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Synthesis and Electrochemical Study of Acetyl- and Carbomethoxycyclopentadienylcarbonyl Chromium Complexes

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Abstract

The salts C_5H_4RNa react with $Cr(CO)_6$ giving the carbonylate salts $[\eta\text{-}C_5H_4RCr(CO)_3]Na$ (R = $COCH_3$ (1), CO_2CH_3 (2)). By reaction of 1 and 2 with $Hg(CN)_2$ the symmetrical mercurials $[\eta\text{-}C_5H_4RCr(CO)_3]_2Hg$ (R = $COCH_3$ (3), CO_2CH_3 (4)) are obtained. The oxidation of 1 and 2 with Fe^{3+} gives rise to the dimers $[\eta\text{-}C_5H_4RCr(CO)_3]_2$ (R = $COCH_3$ (5), CO_2CH_3 (6)). The compounds are characterized by IR and ^1H NMR spectroscopy.

The electrochemical behaviour of these complexes has been studied in THF solution, using cyclic voltammetry and coulometry.

Introduction

Among complexes with stoichiometry $[\eta\text{-}C_5H_4RM(CO)_3]_2$ (M = Cr, Mo, W; R = H, alkyl) chromium derivatives have been less extensively studied than the molybdenum and tungsten analogues, perhaps because they are less stable to air and consequently more difficult to handle.

These dimers can be obtained by oxidation of $[\eta\text{-}C_5H_4RM(CO)_3]^-$ achieved by chemical reagents [1, 2] or by electrochemical methods [3]. If oxidation is achieved electrolytically, then the nature of the product depends on the electrode used: at a Pt electrode $[\eta\text{-}C_5H_4RM(CO)_3]_2$ is formed, but over mercury, the oxidized product is $[\eta\text{-}C_5H_4RM(CO)_3]_2Hg$. The electrochemical behaviour of these complexes has been the subject of several studies [4–8].

For the chromium, dimers with alkyl-ring substituents have been previously examined [9–12], but no compounds containing electron-withdrawing substituents (e.g. CHO, $COCH_3$ or CO_2CH_3) have been described.

The mercury complexes are among the most air stable and thermally stable metal carbonyl derivatives. Edelman and Behrens reported the synthesis of symmetrical mercurials $[\eta\text{-}C_5H_4CHOM(CO)_3]_2Hg$ (M = Cr, Mo, W) by reaction of $C_5H_4CHOM(CO)_3^-$ with $Hg(CN)_2$ [13]. Chaloyard and El Mur reported the analogous acetyl and carbomethoxy derivatives of molybdenum and tungsten obtained by electrochemical oxidation but the IR and ^1H NMR spectra are not given [14].

We extend the early works to a study of the dimers $[\eta\text{-}C_5H_4RCr(CO)_3]_2$ and mercurials $[\eta\text{-}C_5H_4RCr(CO)_3]_2Hg$ with electron-withdrawing groups in the cyclopentadienyl ring (R = $COCH_3$, CO_2CH_3).

Experimental

All reactions were carried out under oxygen-free N_2. Solvents were dried and deoxygenated. $Hg(CN)_2$ and $Cr(CO)_6$ were purchased from standard chemicals. Acetyl and carbomethoxycyclopentadienylsodium were prepared according to literature procedures [15–17]. Chromium was determined by atomic absorption with a Perkin-Elmer 372 spectrophotometer.

The IR spectra were recorded with a Nicolet 5DX spectrometer using Nujol mulls between CsI windows. For spectra in solution NaCl windows were used. ^1H NMR spectra were recorded with a Bruker WM-200-SY spectrometer.

The electrochemical measurements were performed in the experimental conditions previously reported [18]. Tetrahydrofuran was distilled from sodium benzophenone ketyl under nitrogen immediately before use.

$[\eta\text{-}C_5H_4COCH_3Cr(CO)_3]Na$ (1)

Sodium acetylcyclopentadienide (0.58 g, 4.5 mmol) and chromium hexacarbonyl (1.19 g, 5.4

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mmol) were added to a 100 ml three-necked flask equipped with nitrogen inlet, stirrer and reflux condenser. To this was added 30 ml of diglyme and the mixture refluxed for 8 h. The resulting solution of η-$C_5H_4COCH_3Cr(CO)_3Na$ was cooled to room temperature and the solvent was removed by distillation under reduced pressure. A reddish residue was obtained.

