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PREPARATION AND PROPERTIES OF ACETYLIODOTRICARBONYLCOBALTATE; A NOVEL PRODUCT FROM THE REACTION OF METHYL IODIDE WITH TETRACARBONYLCOBALTATE

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Summary

The reaction of PPN[$\mathrm{Co(CO)_4}$] with an excess of methyl iodide in THF at 0°C gives almost quantitatively PPN[$\mathrm{Co(CO)_3\{C(O)CH_3\}I}$], which has been shown by X-ray crystallography and spectroscopic measurements to adopt a trigonal bipyramidal structure with three carbonyls in the equatorial plane; it reacts with hydrogen or with sulfuric acid to give acetaldehyde, and with methanol/pyridine to give methyl acetate. The new anion is of interest as a potential intermediate in the cobalt/iodine catalyzed carbonylation or hydrocarbonylation of methanol.

Introduction

The alkylation of cobalt by methyl iodide is an essential step in the cobalt/iodine catalyzed hydrocarbonylation of methanol to give acetaldehyde [1–3], as well as in the carbonylation of methanol to give acetic acid [4]. Hieber et al. showed that $\mathrm{Na[Co(CO)_4]}$ reacted with MeI to give methyltetracarbonylcobalt (**1**), [5], which under CO gives the more stable acetyl complex, **2**, [6] eq. 1:

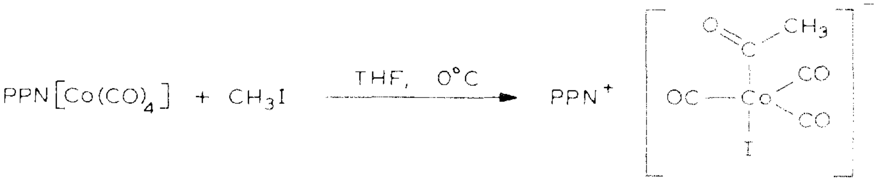
$$\mathrm{Na[Co(CO)_4]} + \mathrm{CH_3I} \xrightarrow[-\mathrm{NaI}]{\mathrm{Et_2O,\ 0^\circ C}} \underset{(\mathbf{1})}{\mathrm{CH_3Co(CO)_4}} \xrightarrow{\mathrm{CO}} \underset{(\mathbf{2})}{\mathrm{Co(CO)_4\{C(O)CH_3\}}} \qquad (1)$$

Substitution of CO in **2** by ligands such as phosphines and phosphites leads to more stable acetyl complexes, numerous examples of which have been prepared [7] and some used as model compounds for mechanistic studies in methanol hydrocarbonylation [8]. To our knowledge, no example is known where a CO ligand in **2** has been replaced by a halide ion to give an anionic cobalt acetyl complex, although analogous complexes with other metals have been reported, e.g. for manganese [9]. Anionic complexes such as $[M(CO)_2\{C(O)CH_3\}(I)_3]^-$, where M = Rh or Ir, have been proposed as intermediates in the catalytic carbonylation of methanol [10,11]. We now report on the facile and almost quantitative formation of the iodide substituted analogue of **2** as well as on model reactions with this new complex anion, which emphasize its relevance as a potential intermediate in catalytic carbonylation/hydrocarbonylation reactions.

Results and discussion

Salts with bulky cations have been shown to be efficient promoters for the cobalt/iodine catalyzed hydrocarbonylation of methanol in solvents such as 1,4-dioxane, THF or diglyme [12]. This strong influence can be related to anionic intermediates in the catalytic cycle. Furthermore, kinetic investigations [13] as well as model reactions with deuterium labelled reagents [3] indicate that the alkylation of cobalt with methyl iodide, as in eq. 1, is the rate-determining step in methanol hydrocarbonylation. In situ IR studies during reactions have established that $[Co(CO)_4]^-$ is present as the major cobalt carbonyl compound in this latter process [14]. We therefore decided to study the effects of various solvents and cations on the reaction of methyl iodide with tetracarbonylcobaltates. We were surprised to find that the reaction took a different course from that shown in eq. 1 when tetracarbonylcobaltates with large cations were used.

