Reactivity of $[\mathrm{Co_4(CO)_{12}}]$.† Synthesis and Characterization of Tetracobalt Carbonyl Anions of General Formula $[\mathrm{Co_4(CO)_{11}X}]^-$

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Salts of the green-brown anions $[\mathrm{Co_4(CO)_{11}X}]^-$ (X = Br, I, or SCN) have been obtained at −70 °C starting from $[\mathrm{Co_4(CO)_{12}}]$ and tetrasubstituted ammonium ($[\mathrm{NEt_4}]$Br or $[\mathrm{NEt_4}]$I) or phosphonium {$[\mathrm{PMePh_3}]$Br, $[\mathrm{N(PPh_3)_2}]$I, or $[\mathrm{N(PPh_3)_2}]$[SCN]} salts. Using sodium alkoxides or propylamine, formation of purple-red solutions containing, on the basis of the i.r. spectra, similar monosubstituted anions (X = COOMe, COOPr^i, or CONHPr^n) has been observed. The transformation of $[\mathrm{Co_4(CO)_{12}}]$ into $[\mathrm{Co_2(CO)_8}]$ has been studied in Pr^{i}OH at room temperature under carbon monoxide. The considerable acceleration of the rate of this reaction by halide ions is in agreement with the ready decomposition observed for all the $[\mathrm{Co_4(CO)_{11}X}]^-$ anions in Lewis-base solvents.

ALTHOUGH several cobalt carbonyl anions have been characterized, *e.g.* $[\mathrm{Co(CO)_4}]^-$,[1] $[\mathrm{Co_3(CO)_{10}}]^-$,[2] $[\mathrm{Co_6(CO)_{15}}]^{2-}$,[3] $[\mathrm{Co_6(CO)_{14}}]^{4-}$,[4] and $[\mathrm{Co_6(CO)_{15}H}]^-$,[5] no tetranuclear anionic species have so far been reported. The experimental observation that degradation of $[\mathrm{Co_4(CO)_{12}}]$ to $[\mathrm{Co_2(CO)_8}]$ by carbon monoxide (25 °C, 1 atm) ‡ in Pr^{i}OH as solvent is considerably accelerated by the presence of trace amounts of halide ions suggested that tetranuclear species of general formula $[\mathrm{Co_4(CO)_{11}X}]^-$ could exist, and that the present gap in the literature might be ascribed to their low stability under the usual experimental conditions.

RESULTS AND DISCUSSION

Synthesis and Isolation of Salts of the $[\mathrm{Co_4(CO)_{11}X}]^-$ *Anions*.—(*a*) X = Br, I, *or* SCN. In dichloromethane $[\mathrm{Co_4(CO)_{12}}]$ reacts with a stoicheiometric amount of iodide at 0 °C according to equilibrium (1). Under

$$[\mathrm{Co_4(CO)_{12}}] + \mathrm{I}^- \rightleftharpoons [\mathrm{Co_4(CO)_{11}I}]^- + \mathrm{CO} \qquad (1)$$

carbon monoxide at atmospheric pressure, similar amounts of $[\mathrm{Co_4(CO)_{12}}]$ and $[\mathrm{Co_4(CO)_{11}I}]^-$ are present, but the equilibrium can be completely shifted to the right under a nitrogen atmosphere. A microcrystalline precipitate of $[\mathrm{NEt_4}][\mathrm{Co_4(CO)_{11}I}]$ has been obtained on simple addition of n-heptane under stirring, and the analytical results indicate a $\mathrm{NEt_4}^+$: Co : I ratio of 1.0 : 3.85 : 0.9 (calc. 1 : 4 : 1).

Solutions of $[\mathrm{NEt_4}][\mathrm{Co_4(CO)_{11}I}]$ in dichloromethane at −70 °C are stable for several days, while at room temperature complete decomposition takes place in a couple of days, probably according to reaction (2) (B = Lewis base). A similar decomposition is observed when

$$3\,[\mathrm{Co_4(CO)_{11}I}]^- + 4n\mathrm{B} \longrightarrow 4\,[\mathrm{CoB}_n][\mathrm{Co(CO)_4}]_2 + 3\,\mathrm{I}^- + \mathrm{CO} \qquad (2)$$

using excess of iodide ion in the synthesis (1) at room temperature.

