

Communication

# Benzoyl-substituted ( $\eta^6$ -arene)tricarbonylchromium complexes: Synthesis and structure

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Dedicated to Stefano Maiorana on the occasion of his 70th birthday.

## Abstract

Lithiation of chloro- and methoxy-( $\eta^6$ -benzene)tricarbonylchromium complexes yielded, after electrophilic quench with a Weinreb amide, the corresponding benzoyl-substituted complexes. One of them has been investigated by an X-ray diffraction study.

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## 1. Introduction

The coordination of an arene to metal carbonyl moieties [M(CO)<sub>3</sub>] strongly modifies the reactivity of the arene ligand. In particular, the arene complexes of chromium have been the subject of extensive development due to their significant applications in organic synthesis [1]. Furthermore, an expanding area of the use of metal carbonyls has been developed in bioorganometallic chemistry, increasing the potential of Cr complexes in such a field [2,3].

In the course of our research into organochromium and organomanganese complexes [4] we were interested in one of the major changings of the coordinated arene: the acidification of the hydrogens attached to the aromatic ring which strongly facilitates the direct proton abstraction followed by electrophilic trapping. This reaction has been extensively explored in (arene)Cr(CO)<sub>3</sub> complexes and has been the subject of several reviews [5]. Different types

of electrophiles have been reported for the anion trapping step. Among them, electrophilic halide sources, alkylating agents, heteroatom nucleophiles were widely used. Carbonyl compounds including aldehydes, acid chlorides, anhydrides, esters, amides, ketones were reported to react with lithiated (arene)Cr(CO)<sub>3</sub> complexes [5c].

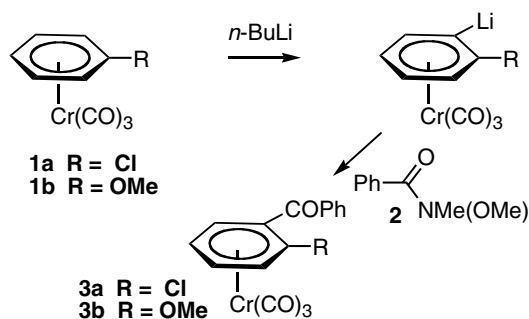
In the course of our research into the functionalization of organochromium complexes we were interested in the preparation of such complexes substituted by a keto group [6,7]. This communication describes the easy syntheses of benzoyl-substituted ( $\eta^6$ -arene tricarbonylchromium) complexes by lithiation/electrophilic quench sequence using a Weinreb amide as the electrophile.

## 2. Results and discussion

The reaction of the anions of complexes **1a,b**, obtained by addition at low temperature of *n*-BuLi to the corresponding complexes, with the Weinreb amide **2** [8] led to the formation of two new complexes substituted by a benzoyl group: **3a** in 43% yield and **3b** in 46% yield (Scheme 1). This reaction is highly regioselective: only the *ortho*-substituted

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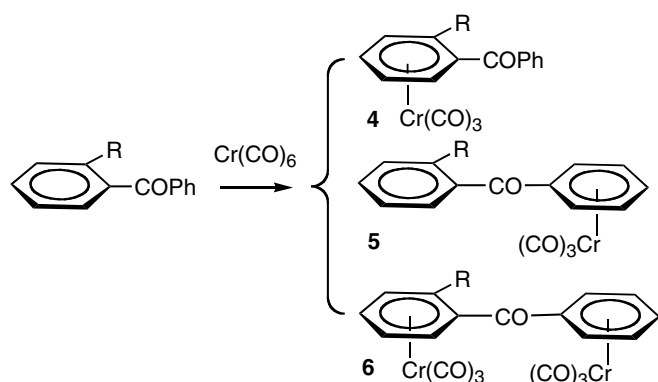


Scheme 1.

compounds were isolated. Although the yields were not entirely satisfying, this reaction represents a significant improvement in the synthesis of such complexes. Indeed, the preparation of **3a** or **3b** by direct coordination of the corresponding free ligands to  $\text{Cr(CO)}_3$  resulted in the formation of three compounds difficult to purify by silica gel chromatography column: two complexes (**4** and **5**), where the chromium entity  $\text{Cr(CO)}_3$  coordinated the substituted or the unsubstituted arene ring, and the last one (**6**), a bimetallic compound, where the chromium entity coordinated the two arene rings at the same time [9] (Scheme 2).

Several years ago [6], we achieved the synthesis of  $\eta^6$ -(2-thiophenyl) carbonylarenetricarbonylchromium complexes using palladium-catalyzed process under a carbon monoxide atmosphere and a judicious choice of reaction conditions. But this methodology needs the presence of an halogen substituent on the arene ring of the starting material to allow the insertion of the palladium active species into the C–halogen bond, thus limiting the choice of the starting complexes.

