Journal of Organometallic Chemistry, 396 (1990) 339–353
Elsevier Sequoia S.A., Lausanne
JOM 21130

Site selectivity and competitive CO attack in $Co_4(CO)_{10}(\mu_4\text{-PPh})_2$ using methanolic $[Et_4N][OH]$

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(Received April 3rd, 1990)

Abstract

The reaction between the tetracobalt cluster $Co_4(CO)_{10}(\mu_4\text{-PPh})_2$ (**1**) and $[Et_4N][OH]$ (1.1 equivalents of a 1.3 *M* solution in MeOH) has been examined in THF at −78 °C. Low-temperature IR analysis reveals the presence of both the hydroxycarbonyl cluster $[Co_4(CO)_9(\mu_4\text{-PPh})_2(CO_2H)^-]$ [$\mathbf{2}^-$] and the methoxycarbonyl cluster $[Co_4(CO)_9(\mu_4\text{-PPh})_2(CO_2Me)^-]$ [$\mathbf{3}^-$] as a result of hydroxide and methoxide attack, respectively, on a terminal carbonyl group in **1**. IR band-shape analysis indicates that [$\mathbf{2}^-$] and [$\mathbf{3}^-$] exist in a 77 : 23 ratio at −72 °C. Addition of excess [Li^+] (as $[CF_3SO_3][Li]$) to solutions of [$\mathbf{2}^-$] and [$\mathbf{3}^-$] affords [$\mathbf{3}^-$] in quantitative yield at −72 °C. The thermal stability and reactivity of these anionic clusters are discussed and comparisons made to the structural similar formyl and acetyl clusters derived from **1**.

Introduction

Polynuclear clusters have been extensively investigated in the homogeneously catalyzed activation of carbon monoxide [1]. Of the many CO reduction reactions studied, considerable effort has been devoted to the water-gas shift reaction [2–13] based on its industrial importance in the generation of hydrogen from water-gas [14]. For reactions conducted under alkaline conditions, hydroxide attack on a coordinated M–CO group to yield an intermediate hydroxycarbonyl complex, $[M\text{–}CO_2H^-]$, continues to serve as an entry point into the water-gas shift cycle. Decarboxylation of the hydroxycarbonyl complex generates the corresponding anionic metal hydride, $[M\text{–}H^-]$, which upon protonation gives a metal dihydride (MH_2) and hydroxide. Reductive elimination of hydrogen, followed by CO uptake, regenerates the initial metal carbonyl complex [15]. Alternatively, evidence exists for a hydride dissociation/CO uptake pathway [16]. In this reaction the liberated hydride reacts with added water to generate hydrogen and hydroxide. Regardless of

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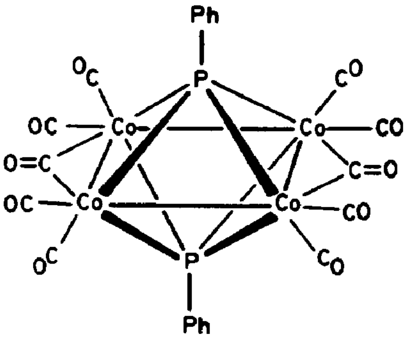
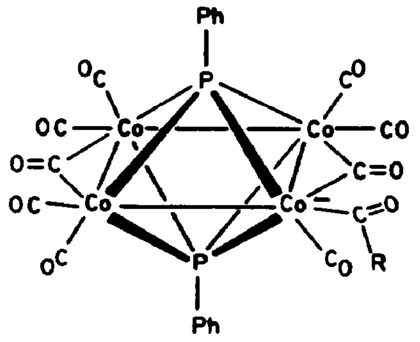
the nature of the hydrogen producing step, regeneration of the initial carbonyl complex allows for continuous water-gas shift catalysis according to Eq. 1.