Addition of cooled methyl iodide to a solution of $PPN[Co(CO)_4]$ (**3**) [PPN = $(Ph_3P)_2N$] in dry THF stirred at 0°C under argon resulted in rapid and selective formation of the novel anionic complex, acetyliodotricarbonylcobaltate (**4**). Disappearance of the IR absorption at 1890 cm^{-1} due to $[Co(CO)_4]^-$ showed that the reaction was complete in 10 min: pure **4** was obtained in almost quantitative yield by evaporating off the solvent and excess of methyl iodide. Slow diffusion of pentane into a THF solution of **4** yielded a crystalline sample; the analogous reaction of methyl iodide with ^{13}CO labelled **3** yielded the complex $[PPN][Co(^{13}CO)_3\{^{13}C(O)CH_3\}I]$ (**4a**).

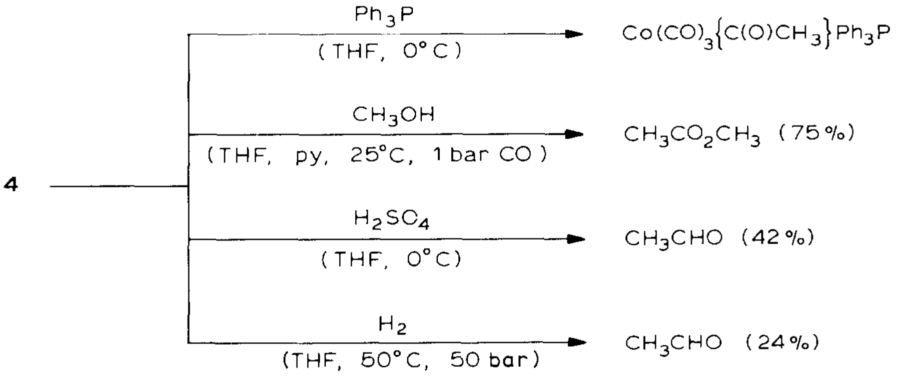


(2)

(4)

Complex **4** has a trigonal bipyrimidal structure with three equivalent carbonyl ligands in the equatorial plane as revealed by the infrared spectrum of **4** ($A_1 + E$, pseudo-C_3 structure) [15], the ^{13}C NMR of **4a**, which shows only one resonance due to the carbonyl ligands, and by X-ray crystallography. Although the X-ray study confirmed this structure, reliable bond angles and distances could not be determined because of the lability of the complex at room temperature.

The formation of **4** depends both on the counterion and on the solvent. Whereas reaction of methyl iodide with **3** in THF or in acetonitrile yields exclusively **4**,



SCHEME 1. Stoichiometric model reactions with the anionic complex **4**.

reaction in methylene chloride gives a mixture of **2** and **4**. Use of $K[Co(CO)_4]$ in THF leads to the formation of **2** instead of **4**, as shown by IR spectroscopy.

Complex **4** is reasonably stable in the absence of oxygen at temperatures $\leqslant 0°C$ and is very soluble in THF or acetonitrile, but very concentrated solutions tend to decompose with separation of (PPN)I.

Anionic acetyl complexes such as **4** are of interest as potential intermediates in the cobalt/iodine catalyzed hydrocarbonylation of methanol, in which a strong influence of the cation has been recently established [12]. We therefore studied the chemical properties of **4**, and the outcomes of some model stoichiometric reactions are summarized in Scheme 1.

A solution of **4** in THF at 0°C reacts slowly with triphenylphosphine to give $Co(CO)_3\{C(O)CH_3\}(PPh_3)$ (**5**) [16]. Reaction with CO (1 bar) in THF gave a mixture of **2**, **3**, and **4** (IR). Carbonylation in methanol/pyridine (1 bar CO, 25°C, 1 h) gives methyl acetate in 75% yield (GLC) along with $[Co(CO)_4]^-$. Hydrogenation of **4** in THF (50 bar H_2, 50°C, 5 h) gives acetaldehyde (24% yield), and hydrolysis with sulfuric acid (THF, 0°C) gives acetaldehyde in 42% yield (GLC).

