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Reductive elimination of dimethylcarbonate from (dimethoxycarbonyl)tricarbonyl cobaltates. Isolation and crystal structures of $Cs[Co(COOCH_3)_2(CO)_3]$ and $K[(dibenzo\text{-}18\text{-}crown\text{-}6)][Co(COOCH_3)_2(CO)_3]$ *

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Abstract

Salts of the anion $[Co(COOCH_3)_2(CO)_3]^-$ with Cs^+ and K^+ (with the latter cation complexed by dibenzo-18-crown-6 ether) have been isolated and structurally characterized. In the trigonal bipyramidal cobaltate two C-coordinated $COOCH_3$ groups occupy *trans*-axial positions. There are ionic interactions between the cation and the terminal oxygen atoms of methoxycarbonyl involving both of the coordinated $COOCH_3$ groups in the case of the Cs salt but only one of them in the case of the K salt. One methoxy group of the anion $[Co(COOCH_3)_2(CO)_3]^-$ is strongly nucleophilic, as shown by the reactions with $Co_2(CO)_8$ or CO_2. Under an inert atmosphere $[Co(COOCH_3)_2(CO)_3]^-$ undergoes elimination of dimethylcarbonate.

The oxidative carbonylation of alcohols to give dialkyloxalates represents a step in a syngas-based route to ethylene glycol. The alcohol/CO coupling has been accomplished only with palladium-based catalysts and the intermediates appear to be (dialkoxycarbonyl)-complexes that can undergo reductive elimination of dialkyl oxalates [1]. Most often, however, the elimination of dialkyloxalates requires the action of oxidizing agents, which also give some organic side products [2,3].

We now report the isolation and the characterization of the anionic (dialkoxycarbonyl)-complex $[Co(COOCH_3)_2(CO)_3]^-$ as its cesium (**1**) and potassium [dibenzo-18-crown-6] (**2**) salt, and on the selective elimination of dimethylcarbonate from it.

Compound **1** is formed in quantitative yield by adding $CsOCH_3$ to a THF solution of $Co(COOCH_3)(CO)_4$ (**3**) [4] at room temperature under a CO atmosphere

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* Dedicated to the memory of Piero Pino.

(eq. 1). Colorless crystals are obtained by adding $(C_2H_5)_2O$ to the solution. Pályi et al. [5] previously suggested the existence of the anion **1** on the basis of IR spectroscopy after they carried out a reaction similar to eq. 1 but with $NaOCH_3$ in the presence of 15-crown-5. However, further characterization was prevented by the fast thermal decomposition of the product. It is now evident that the stability of **1** is strongly dependent upon the CO pressure and on the nature of the cation.

$$\underset{(\mathbf{3})}{Co(COOCH_3)(CO)_4} + CsOCH_3 \xrightarrow[\text{THF}]{\text{CO atm.}} \underset{(\mathbf{1})}{Cs[Co(COOCH_3)_2(CO)_3]} \qquad (1)$$

The structure of $Cs[Co(COOCH_3)_2(CO)_3]$ was determined by X-ray diffraction [6*]. Each anion (Fig. 1) is almost trigonal bipyramidal, with two η^1-coordinated alkoxycarbonyl groups in axial positions. The average $Co-COOCH_3$ bond, 1.96(2) Å, is ca. 0.2 Å longer than the average Co–CO bond, suggesting that there is very little $Co(d_\pi)-C(p_\pi)$ interaction with the alkoxycarbonyl groups. Although the two CO_2 planes are skew by ca. 30°, the two methoxy groups are closer to an eclipsed than to a staggered disposition. This is probably a consequence of the stabilizing ionic interactions that each Cs^+ cation forms with the terminal oxygen atoms of $COOCH_3$ from four different complex anions. The contacts are short [in the range 3.00(1) and 3.07(1) Å] and involve equally the *trans*-methoxycarbonyl groups of any anion. The latter feature is fully consistent with the unique broad band at ca. 1610 cm^{-1} observed in the IR spectrum of the solid.