The corresponding $[\mathrm{Co_4(CO)_{11}Br}]^-$ anion has been synthesized at −70 °C from a suspension of $[\mathrm{Co_4(CO)_{12}}]$ in dichloromethane and an equimolar amount either of $[\mathrm{NEt_4}]$Br or $[\mathrm{PMePh_3}]$Br; the $[\mathrm{Co_4(CO)_{11}(SCN)}]^-$ anion has been similarly obtained from $[\mathrm{N(PPh_3)_2}]$[SCN]. All these derivatives are green-brown and have been isolated in a microcrystalline state by addition of n-heptane with stirring at −70 °C. These anions are more labile than the corresponding $[\mathrm{Co_4(CO)_{11}I}]^-$, and, at room temperature, decomposition according to (2) is generally complete in a few hours. In all cases disproportionation is greatly accelerated when working in Lewis-base solvents such as methanol, isopropyl alcohol, tetrahydrofuran, acetone, and acetonitrile.

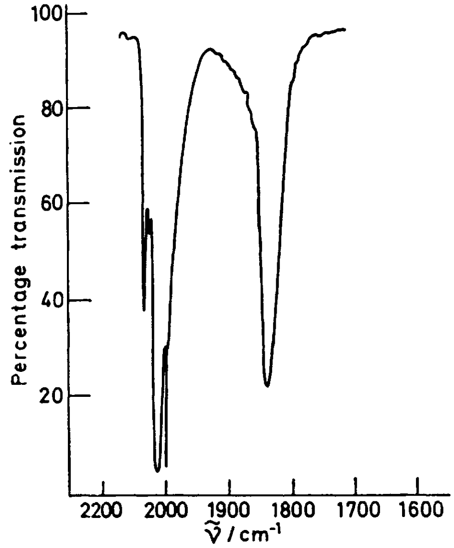

FIGURE 1 Infrared spectrum of $[\mathrm{NEt_4}][\mathrm{Co_4(CO)_{11}I}]$ in $\mathrm{CH_2Cl_2}$

The i.r. spectrum of $[\mathrm{NEt_4}][\mathrm{Co_4(CO)_{11}I}]$ in $\mathrm{CH_2Cl_2}$ is shown in Figure 1. The weak absorption around 2 050 cm^{-1} is probably due to $[\mathrm{Co_4(CO)_{12}}]$ as impurity. The i.r. data are collected in the Table. The similarities in colour and in the i.r. spectra of the $[\mathrm{Co_4(CO)_{11}X}]^-$ (X = Br, I, or SCN) derivatives suggest that all these anions in solution adopt mainly the same conformation with the X substituent replacing a terminal carbonyl

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† Tri-μ-carbonyl-nonacarbonyl-*tetrahedro*-tetracobalt.

‡ Throughout this paper: 1 atm = 101 325 Pa.

group of the apical cobalt atom, as has been found in the solid-state structure of the $[Co_4(CO)_{11}I]^-$ anion.[6]

(*b*) X = COOMe, $COOPr^i$, *or* $CONHPr^n$. Since tetranuclear alkoxycarbonyl derivatives of rhodium are more stable than the corresponding $[Rh_4(CO)_{11}X]^-$ (where X is a halide or a pseudohalide), whose formation could not be detected probably as a result of rapid condensation to $[Rh_6(CO)_{15}X]^-$ anions,[7,8] the synthesis of tetranuclear cobalt alkoxycarbonyl derivatives has been investigated.

Infrared carbonyl stretching bands (±5 cm^{-1}) of the $[Co_4(CO)_{11}X]^-$ anions

Anion	Solvent [a]	ν(CO)
$[Co_4(CO)_{11}I]^-$	CH_2Cl_2	2 070vw, 2 020s, 2 000(sh), 1 835ms
$[CO_4(CO)_{11}Br]^-$	CH_2Cl_2	*b*, 2 020s, 2 000(sh), 1 835ms
$[CO_4(CO)_{11}(SCN)]^-$	CH_2Cl_2	2 070vw, 2 030s, 2 000(sh), 1 840ms [c]
$[Co_4(CO)_{11}(COOMe)]^-$	thf	2 070w, 2 020s, 2 000ms, 1980(sh), 1 830m, 1 640w
$[Co_4(CO)_{11}(COOPr^i)]^-$	thf	2 070w, 2 020s, 2 000ms, 1 980(sh), 1 830m, 1 635w
$[Co_4(CO)_{11}(CONHPr^n)]^-$	thf	*b*, 2 020s, 2 000(sh), 1 990(sh), 1 830m, 1 700mw

[a] thf = Tetrahydrofuran. [b] Obscured by the presence of $[Co_4(CO)_{12}]$ impurity. [c] Further absorption at 2 100 cm^{-1} attributed to the SCN ligand.