$$H_2O + CO \rightleftharpoons H_2 + CO_2 \qquad (1)$$

While polynuclear hydroxycarbonyl complexes of the form $[M_x(CO)_{n-1}(CO_2H)^-]$ are undoubtedly formed in the reaction between hydroxide and $M_x(CO)_n$, their spectral observation is lacking due to the ease associated with the CO_2 decarboxylation step. As part of our interest in the spectral characterization and reactivity studies of thermally unstable organometallic species and their possible intervention in catalytic cycles [17–19], we report our results on the reaction between the tetracobalt cluster $Co_4(CO)_{10}(\mu_4\text{-}PPh)_2$ (1) and methanolic $[Et_4N][OH]$ which affords the thermally unstable hydroxycarbonyl and methoxycarbonyl clusters $[Co_4(CO)_9(\mu_4\text{-}PPh)_2(CO_2H)^-]$ and $[Co_4(CO)_9(\mu_4\text{-}PPh)_2(CO_2Me)^-]$, respectively. The selection of cluster **1** was based on its reported hydroformylation activity [20] in addition to an earlier study which outlined the reactivity of **1** with various hydridic and alkyllithium reagents [21,22]. The present study allows for a direct reactivity comparison between the structurally similar formyl, acetyl, hydroxycarbonyl, and methoxycarbonyl clusters.





R = OH,OMe.H,Me

Results

I. Reaction of $[Et_4N][OH]$ and $[MeO][Li]$ with $Co_4(CO)_{10}(\mu_4\text{-}PPh)_2$

The reaction of $Co_4(CO)_{10}(\mu_4\text{-}PPh)_2$ with 1.1 equiv. of $[Et_4N][OH]$ (1.3 *M* in MeOH) in THF at −78 °C yields the anionic clusters $[Co_4(CO)_9(\mu_4\text{-}PPh)_2(CO_2H)^-]$ $[2^-]$ and $[Co_4(CO)_9(\mu_4\text{-}PPh)_2(CO)_2Me)^-]$ $[3^-]$ immediately and in quantitative yield (combined yield). Low-temperature IR analysis (THF solvent) revealed terminal carbonyl stretching bands at 2037(m), 2002(vs), 1983(s), and 1976(s) cm^{-1} in addition to a broad μ_2-bridging CO band at 1838(m) cm^{-1} as shown in Fig. 1a. A single μ_2-bridging CO band is inconsistent with a hydroxide/methoxide attack at a terminal CO group based on symmetry considerations associated with inequivalent μ_2-bridging CO groups [23–25]. However, closer inspection of the μ_2-CO band in Fig. 1a reveals that it is actually composed of two overlapping bands. On the basis of previous work, we can readily assign the shoulder at ~ 1848 cm^{-1} to the μ_2-CO

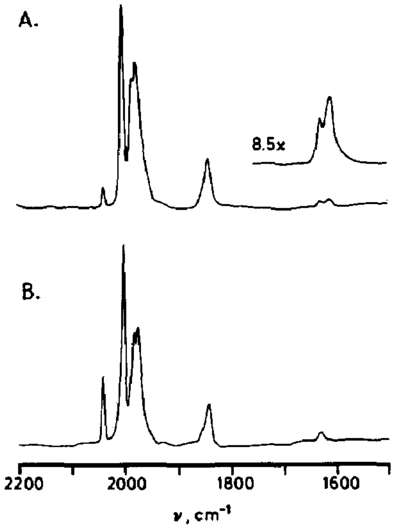


Fig. 1. Infrared spectra of the carbonyl region for (a) $[\mathrm{Co_4(CO)_9(\mu_4\text{-}PPh)_2(CO_2H)}^-]$ and $[\mathrm{Co_4(CO)_9(\mu_4\text{-}PPh)_2(CO_2Me)}^-]$ and (b) $[\mathrm{Co_4(CO)_9(\mu_4\text{-}PPh)_2(CO_2Me)}][\mathrm{Li(15\text{-}crown\text{-}5)}]$. Both spectra were recorded in THF at −72 °C.