By contrast this band is split into two bands (at 1600 and 1635 cm^{-1}) in the spectrum recorded for a THF solution of **1**, suggesting that only one methoxycarbonyl group is preferentially involved in ion pairing. To confirm this we also studied the structure [8*] of $[K(\text{dibenzo-18-crown-6})][Co(COOCH_3)_2(CO)_3]$ (**2**), which in the solid state shows IR bands at 1600 and 1625 cm^{-1}. The gross structural features of cobaltate in **2** are not very different from those in **1** (Fig. 2), but it is evident that a terminal oxygen atom of a $COOCH_3$ group forms a bond with the K^+ ion surrounded by the crown ether [K–O(5) = 2.77(1) Å]. The Co–C–O–K bonding network compares well with that present in the compound $[Co(^n\text{Pr-salen})K(CO_2)(THF)_n]$, a rare $M-\eta^1-CO_2$ adduct [9]. In **2** the *trans*-axial $COOCH_3$ groups are almost staggered, and the group free from ion pairing with K^+ can strongly vibrate, as shown by the appearance of two peaks for the terminal oxygen atom in the ΔF maps.

Neutral (dialkoxycarbonyl)-complexes lose one methoxy group when reacted with strong electrophiles such as $CF_3SO_3CH_3$ and C_3SO_3H [10]. In the case of **1** one methoxy group leaves readily, and is strongly nuclephilic; e.g., **1** reacts with equimolar amounts of $Co_2(CO)_8$ in THF solution under a CO atmosphere to give $[Co(CO)_4]^-$ and **3** (see eq. 2).

$$Cs[Co(COOCH_3)_2(CO)_3] + Co_2(CO)_8 + CO \rightarrow$$
$$2Co(COOCH_3)(CO)_4 + Cs[Co(CO)_4] \qquad (2)$$

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* Reference number with asterisk indicates a note in the list of references.

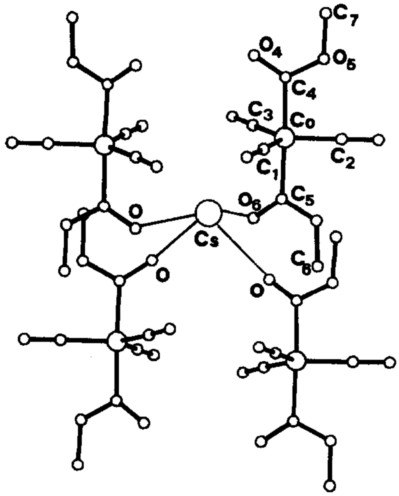

Fig. 1. A cesium cation forms short contacts [in the range 3.00–3.07(9) Å] with terminal oxygen atoms of methoxycarbonyl groups from four different $[Co(COOCH_3)_2(CO)_3]^-$ anions. Selected bond distances (Å): Co–C(1) 1.76(2), Co–C(2) 1.80(2), Co–C(3) 1.75(2), Co–C(4) 1.96(1), Co–C(5) 1.96(1), C–O (carbonyl) 1.15(3) ave., C(4)–O(4) 1.21(2), C(4)–O(5) 1.37(2), C(5)–O(6) 1.24(1), C(5)–O(7) 1.33(1), C(6)–O(7) 1.46(1). Angles (°): C(4)–Co–C(5) 177.7(5), O(4)–C(4)–O(5) 118.6(1.1), O(6)–C(5)–O(7) 119.0(1.1), C(4)–O(5)–C(7) 118.4(1.0), C(5)–O(7)–C(6) 117.4(1.1).

Furthermore, a THF solution of **1** reacts instantaneously with carbon dioxide to give **3**, along with a precipitate of $CsOCOOCH_3$.