Dropwise addition at −70 °C of a standard solution of a sodium alkoxide to an alcoholic suspension of $[Co_4(CO)_{12}]$ under a nitrogen atmosphere resulted in the formation of a red-violet solution [reaction (3), R = Me or Pr^i]. The reaction is complete after addition of a slight excess of sodium alkoxide and requires anhydrous conditions because of ready hydrolysis according to (4),

$$[Co_4(CO)_{12}] + Na(OR) \xrightarrow[-70\,^{\circ}C]{ROH} Na[Co_4(CO)_{11}(COOR)] \quad (3)$$

$$[Co_4(CO)_{11}(COOR)]^- + H_2O \longrightarrow [Co_4(CO)_{12}] + ROH + OH^- \quad (4)$$

followed by the usual reaction between $[Co_4(CO)_{12}]$ and hydroxide ions. As shown in Figure 2, the formulation as tetranuclear alkoxycarbonyl derivatives is supported by the similarity of the i.r. spectra to those of the corresponding rhodium [7] and iridium [9] derivatives. Unfortunately, even under anhydrous conditions, both the cobalt species readily decompose to $[Co(CO)_4]^-$ on warming to room temperature, and it has only been possible to isolate microcrystals of $[N(PPh_3)_2][Co_4(CO)_{11}(COOMe)]$ by addition of $[N(PPh_3)_2]_2[SO_4]$ at −70 °C and by precipitation with stirring using di-isopropyl ether–pentane (1 : 1).

There is also i.r. evidence that dropwise addition of n-propylamine to a methanolic suspension of $[Co_4(CO)_{12}]$ at −70 °C results in the formation of the corresponding carbamoyl derivative, as expected from reaction (5). The stability of this derivative is comparable to that of the corresponding alkoxycarbonyl

$$[Co_4(CO)_{12}] + 2\ NH_2Pr^n \longrightarrow [NH_3Pr^n][Co_4(CO)_{11}(CONHPr^n)] \quad (5)$$

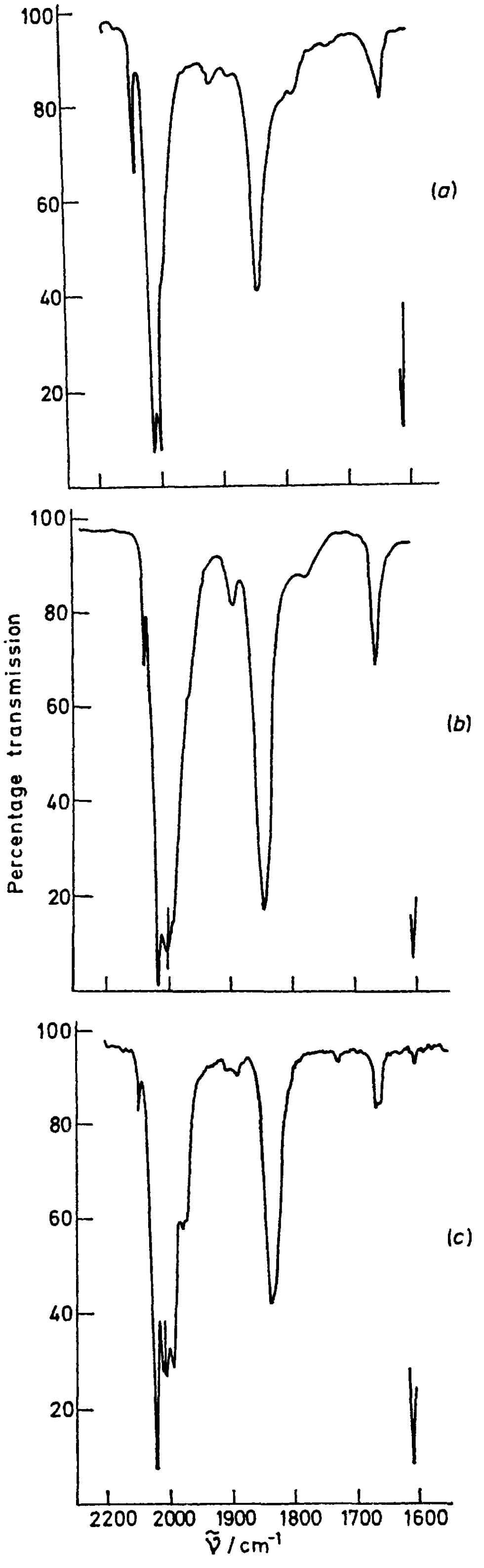

FIGURE 2 Comparison of the i.r. spectra of the $[N(PPh_3)_2]^+$ salts of $[Co_4(CO)_{11}(COOCH_3)]^-$ (*a*), $[Rh_4(CO)_{11}(COOCH_3)]^-$ (*b*),[7] and $[Ir_4(CO)_{11}(COOCH_3)]^-$ (*c*) [9] in the thf solution

derivatives and, therefore, no attempt was made to isolate it.