group opposite the site of the hydroxycarbonyl/methoxycarbonyl functionality [23–25]. The two weak intensity bands at 1624(w) and 1606(w) cm^{-1} have been assigned to the methoxycarbonyl and hydroxycarbonyl moieties of clusters $[\mathbf{3}^-]$ and $[\mathbf{2}^-]$, respectively. Equation 2 illustrates the observed reaction.

$$\mathrm{Co_4(CO)_{10}(\mu_4\text{-}PPh)_2} \xrightarrow{[\mathrm{Et_4N}][\mathrm{OH}]/\mathrm{MeOH}} \mathrm{Co_4(CO)_9(\mu_4\text{-}PPh)_2(CO_2H)}^- + \mathrm{Co_4(CO)_9(\mu_4\text{-}PPh)_2(CO_2Me)}^- \tag{2}$$

The ratio of $[\mathrm{Co_4(CO)_9(\mu_4\text{-}PPh)_2(CO_2H)}^-]$ and $[(\mathrm{Co_4(CO)_9(\mu_4\text{-}PPh)_2(CO_2Me)}^-]$ obtained in the reaction between **1** and $[\mathrm{Et_4N}][\mathrm{OH}]$ was determined by measuring

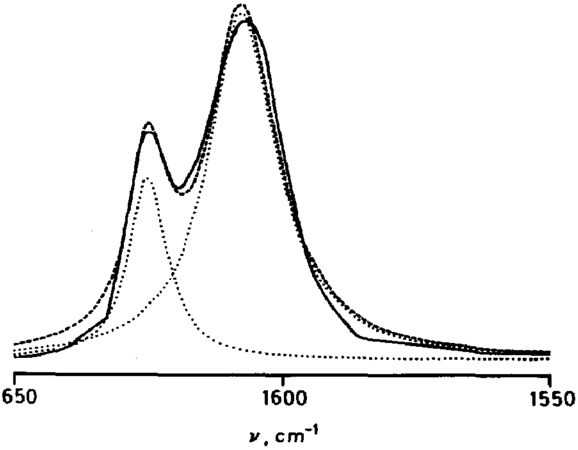


Fig. 2. Expanded infrared spectral view of the acid/ester C–O stretching region (THF, −72 °C) for the experimental (———), resolved bands (······), and the theoretical curve (------) for both the acid and the ester.

Table 1

Infrared spectral data in the carbonyl region for the anionic clusters [$Co_4(CO)_9(\mu_4\text{-}PPh)_2\{C(O)R\}^-$] [a]

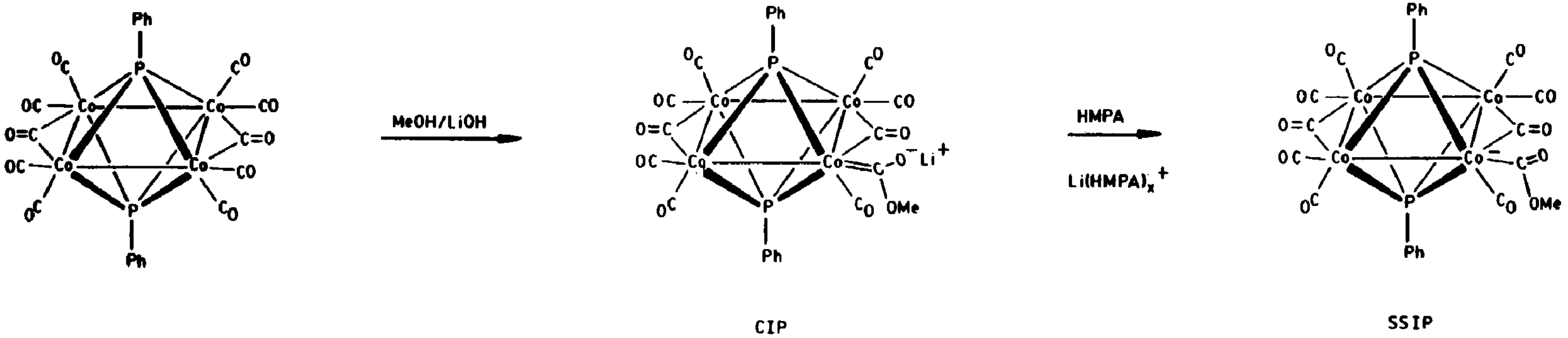
R	OH/OMe [*] mixture	OMe [b]	OMe [c]	H [d]	Me [d]
C(O)R	1624 (OMe, w) 1606 (OH, w)	1624 (w)	1580 (w)	1575 (w)	1574 (w)
bridging carbonyls	1848 (sh) 1838 (m)	1847 (sh) 1837 (m)	1842 (m)	1847 (m)	1840 (m)
terminal carbonyls	2037 (m) 2002 (vs) 1983 (s) 1976 (s) 1960 (sh)	2039 (m) 2001 (vs) 1982 (s) 1974 (s)	2042(m) 2002 (vs) 1988 (s) 1979 (s)	2041 (s) 2005 (vs) 1991 (vs) 1980 (s)	2039 (m) 2000 (vs) 1988 (s) 1979 (s) 1961 (sh)