Anal. Calc. for $C_{10}H_7CrNaO_4$: C, 45.11; H, 2.63; Cr, 19.54. Found: C, 44.72; H, 2.70; Cr, 18.80%.

IR (diglyme): ν(CO) 1905vs, 1897sh, 1800vs, 1794vs, 1780sh, 1650m cm^{-1}.

[η-$C_5H_4CO_2CH_3Cr(CO)_3$]Na (2)

The procedure described above was used but with sodium carbomethoxycyclopentadienide (0.46 g, 3.1 mmol) and chromium hexacarbonyl (0.83 g, 3.7 mmol) as reactants. A brown–yellow residue was obtained.

Anal. Calc. for $C_{10}H_7CrNaO_5$: C, 42.55; H, 2.48; Cr, 18.43. Found: C, 42.30; H, 2.51; Cr, 17.90%.

IR (diglyme): ν(CO) 1903vs, 1800vs, 1794vs, 1764sh, 1700m cm^{-1}.

[η-$C_5H_4COCH_3Cr(CO)_3]_2$Hg (3)

Sodium acetylcyclopentadienide (1.19 g, 9.1 mmol) and chromium hexacarbonyl (2.42 g, 11 mmol) were added to a 250 ml three-necked flask equipped with nitrogen inlet, stirrer and reflux condenser. To this was added 50 ml of diglyme and the mixture refluxed for 8 h. The resulting solution of η-$COCH_3C_5H_4Cr(CO)_3Na$ was cooled to room temperature and poured into 120 ml of an aqueous solution of 3.05 g (12.0 mmol) of mercury(II) cyanide. A yellow–gold precipitate of the mercury derivative formed. This was filtered off, washed several times with water, and dried in vacuum. The product was purified from acetone/water. The yield was 1.17 g (39%).

Anal. Calc. for $C_{20}H_{14}HgCr_2O_8$: C, 34.95, H, 2.03; Cr, 15.14. Found: C, 33.81; H, 2.26; Cr, 14.48%.

IR ($CHCl_3$): ν(CO) 1994vs, 1972sh, 1966vs, 1908sh, 1892vs, 1684vs cm^{-1}. IR (Nujol): ν(CO) 1987vs, 1955vs, 1912sh, 1897sh, 1869vs, 1681s cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.49 (br.s, 2H, $H_{2,5}$), 5.08 (br.s, 2H, $H_{3,4}$), 2.32 (s, 3H, CH_3) ppm.

[η-$C_5H_4CO_2CH_3Cr(CO)_3]_2$Hg (4)

The procedure described above was used, but with $CO_2CH_3C_5H_4Na$ (1.67 g, 11.4 mmol) and $Cr(CO)_6$ (3.02 g, 13.7 mmol) as reactants. Yellow–orange flakes were obtained. The yield was 1.7 g (41.46%).

Anal. Calc. for $C_{20}H_{14}HgCr_2O_{10}$: C, 33.39; H, 1.94; Cr, 14.47. Found: C, 33.26; H, 2.23; Cr, 13.90%.

IR ($CHCl_3$): ν(CO) 1995vs, 1969vs, 1912sh, 1891vs, 1725s cm^{-1}. IR (Nujol): ν(CO) 1992vs, 1961vs, 1912sh, 1875sh, 1869vs, 1717s cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.50 (br.s, 2H, $H_{2,5}$), 5.00 (br.s, 2H, $H_{3,4}$), 3.79 (s, 3H, CH_3).

[η-$C_5H_4COCH_3Cr(CO)_3]_2$ (5)

Sodium acetylcyclopentadienide (2.35 g, 18.0 mmol) and chromium hexacarbonyl (4.70 g, 21.3 mmol) were added to a 250 ml three-necked flask equipped with nitrogen inlet, stirrer and reflux condenser. To this was added 100 ml of diglyme and the mixture heated to reflux for 7.30 h. The reaction mixture was cooled and stirred. To it was added a solution of hydrated ferric sulphate (7.23 g) in water (90 ml) and acetic acid (5.5 ml) over a period of *ca.* 30 min. A green powder was obtained. This was filtered off, washed with water, methanol and pentane, and dried in vacuum. The yield was 0.6 g (13.68%).

Anal. Calc. for $C_{20}H_{14}Cr_2O_8$: C, 49.38; H, 2.28; Cr, 21.39. Found: C, 48.71; H, 3.25; Cr, 20.86%.