The formation of **4** corresponds formally to an oxidative addition of methyl iodide to $[Co(CO)_4]^-$ followed by methyl migration. This type of reaction is known for Co^I complexes such as $CpCo(CO)(PPh_3)$ but it has not previously been described for Co^{-I} compounds. Presumably, the reaction involves methylation of $[Co(CO)_4]^-$ in the rate-determining step to give **1**, and this is followed by fast methyl migration and coordination of iodide, as in eqs. 3 and 4.

$$[Co(CO)_4]^- + CH_3I \xrightarrow[-I^-]{\text{slow}} CH_3Co(CO)_4 \xrightarrow{\text{fast}} Co(CO)_3\{C(O)CH_3\} \qquad (3)$$

$$Co(CO)_3\{C(O)CH_3\} \xrightarrow[+I^-]{\text{fast}} [Co(CO)_3\{C(O)CH_3\}I]^- \qquad (4)$$

A corresponding sequence has been established by Calderazzo et al. in the synthesis of $[Mn(CO)_4\{C(O)CH_3\}I]^-$ [9]. The role of the THF is probably to stabilize the coordinatively unsaturated intermediate, as suggested previously by Cotton et al. [18].

Experimental

All reactions were carried out under oxygen-free argon. PPN[Co(CO)$_4$] [19] and K[Co(CO)$_4$] [20] were prepared by published methods. All other reagents were commercially available and were degassed or distilled before use. THF was freshly dried from Na/K alloy.

IR spectra were recorded on a Perkin–Elmer 577 instrument using CaF$_2$ windows (path length 0.1 mm). ^{1}H NMR spectra were recorded at 90 MHz on a Varian EM 390 spectrometer and ^{13}C NMR spectra on a Bruker WH 200. Quantitative GLC determinations were carried out on a Siemens Sichromat 1/Spectra Physics 4000 instrument using a 100 m Carbowax 1500 capillary (ID 0.25 mm) at 40°C and 1.5 bar N$_2$. Toluene was used as the internal standard and response factors were 3.12 for acetaldehyde and 3.15 for methyl acetate.

*Preparation of [PPN][Co(CO)$_3${C(O)CH$_3$}I]$_2$ (**4**)*

Cooled methyl iodide (100 mmol) was added to a stirred yellow solution of PPN[Co(CO)$_4$] (**3**) (1.0 mmol), in dry THF (5 ml), at 0°C in a Schlenk tube (100 ml). The mixture turned dark brown, and disappearance of the IR absorption at 1890 cm^{-1} due to [Co(CO)$_4$]$^-$ showed that the reaction was complete after 10 min. Pure **4** was obtained as a microcrystalline brown solid in almost quantitative yield by concentrating the dark brown solution to 2–3 ml at 0°C/2 mmHg, and then evaporating off residual solvent in a stream of argon.

IR (THF, 0.1 mm, $\tilde{\nu}$ (cm^{-1})) ν(CO): 2029w, 1953vs, 1933vs; ν(Acyl): 1657s. ^{1}H NMR (THF-d_8, δ(ppm)): 2.27 (s, 3H), 7.3–7.8 (m, 30H). Analysis: Found: C, 58.02; H, 3.96; N, 1.66; I, 14.71; P, 7.17; Co, 6.94. Calcd. C, 57.83; H, 3.91; N, 1.65; P, 7.28; I, 14.90; Co, 6.92%. m.p. (sealed tube, uncorr.): 95–98°C (decomposition to green compound).

Crystalline **4** was obtained by adding 20 ml of dry THF after the reaction mixture had been concentrated to 2–3 ml then allowing n-pentane (50 ml) to diffuse in slowly. Crystallization during several days at −10°C gave brown cubic crystals of **4**.