[a] All spectra recorded in THF at −72 °C unless otherwise noted. [b] Solvent-separated ion pairs. [c] [Li^+] contact ion pairs. [d] Recorded at room temperature in THF. See Ref. 21.

the area under the overlapping low frequency acid and ester C–O stretching bands. In order to avoid undue error from these low intensity bands, the IR band-shape analysis was performed on a 1.6×10^{-2} *M* solution (THF) of $Co_4(CO)_{10}(\mu_4\text{-}PPh)_2$. An abbreviated view of the acid and ester carbonyl bands from 1650 to 1550 cm^{-1} for [2^-] and [3^-] prepared at this higher concentration is shown in the inset accompanying Fig. 1a while Fig. 2 displays the experimental and resolved spectra of these acid and ester bands. A 77 : 23 ratio of [2^-] to [3^-] at −72 °C is readily computed from the area under each band. This ratio of acid to ester is lower than that recently observed for similarly conducted experiments using $Fe(CO)_5$ [26] and $Cr(CO)_6$ [27] which display an acid/ester ratio of 95 : 5 and 98 : 2, respectively.

Unequivocal proof for the presence of the methoxycarbonyl cluster [3^-] was established by its independent synthesis. Treatment of $Co_4(CO)_{10}(\mu_4\text{-}PPh)_2$ in THF at −78 °C with 1.1 equiv of [MeO][Li] (1.3 *M* in MeOH) gives [3][Li] which exists as a contact ion pair in solution. The reaction is quantitative as the parent cluster's CO stretching bands are shifted to lower frequency consistent with the formation of the anionic methoxycarbonyl cluster. The IR spectrum of [3][Li] recorded at −72 °C is similar to the mixture of [2^-] and [3^-] obtained using [Et_4N][OH] as demonstrated by the IR frequencies given in Table 1. All of the terminal and bridging CO bands of [3][Li] are observed to be ~ 1–6 cm^{-1} higher in frequency relative to [2][Et_4N] and [3][Et_4N] while the ester C–O stretch is shifted 44 cm^{-1} to lower frequency. This is exactly the behavior expected for a carbonyl oxygen–[Li^+] contact ion pair (CIP) where π electron density is polarized towards the ester carbonyl oxygen involved in ion pairing with the [Li^+] gegencation [28]. The [Li^+]-ester interaction leads to a lowering of the C-O stretching frequency of the participatory ester functionality with concomitant strengthening (i.e., high frequency shift) of the remaining CO groups [28,29].