IR (Nujol): ν(CO) 2002sh, 1946vs, 1917vs, 1909vs, 1819m, 1686m cm^{-1}.

[η-$C_5H_4CO_2CH_3Cr(CO)_3]_2$ (6)

The procedure described above was used, but with sodium carbomethoxycyclopentadienide (2.36 g, 16.1 mmol) and $Cr(CO)_6$ (4.26 g, 19.3 mmol) as reactants. A green powder was obtained. The yield was 0.7 g (16.74%).

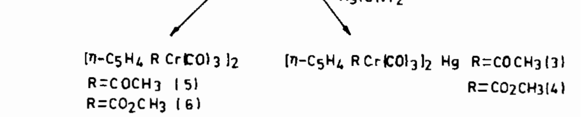
Anal. Calc. for $C_{20}H_{14}Cr_2O_{10}$: C, 46.33; H, 2.70; Cr, 20.07. Found: C, 45.70; H, 3.01; Cr, 19.25%.

IR (Nujol): ν(CO) 2002sh, 1966s, 1952sh, 1919sh, 1911vs, 1802m, 1717s cm^{-1}.

Results and Discussion

The carbonylate ions [η-$C_5H_4RCr(CO)_3]^-$ (R = $COCH_3$ (1), CO_2CH_3 (2)) were obtained by reaction of $C_5H_4R^-$ with $Cr(CO)_6$ in diglyme under refluxing conditions for several hours (Scheme 1). The anions are more stable to the oxidizing agents than the unsubstituted-ring analogues. Thus, the solutions can be handled in air for at least a short period, and in a solid state under inert atmospheres do not deteriorate over several months.

The symmetrical mercurials [η-$C_5H_4RCr(CO)_2]_2$-Hg, were prepared by treatment of a diglyme solution of η-$C_5H_4RCr(CO)_3Na$ with an aqueous solution of



Scheme 1.

mercury cyanide [19]. The compounds are a yellow–gold powder (R = $COCH_3$ (3)) and yellow–orange flakes (R = CO_2CH_3 (4)), air-stable, analogous with the formyl derivative obtained by Edelman and Behrens [13], and soluble in organic solvents.

The oxidation of the sodium salts of the anions 1 and 2 in diglyme solution with aqueous ferric sulphate solution gives rise to the $[\eta\text{-}C_5H_4RCr(CO)_3]_2$ (R = $COCH_3$ (5), CO_2CH_3 (6)) complexes. These dimers are green powders unstable in air and slighly soluble in organic solvents.

The IR of all complexes show ν(CO) frequencies characteristic of terminal, $COCH_3$ and CO_2CH_3 ligands [20]. The M–CO stretching modes of the complexes appear at higher frequencies than the corresponding bands when R = H or alkyl [21, 9–12], presumably due to the electron-withdrawing properties of the $COCH_3$ and CO_2CH_3 substituents in the ring.

The ^1H NMR spectra of monosubstituted cyclopentadienyl metal compounds vary greatly in complexity, depending upon the transition metal and the nature of the substituent. In general, compounds with substituents other than simple alkyl groups exhibit an A_2B_2 pattern for the cyclopentadienyl protons [22]. The spectrum consists of a pair of apparent triplets, in which the downfield triplet has been assigned to the $H_{2,5}$ protons.

The ^1H NMR of the mercury complexes 3 and 4 each display two broad singlets due to the four ring hydrogens and a singlet arising from the three protons of the $COCH_3$ and CO_2CH_3 groups in the usual range for acetyl and carbomethoxycyclopentadienyl chromium complexes [16].

The spectra of the dimers $[\eta\text{-}C_5H_4RCr(CO)_3]_2$ (R = $COCH_3$, CO_2CH_3) could not be obtained because they are slighly soluble in organic solvents.

Electrochemical Studies

The electrochemistry of the compounds was investigated in THF with 0.1 M $[NBu^n{}_4]PF_6$ as supporting electrolyte. Electrochemical parameters of the complexes are summarized in Table I.

The cyclic voltammograms of complexes 3 and 4 show cathodic (A) and anodic (B′) peaks but they are not associated with a reversible process, because of a large peak separation and a i_{pa}/i_{pc} value much smaller than unity (Fig. 1).