The most striking feature of the monosubstituted tetranuclear cobalt anions $[Co_4(CO)_{11}X]^-$ is that they are green-brown when X = Br, I, or SCN, and purple-red when X = COOMe, $\mathrm{COOPr^i}$, or $\mathrm{CONHPr^n}$. This marked colour change is rather surprising and does not have a parallel in the iridium case where, for instance, both $[Ir_4(CO)_{11}Br]^-$ and $[Ir_4(CO)_{11}(COOMe)]^-$ are yellow and have been shown by *X*-ray analysis to be isostructural, with the X substituent in an axial position under the bridged basal plane.[9,10] The most simple interpretation would be that the $[Co_4(CO)_{11}X]^-$ species with X = COOMe, $\mathrm{COOPr^i}$, or $\mathrm{CONHPr^n}$ are not isostructural with those with X = Br, I, or SCN. This is indeed likely. Thus, while a combination of electronic and steric factors has been assumed to favour apical substitution in the solid-state structure of $[Co_4(CO)_{11}I]^-$,[6] the basal-substituted structure found for the $[Ir_4(CO)_{11}X]^-$ (X = Br or COOMe) derivatives[9,10] seems more favourable even for $[Co_4(CO)_{11}X]^-$, when X is a bulky polyatomic substituent such as COOMe, $\mathrm{COOPr^i}$, or $\mathrm{CONHPr^n}$, owing to the larger cone angle of the substituent. As shown by the structural data for the $[Co_4(CO)_{11}I]^-$ anion,[6] a substituent in an axial position, under the bridged basal plane, would profit from two particularly long C • • • C non-bonding contacts. However, although the different colours of the $[Co_4(CO)_{11}X]^-$ anions, observed both in solution and in the solid state, may be accounted for by the prevalence of the apical-substituted (X = Br, I, or SCN) or of the basal-substituted (X = COOMe, $\mathrm{COOPr^i}$, or $\mathrm{CONHPr^n}$) isomer, we cannot rule out alternative explanations based, for instance, on charge-transfer bands.

The Transformation of $[Co_4(CO)_{12}]$ *into* $[Co_2(CO)_8]$.—In 1952 Wender *et al.*[11] reported the now well known disproportionation of $[Co_2(CO)_8]$ in Lewis-base solvents [equation (6)]. This reaction was later shown to be

$$3\,[Co_2(CO)_8] + 2nB \rightleftharpoons 2\,[CoB_n][Co(CO)_4]_2 + 8\,CO \quad (6)$$

reversible.[12] The same authors discovered the direct transformation of $[Co_2(CO)_8]$ into $[Co_4(CO)_{12}]$ when working in $\mathrm{Bu^tOH}$.[11] In 1968, a similar transformation was observed in $\mathrm{Pr^iOH}$ and the equilibrium (7) was proposed.[3] Equilibrium (7) can actually provide a

$$2\,[CoB_n][Co(CO)_4]_2 + [Co_2(CO)_8] \rightleftharpoons 2\,[Co_4(CO)_{12}] + 2nB \quad (7)$$

simple explanation both for the disproportionation of $[Co_4(CO)_{12}]$ into $[CoB_n][Co(CO)_4]_2$ observed in the usual Lewis-base solvents,[3] and for the transformation of $[Co_2(CO)_8]$ into $[Co_4(CO)_{12}]$ when the cobalt(II) cation is destabilized by insufficient solvation in a weakly basic and sterically demanding solvent. We, therefore, expected that, if reaction (6) could be shifted to the left in mild conditions, a transformation of $[Co_4(CO)_{12}]$ into $[Co_2(CO)_8]$ could be obtained throughout reactions (6) and (7). This transformation is indeed observed on treating $[Co_4(CO)_{12}]$ in $\mathrm{Pr^iOH}$ with carbon monoxide (25 °C, 1 atm).[13]

At room temperature this reaction is slow (*ca.* 4 d), whereas at 55 °C the equilibrium corresponding to the sum of reactions (6) and (7) lies essentially on the side of $[Co_4(CO)_{12}]$ and no transformation can be observed. At 40 °C the reaction is more rapid but not complete. It is considerably accelerated at room temperature (12—48 h) in the presence of trace amounts of halide ions derived from salts such as LiCl, LiI, and $[NBu_4]I$. Because the formation and subsequent rapid decomposition at room temperature of the $[Co_4(CO)_{11}I]^-$ anion has also been observed in $\mathrm{Pr^iOH}$, it seems probable that $[Co_4(CO)_{11}I]^-$ and the related anions are involved in the activation of $[Co_4(CO)_{12}]$ according to reactions (1) and (2). The expected associated increase in the rate of transformation of $[Co_4(CO)_{12}]$ into cobalt(II) bis(tetracarbonylcobaltate) will be consistent with reaction (7) being rate determining in $\mathrm{Pr^iOH}$.