Treatment of the contact ion pairs (CIP) of [3][Li] with excess 15-crown-5 or HMPA (~ 10 equiv.) effected the complete disruption of the [Li^+] contact ion pairs. The resulting solvent-separated ion pairs (SSIP) of [3^-] facilitate the direct spectral comparison with the same ions obtained using [Et_4N][OH] since the solvated [$Li \cdot (HMPA)_x^+$] and [$Li(15\text{-crown-}5)^+$] ions exhibit minimal contact ion pairing



Scheme 1

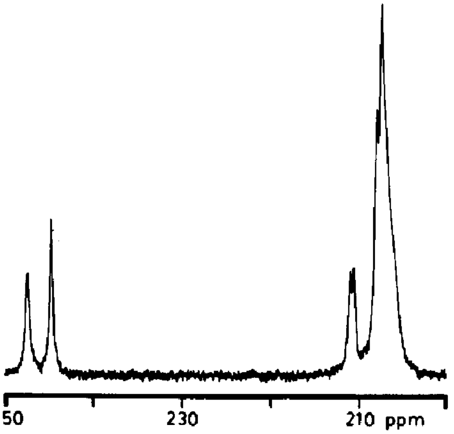


Fig. 3. $^{13}C\{^{1}H\}$ NMR spectrum of the carbonyl region of $[Co_4(CO)_9(\mu_4\text{-}PPh)_2(CO_2H)^-]$ and $[Co_4(CO)_9(\mu_4\text{-}PPh)_2(CO)_2Me)^-]$ in THF/benzene-d_6 (4:1 v/v) at −78° C.

[28,30]. Figure 1b shows the low-temperature IR spectrum recorded after the addition of 15-crown-5 to [3][Li]. Comparison of Fig. 1a and 1b reveal virtually identical spectra in the terminal and bridging carbonyl region. The similarity between these spectra suggests that the acid and ester moieties possess comparable electronic and steric properties, manifesting itself in comparable metal carbonyl C–O stretching perturbations. The low-frequency C–O band at 1624 cm^{-1} in Fig. 1b is readily ascribed to the ester moiety of $[3^-]$. It is this latter ester band which provides the unequivocal proof for the presence of the methoxycarbonyl cluster $[3^-]$ in $[Et_4N][OH]$ reaction. Accordingly, we assign the C–O stretching band at 1606 cm^{-1} in Fig. 1a to the hydroxycarbonyl cluster $[2^-]$. Scheme 1 illustrates the transformations observed with $[3^-]$.

^{13}C NMR examination of $[2^-]$ and $[3^-]$ obtained from ^{13}CO enriched $Co_4(CO)_{10}(\mu_4\text{-}PPh)_2$ [31] and $[Et_4N][OH]$ establishes the reaction as arising from a hydroxide/methoxide attack at a terminal carbonyl group. Figure 3 shows the $^{13}C\{^{1}H\}$ NMR spectrum recorded at −78°C. At first glance, the observed ^{13}C resonances at δ 247.8 (1C), 244.8 (1C), 211.1 and 210.7 (1C, combined) and 207.5 (7C) suggest the presence of only one anionic cluster of the form $[Co_4(CO)_9(\mu_4\text{-}PPh)_2(CO_2X)^-]$ (where $X = H$ or Me). However, as shown by the two distinct ν(CO) bands for the acid and ester functionalities (vide supra), we propose that the observed ^{13}C NMR spectrum actually represents a composite spectrum formed by the superposition of the terminal and bridging CO groups of $[2^-]$ and $[3^-]$. The lack of observable resolution in the IR spectrum containing $[2^-]$ and $[3^-]$ is also seen in the ^{13}C NMR spectrum. Accordingly, we assign the resonance at lowest field (δ 247.8) to the μ_2-CO group adjacent to the ancillary CO_2H/CO_2Me group while the other low-field resonance (δ 244.8) represents the remaining μ_2-CO group. The observed chemical shift difference between these two groups results from the increased charge density at the hydroxy/methoxy carbonyl-substituted cobalt center which causes the adjacent μ_2-CO group to experience a greater degree of π backbonding relative to the other μ_2-CO group [32,33]. The unresolved resonance centered at δ 207.5 represents the seven terminal CO groups associated with $[2^-]$ and $[3^-]$ and is in agreement with the unresolved nature and the chemical shift reported for the analogous formyl and acetyl clusters $[Co_4(CO)_9(\mu_4\text{-PPh})_2(CHO)^-]$ $[4^-]$ and $[Co_4(CO)_9(\mu_4\text{-PPh})_2(COMe)^-]$ $[5^-]$ [21]. The partially resolved resonances at δ 211.1 and 210.7, which taken together integrate for one carbon, are tentatively assigned to the acid and ester carbon of $[2^-]$ and $[3^-]$. No attempt has been made to assign a specific resonance to these groups.