$^1\text{H}$  NMR spectra of complexes **3a** and **3b** exhibit well resolved doublets and triplets for the  $\text{H}_3$ – $\text{H}_6$  protons. As expected, the conformations in solution of the major isomers of both complexes are anti-eclipsed with respect with the keto group [10]. For the anisole derivative **3b**, there is a synergic effect between the methoxy and the keto groups. Indeed, the electron-donating methoxy group favours a conformation which eclipses this substituent and the elec-



Scheme 2.

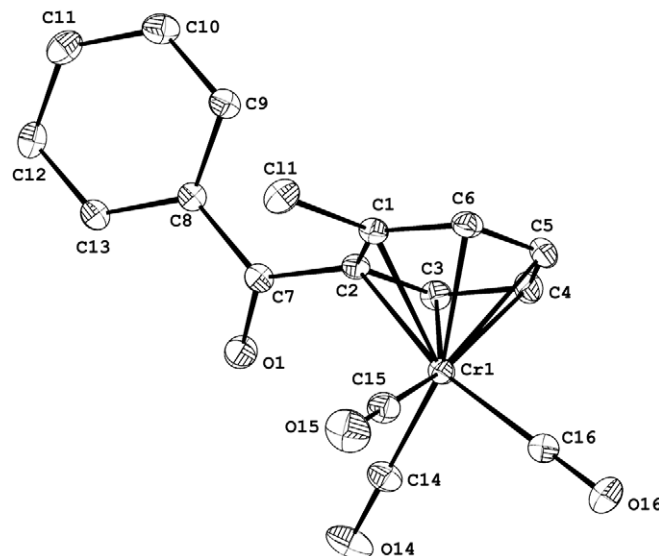
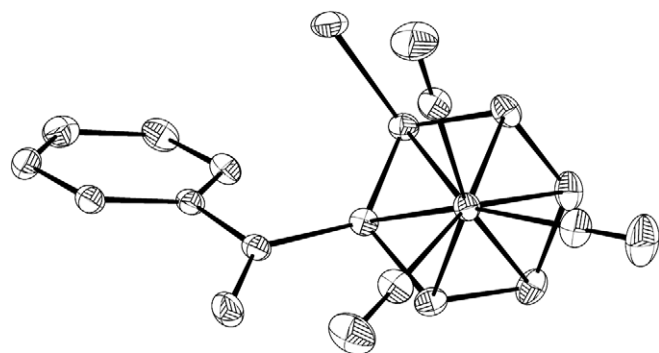


Fig. 1. Two views of the ORTEP diagram of **3a**. Selected bond lengths (Å) and angles (°): Cr–C<sub>1</sub>, 2.216(2); Cr–C<sub>2</sub>, 2.230(2); Cr–C<sub>3</sub>, 2.204(2); Cr–C<sub>4</sub>, 2.229(2); Cr–C<sub>5</sub>, 2.219(2); Cr–C<sub>6</sub>, 2.222(2); Cr–O, 1.225(3); C<sub>2</sub>–C<sub>7</sub>, 1.525(3); C<sub>7</sub>–C<sub>8</sub>, 1.492(3).

tron-withdrawing benzoyl group favours a conformation which anti-eclipses the carbonyl residue. Thus, the difference of chemical shifts between the  $\text{H}_4$  and  $\text{H}_5$  protons is larger in **3b**: 0.74 ppm than in **3a**: 0.62 ppm.

We obtained some monocrystals of complex **3a** and subjected them to X-ray analysis. Two views of ORTEP diagram as well as selected bond lengths are reported Fig. 1. The torsion angles  $\text{C1-C10-Cr-C15}$ ,  $\text{C5-C10-Cr-C16}$ , and  $\text{C3-C10-Cr-C14}$  are  $21.45^\circ$ ,  $19.80^\circ$ , and  $20.61^\circ$ , respectively (C10 being the center of the six-membered ring). The free arene plane is not parallel to the coordinated arene plane, with a dihedral angle value of  $68^\circ$ . The carbonyl function, which lies almost in the plane of the uncoordinated arene ring, is pointing out in the direction of the  $\text{Cr(CO)}_3$  entity with a dihedral angle of  $46^\circ$  with the coordinated arene ring. It is interesting to note that, in the case of the  $[\eta^6$ -(2-thiophenyl)carbonyl-*p*-methoxybenzene]-tricarbonylchromium complex [6], the carbonyl function was found to point in the direction opposite to the  $\text{Cr(CO)}_3$  moiety with a dihedral angle of  $14^\circ$  with the six-membered arene ring.