Crystal data. a 12.108(3), b 22.348(6), c 17.946(3) Å, β 92.74 (3)°, V 4850.61 Å^3, space group: $P2_1/c$, $R = 0.19$, observed reflections: 9278, 40% decomposition.

*Preparation of [PPN][Co(^{13}CO)$_3${^{13}C(CO)CH$_3$}I] (**4a**)*

Reaction of ^{13}CO labelled **3** (ca. 80% enriched) with methyl iodide as described above yielded the analogous complex **4a**.

IR (THF, 0.1 mm, $\tilde{\nu}$ (cm^{-1})) ν(CO): 1976w, 1907vs, 1887vs; ^{13}C NMR (THF-d_8, δ (ppm)): 241.8 (COCH$_3$), 201.3 (CoCO).

*Reaction of **4** with Ph$_3$P*

Addition of a solution of Ph$_3$P (0.05 mmol) in THF (5 ml) to a stirred solution of **4** (0.05 mmol) in THF (5 ml) kept at 0°C caused rapid decolourization of the brown mixture and a yellow precipitate ([PPN]I) was formed. The IR spectrum of the solution showed quantitative formation of Co(CO)$_3${C(CO)CH$_3$}(Ph$_3$P) (**5**) [14].

IR (THF, 0.1 mm, $\tilde{\nu}$ (cm^{-1})) ν(CO): 2055w, 1982vs, 1962vs; ν(Acyl): 1681s.

*Reaction of **4** with sulfuric acid*

H$_2$SO$_4$ (10 mmol) was added with stirring to a solution containing freshly prepared **4** (1.0 mmol) in THF (10 ml) kept at 0°C. After 1 h stirring, during which the colour of the mixture changed from dark brown to green and the IR absorptions of **4** disappeared, toluene (139.4 mg) was added as the internal standard and the mixture was analyzed by GLC. Acetaldehyde was formed selectively with a yield of 18.4 mg corresponding to 41.8 mol% based on **4**.

Reaction of ***4*** *with hydrogen*

A solution of **4** (1.0 mmol) in THF (10 ml) was transferred under an inert atmosphere into a stainless steel autoclave. Hydrogenation was carried out at 50°C under 50 bar H_2 with magnetic stirring for 5 h. After cooling and depressurizing, the volatile material was separated at reduced pressure/room temperature by flash distillation and analyzed by GLC using toluene (90.2 mg) as the internal standard. Acetaldehyde was detected in a yield of 10.3 mg (23.4 mol% based on **4**) along with trace amounts of acetone.

Reaction of ***4*** *with methanol/pyridine*

A solution of **4** (0.5 mmol) in THF (5 ml) was stirred at 25°C under CO. After addition of methanol (50 mmol) and pyridine (5 mmol) the colour of the solution changed within 2 min from brown to pale green. Stirring was continued for 1 h then the volatile material was separated by flash distillation as described above, and analyzed by GLC using toluene (106.6 mg) as the internal standard. The yield of methyl acetate was 27.9 mg, corresponding to 75.4 mol% based on **4**. A THF solution of the yellow residue showed a strong IR absorption at about 1895 cm^{-1}, characteristic of $[Co(CO)_4]^-$.

Reaction of ***4*** *with CO*

CO was bubbled slowly through a stirred solution of **4** (0.5 mmol) in THF (5 ml) kept at 0°C. The colour of the brown solution slowly faded and a yellow precipitate formed. After 1.5 h the solution showed IR absorptions due to **4**, $[Co(CO)_4]^-$ (1895 cm^{-1}), and **2** ($\bar{\nu}$ (cm^{-1}): 2110w, 2055ss, 2022ss, 1712s) [6].

Reaction of $K[Co(CO)_4]$ *with* CH_3I

Cooled CH_3I (50 mmol) was added with stirring to a yellow solution of $K[Co(CO)_4]$ [13] (0.5 mmol) in THF (10 ml) kept at 0°C. The solution turned dark brown and the IR spectrum showed that after 10 min almost complete conversion of $[Co(CO)_4]^-$ to **2** had occurred, and no **4** could be detected.

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