Conclusions.—The present work has shown that anionic tetranuclear cobalt carbonyl species $[Co_4(CO)_{11}X]^-$ do exist even if they are unstable under the usual experimental conditions. It is, therefore, possible that tetranuclear hydrides or their anionic derivatives are responsible for the stoicheiometric hydroformylation reaction which occurs with $[Co_4(CO)_{12}]$ under hydrogen in an alcoholic medium,[14] as well as for the change in rate and product distribution observed when carrying out catalytic hydroformylation at low partial pressure of CO.[15]

EXPERIMENTAL

Preparations.—$[NEt_4][Co_4(CO)_{11}I]$. The compound $[Co_4(CO)_{12}]$ (0.77 g) was suspended in CH_2Cl_2 (25 cm^3) under nitrogen and cooled to 0 °C. Solid tetraethylammonium iodide (0.35 g) was slowly added with stirring. After 1 h, the resulting dark green-brown solution was allowed to warm to room temperatue and then filtered. Solid microstalline $[NEt_4][Co_4(CO)_{11}I]$ was precipitated by addition of n-heptane (40 cm^3) with stirring. The solid was filtered off, washed with n-heptane (20 cm^3), and dried *in vacuo*. Yield *ca.* 80% {Found: Co, 29.3; I, 15.0; NEt_4, 16.85. Calc. for $[NEt_4][Co_4(CO)_{11}I]$: Co, 29.45; I, 15.85; NEt_4, 16.3%}.

$[N(PPh_3)_2][Co_4(CO)_{11}(SCN)]$. The compound $[Co_4(CO)_{12}]$ (0.34 g) was suspended in CH_2Cl_2 (10 cm^3) under nitrogen and cooled to −70 °C. A solution of $[N(PPh_3)_2][SCN]$ (0.47 g) in CH_2Cl_2 (2 cm^3) was added dropwise with stirring. After 2 h the resulting dark green-brown solution was filtered, and $[N(PPh_3)_2][Co_4(CO)_{11}(SCN)]$ was precipitated by addition of n-heptane (20 cm^3). The salt $[PMePh_3][Co_4(CO)_{11}Br]$ was obtained analogously starting from $[Co_4(CO)_{12}]$ (0.32 g) and $[PMePh_3]Br$ (0.31 g). The solid isolated contained $[PMePh_3][Co(CO)_4]$ and $[Co_4(CO)_{12}]$ as impurities.

$[N(PPh_3)_2][Co_4(CO)_{11}(COOCH_3)]$. The compound $[Co_4(CO)_{12}]$ (0.96 g) was suspended in anhydrous methanol (12 cm^3) under nitrogen and cooled to −70 °C. A solution of (0.422 mol dm^{-3}, 4 cm^3) of $Na(OCH_3)$ in methanol was added dropwise with stirring. After 2 h a purple-red solution resulted and solid $[N(PPh_3)_2]_2[SO_4]$(1.01 g) was added. After filtration at low temperature, $[N(PPh_3)_2]$-$[Co_4(CO)_{11}(COOCH_3)]$ was precipitated as lustrous violet microcrystals by addition of pentane–di-isopropyl ether (1 : 1, 50 cm^3).

Transformation of $[Co_4(CO)_{12}]$ *into* $[Co_2(CO)_8]$.—(*a*) The compound $[Co_4(CO)_{12}]$ (0.34 g) and LiCl (0.002 5 g) were suspended in anhydrous Pr^iOH (31 cm^3) and stirred under carbon monoxide (1 atm) at room temperature (*ca.* 25 °C). After 24 h the i.r. spectrum showed only the stretching absorptions of $[Co_2(CO)_8]$. The solution was cooled to −70 °C and solid $[Co_2(CO)_8]$ was isolated in 60% yield.

(*b*) The compound $[Co_4(CO)_{12}]$ (0.10 g) and $[NBu_4]I$ (0.005 g) were suspended in anhydrous Pr^iOH (10 cm^3) and stirred under carbon monoxide (1 atm) at room temperature. After 48 h the i.r. spectrum showed only carbonyl stretching absorptions due to $[Co_2(CO)_8]$.

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