Finally, **1** undergoes selective elimination of dimethylcarbonate (eq. 3). The reaction is complete in 3 hours at room temperature under an inert atmosphere; it is

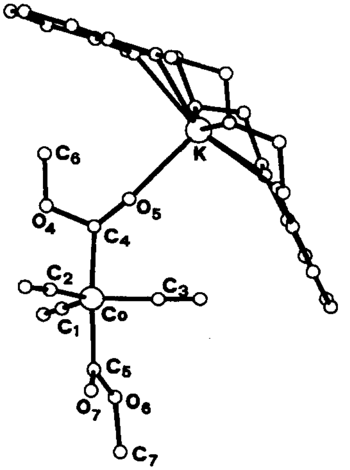

Fig. 2. Drawing of the adduct $[K(dibenzo\text{-}18\text{-}crown\text{-}6)][Co(COOCH_3)_2(CO)_3]$ (**2**). Selected bond distances (Å): Co–C(1) 1.83(2), Co–C(2) 1.80(2), Co–C(3) 1.78(2), Co–C(4) 1.97(1), Co–C(5) 1.93(3), C–O (carbonyl) 1.10(3) ave., C(4)–O(4) 1.37(2), C(4)–O(5) 1.19(2), C(5)–O(6) 1.29(1), C(5)–O(7) 1.43(4), C(7)–O(6) 1.44(2). Angles (°): C(4)–Co–C(5) 175.2(8), O(4)–C(4)–O(5) 117(2), O(6)–C(5)–O(7) 116(2), C(4)–O(4)–C(6) 116(2), C(5)–O(6)–C(7) 122(2).

first order with respect to **1** and is inhibited by CO. These features favour the intermediacy of a methoxy(methoxycarbonyl)cobalt tricarbonyl complex formed by loss ("deinsertion") of CO from the CH_3OOC ligand in **1**.

$$Cs[Co(COOCH_3)_2(CO)_3] \xrightarrow{THF} CO(OCH_3)_2 + Cs[Co(CO)_4] \qquad (3)$$

Supplementary material. Lists of atomic coordinates, and bond distances and angles will be deposited with Cambridge Crystallographic Data Center.

References and notes

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6 *Crystal data* $C_7H_6O_7Co_1Cs_1$: $M = 393.96$, monoclinic, $P2_1/c$, $a = 11.868(4)$, $b = 13.611(5)$, $c = 7.634(3)$ Å, $\beta = 104.07(2)°$, $V = 1196.27$ A^3, $Z = 4$, $d_{calc} = 2.187$ g cm^{-3}, $F(000) = 744$, $\lambda(Mo\text{-}K_\alpha) = 0.7107$, $\mu(Mo\text{-}K_a) = 44.2$. A crystal, sealed in a capillary with dimensions $0.1 \times 0.2 \times 0.3$ mm^3 was mounted on a CAD4 diffractometer. Intensities were collected up to $2\theta = 60°$ [3803 measured reflections of which 1251 had intensities $I > 3\sigma(I)$]. The structure was solved by Patterson and Fourier methods. Empirical absorption corrections were made [7] with min.–max. absorption of 0.69–0.89. All of the non-hydrogen atoms were refined anisotropically. Final R and R_w values were 0.049 and 0.051, respectively.

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8 *Crystal data* $C_{27}H_{30}O_{13}Co_1K_1$: $M = 660.56$, triclinic $P\bar{1}$, $a = 15.955(4)$, $b = 11.208(5)$, $c = 9.435(3)$ Å, $\alpha = 66.53(2)$, $\beta = 77.97(2)$, $\gamma = 80.64(2)°$, $V = 1507.6$ Å^3, $Z = 2$, $d_{calc} = 2.910$ g cm^{-3}, $F(000) = 1368$, $\lambda(Cu\text{-}K_\alpha) = 1.5418$, $\mu(Cu\text{-}K_\alpha) = 129.2$. A crystal, sealed in a capillary with dimensions $0.1 \times 0.1 \times 0.2$ mm^3 was mounted on a PW 1100 diffractometer. Intensities were collected up to $2\theta = 110^3$ [3600 measured reflections, of which 1881 had intensities $I > 3\sigma(I)$]. The structure was solved by Patterson and Fourier methods. The empirical absorption coefficients, [7] are in the range 0.49–0.89. Co, K, O atoms were refined anisotropically. The present R and R_w values are 0.098 and 0.090, respectively. Attempts are still being made to solve the disorder associated with O7 (O8) atom.

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