 0.88, max. trans. 0.98) was applied before averaging symmetry equivalent data ( $R_{\text{int}} = 0.2619$ ). After merging, 5288 independent reflections remained for structure solution by direct method [42]. The structure model was completed by Fourier difference syntheses and refined with full-matrix least-squares on  $F^2$  [43]. Convergence was reached for 5288 reflections and 244 variables at  $wR_2 = 0.1343$  (all data),  $R_1 = 0.0660$  [observations with  $I > 2\sigma(I)$ ]. Max. and min. from a final Fourier map were 0.630 and  $-0.406 \text{ e \AA}^{-3}$ .

Table 4  
Crystal data and structure refinement for  $[\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2][\text{dbcp}] \cdot \text{THF}$  (**1** · THF), and  $[\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2][\text{pcmcp}]$ , (**2**)

Compound	<b>1</b> · THF	<b>2</b>
Empirical formula	C <sub>37</sub> H <sub>37</sub> CrO <sub>3</sub>	C <sub>29</sub> H <sub>31</sub> CrO <sub>10</sub>
Formula weight	581.67	591.54
Temperature (K)	110(2)	
Wavelength (Å)	0.71073	
Crystal system, space group	Rombohedral, $R\bar{3}$	Monoclinic, $P2_1/c$
Unit cell dimensions		
<i>a</i> (Å)	41.243(4)	14.791(5)
<i>b</i> (Å)	41.243(4)	33.218(11)
<i>c</i> (Å)	9.0759(13)	11.069(4)
$\beta$ (°)		91.225(7)
Crystal dimensions (mm)	0.30, 0.05, 0.05	0.71, 0.12, 0.10
<i>V</i> (Å <sup>3</sup> )	13370(3)	5437(3)
<i>Z</i> , calculated density (Mg/m <sup>3</sup> )	18, 1.300	8, 1.445
Absorption coefficient (mm <sup>-1</sup> )	0.421	0.479
<i>F</i> (000)	5526	2472
$\theta$ range (°)	2.3–25.1	1.4–27.5
Limiting indices	$-49 \leq h \leq 49$ ; $-48 \leq k \leq 49$ ; $-10 \leq l \leq 10$	$-19 \leq h \leq 19$ ; $-42 \leq k \leq 43$ ; $-14 \leq l \leq 14$
Reflections collected/unique	49,238/5288 [ $R_{\text{int}} = 0.2619$ ]	61,678/12,432 [ $R_{\text{int}} = 0.0755$ ]
Refinement method	Full-matrix least-squares on $F^2$	
Data/restraints/parameters	5288/9/244	12432/0/735
Goodness-of-fit on $F^2$	0.913	1.051
Final <i>R</i> indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0660$ , $wR^2 = 0.1181$	$R_1 = 0.0510$ , $wR^2 = 0.1083$
<i>R</i> indices (all data)	$R_1 = 0.1719$ , $wR^2 = 0.1343$	$R_1 = 0.0730$ , $wR^2 = 0.1173$
Largest difference peak and hole ( $\text{e \AA}^{-3}$ )	0.630 and $-0.406$	0.421 and $-0.378$

In view of the relatively low number of observed data and the limited resolution of the experiment, only non-hydrogen atoms in the cation were assigned anisotropic displacement parameters in the final refinement.

#### 4.5. X-ray structure determination of $[\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2][\text{pcmcp}]$ (**2**)

Crystal data and parameters of data collection and structure refinement are compiled in Table 4. Data were collected with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) on a Bruker Smart Apex CCD area detector on a D8 goniometer at 110(2) K on a crystal of approximate dimensions  $0.71 \times 0.12 \times 0.10 \text{ mm}$ . A set of 61,678 reflections with indices  $-19 \leq h \leq 19$ ,  $-42 \leq k \leq 43$ ,  $-14 \leq l \leq 14$  were collected with the  $\omega$  scan method in the range  $1.4^\circ \leq \theta \leq 27.5^\circ$ . An empirical absorption correction (min. trans. 0.73, max. trans. 0.95) was applied before averaging symmetry equivalent data ( $R_{\text{int}} = 0.0755$ ). The structure was solved by direct methods [42] and the structural models were completed by Fourier difference syntheses and refined with full-matrix least-squares on  $F^2$  [43].

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#### Appendix A. Supplementary data

*Crystallographic material.* Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC 271156 for  $[\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2][\text{dbcp}] \cdot \text{THF}$  and CCDC 271157 for  $[\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2][\text{pcmcp}]$ . Copies can be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax 441223336033; email: deposit@ccdc.cam.ac.uk or WWW: <http://www.ccdc.cam.ac.uk>). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2005.09.048.

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