TABLE I. Cyclic Voltammetric[a] Data for the Complexes at 200 mV s^{-1}

Compounds	A	B	B'	C
1		−0.11	−0.04	−0.98
2		−0.175	−0.10	−0.89
3	−0.91	−0.105	−0.03	−0.97
4	−0.76	−0.18	−0.11	−0.88

[a] Potential peak *vs.* SCE, volts.

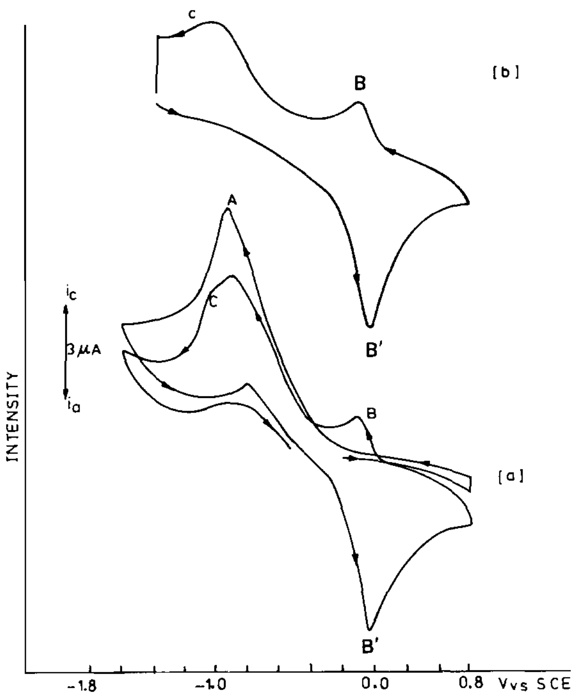
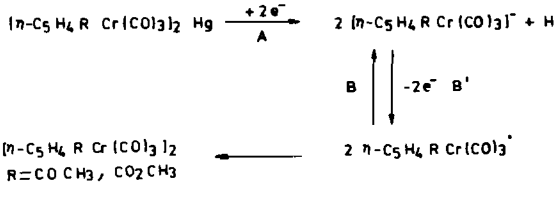


Fig. 1 (a) Multicyclic voltammograms for $[\eta\text{-}C_5H_4COCH_3Cr(CO_3)]_2Hg$ in THF at Pt electrode, scan rate 0.2 V s^{-1}. (b) Cyclic voltammogram for $[\eta\text{-}C_5H_4COCH_3Cr(CO)_3]Na$ in THF solution at Pt electrode, scan rate 0.2 V s^{-1}.

The electrochemical irreversibility of the process corresponding to these peaks is confirmed by the magnitude of the slopes in the plots of E_p *versus* log ν (ν = scan rate) [23] which are significantly larger than those expected for a reversible process. The reductions are irreversible at scan rates as high as 5 V s^{-1}.

Bulk reduction of the complexes carried out at a potential 100 mV more negative than the cathodic potentials results in the removal of 2.0 electron per molecule.

The second cyclic run shows a new little cathodic peak (B) at higher potentials than the first one (A); this peak (A) exhibits a shoulder (C) at more negative potentials and its current peak decreases. The peak separation values, ΔE_p, of the couple B/B′ are close to 70 mV and it can be observed that the current of peak B increases as scan rate increases. Scheme 2 is proposed to account for the results.



Scheme 2.

The release of the anions $[\eta\text{-}C_5H_4RCr(CO)_3]^-$ ($R = COCH_3$, CO_2CH_3) from the electrochemical reductions of the mercury complexes **3** and **4** is supported by cyclic voltammetric studies of the sodium salts **1** and **2** in THF solutions. The cyclic voltammograms of these salts display an anodic peak (B′) and two cathodic peaks (B) and (C) (Fig. 1b).

The potential values of these peaks match the voltages of the B/B′ couple and the shoulder in the multicyclic voltammograms of the respective complexes **3** and **4** (Fig. 1, Table I).

Potentiostatic coulometry indicates a one-electron exchange in the electrochemical oxidation of the anions **1** and **2**.

The electron transfers are diffusion controlled, with oxidation current function ($i_{pa}/\nu^{1/2}$) independent of the scan rate (ν) over the range of the scan rates used. The peak separation, $\Delta E_p \sim 70$ mV, for the pair B/B′, corresponding to one-electron reversible transfer, and the variation of the current peak B with ν, suggest that dimerization follows the electrochemical formation of the radicals.

A similar $E_{rev}C$ mechanism has been reported for the anion $[\eta\text{-}C_5H_5Cr(CO)_3]^-$ [24].

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