### 3. Conclusion

These results address the potentiality of the Weinreb amide **2** in the preparation of benzoyl-substituted ( $\eta^6$ -arene)tricarbonylchromium complexes. This electrophile allows the easy formation of such complexes after a lithiation/electrophilic quench sequence of halogeno- and methoxy-substituted (arene)Cr(CO)<sub>3</sub> complexes. Work is in progress in order to generalize these results to other diversely substituted complexes.

### 4. Experimental

All chemicals were used as supplied, unless noted otherwise. All NMR spectra were obtained on a Bruker 250 or 400 in CDCl<sub>3</sub> and are referenced to external TMS. Elemental analyses were performed by the “Service de microanalyses de l’UPMC”.

#### 4.1. Typical procedure: preparation of complex **3a**

Chlorobenzenetricarbonylchromium **1a** (321 mg, 1.29 mmol) in THF (10 mL) was stirred at  $-78^\circ\text{C}$  in a flask under dry nitrogen. *n*-BuLi (0.72 mL, 1.8 mmol) was added to this yellow solution. The solution became pink then orange. After 90 min, the Weinreb amide PhCON(Me)(OMe) **2** (421 mg, 2.55 mmol) was introduced via a canula at  $-78^\circ\text{C}$  and the reaction mixture stirred for 2 h. This solution was introduced at  $0^\circ\text{C}$  into another flask containing AcOH (11 mL) and water (9 mL) at  $0^\circ\text{C}$ . The mixture was then extracted twice with Et<sub>2</sub>O (2 × 30 mL), with a saturated K<sub>2</sub>CO<sub>3</sub>/H<sub>2</sub>O solution and with a saturated NaCl/H<sub>2</sub>O solution. After evaporation of the organic phase, an orange solid was recovered which was purified by silica gel chromatography column with a petroleum-ether/dichloromethane mixture 100/0 until 0/100 ratio. The orange red solution was evaporated under reduced pressure and recrystallized: 196 mg, 43% yield of **3a**.

$\delta_{\text{H}}$  (CDCl<sub>3</sub>): 7.4–7.9 (5H, m, ArH); 5.67 (1H, d,  $J = 6$  Hz, H<sub>5</sub>); 5.56 (1H, t,  $J = 6$  Hz, H<sub>3</sub>); 5.47 (1H, d,  $J = 6$  Hz, H<sub>6</sub>); 5.05 (1H, t,  $J = 6$  Hz, H<sub>4</sub>). Elemental analysis (C<sub>16</sub>H<sub>9</sub>ClCrO<sub>4</sub> requires): C, 54.55; H, 2.58. Found: C, 54.38; H, 2.49%. MS IC  $m/z$  353 (MH)<sup>+</sup>. IR (CHCl<sub>3</sub>) 1983, 1913, 1652 cm<sup>-1</sup>.

#### 4.2. Complex **3b**

$\delta_{\text{H}}$  (CDCl<sub>3</sub>): 7.3–7.5 (5H, m, ArH); 5.87 (1H, dd,  $J = 7$  and 1 Hz, H<sub>3</sub>); 5.65 (1H, td,  $J = 7$  and 1 Hz, H<sub>5</sub>); 5.06 (1H, br d,  $J = 7$  Hz, H<sub>6</sub>); 4.91 (1H, td,  $J = 7$  and 1 Hz, H<sub>4</sub>); 3.66 (3H, s, OMe). IR (CHCl<sub>3</sub>) 1987, 1917, 1660 cm<sup>-1</sup>.

Elemental analysis (C<sub>17</sub>H<sub>12</sub>CrO<sub>5</sub> requires): C, 58.62; H, 3.48. Found: C, 58.54; H, 3.41%. MS IC  $m/z$  349 (MH)<sup>+</sup>.

Crystal structure data of **3a**: orange-red parallelepiped, C<sub>16</sub>H<sub>9</sub>ClCrO<sub>4</sub>,  $M = 352.67$ , monoclinic, space group P2<sub>1</sub>/c;  $a = 12.203(2)$ ,  $b = 10.447(3)$ ,  $c = 12.760(2)$  Å,  $\alpha = 90^\circ$ ,  $\beta = 116.761(14)^\circ$ ,  $\gamma = 90^\circ$ .  $U = 1452.5(6)$  Å<sup>3</sup>,  $T = 250$  K,

$Z = 4$ ,  $\lambda(\text{Mo-K}\alpha) = 0.71073$  Å, nb of data collected = 12896, nb of unique data collected = 4219, nb of unique data used for refinement  $2162(F_o)^2 > 3\sigma(F_o)^2$ ,  $R(F) = 0.0312$ ,  $R_w(F^2) = 0.0344$ .

### 5. Supplementary material

CCDC 622365 contains the supplementary crystallographic data for **3a**. The data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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