II. Stability and reactivity studies

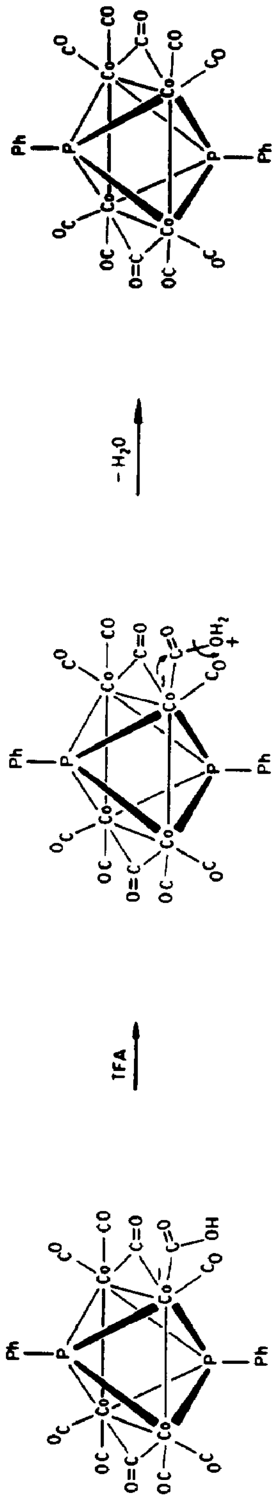
THF solutions containing $[2^-]$ and $[3^-]$ were observed to be stable for a period of at least two weeks when maintained at −78 °C. Warming to room temperature led to the complete decomposition of $[2^-]$ and $[3^-]$ as shown in Eq. 3. IR analysis revealed the presence of the anionic hydride cluster $[Co_4(CO)_9(\mu_4\text{-PPh})_2(\mu_2\text{-H})^-]$, $[6^-]$, and $[Co(CO)_4^-]$ [35] in ca. 20 and 25% yield, respectively, in addition to a small amount of the parent cluster **1** ($< 15\%$). Evident in these solutions is the presence of a considerable amount of insoluble material which presumably represents the unaccounted cobalt, most likely as some form of Co^{2+}, along with bicarbonate based on the broad IR band (KBr pellet) observed at ~ 1600 cm^{-1}. The less than clean decomposition of $[2^-]$ and $[3^-]$ stands in marked contrast to the formyl cluster $[Co_4(CO)_9(\mu_4\text{-PPh})_2(CHO)^-]$ which readily decarbonylates to afford the anionic hydride cluster $[6^-]$ in near quantitative yield [21].

$$[2^-] \text{ and } [3^-] \xrightarrow{\text{warm-up}} \mathbf{1} + Co(CO)_4^- + Co_4(CO)_9(\mu_4\text{-PPh})_2(\mu_2\text{-H})^- \qquad (3)$$

In a separate study the methoxycarbonyl cluster [3][Li] was observed to be stable for a period of at least one week at −78 °C. Warming to room temperature affords $Co_4(CO)_{10}(\mu_4\text{-PPh})_2$ in considerably lowered yield. For example, in situ IR analysis of a ~ 1.0×10^{-3} *M* THF solution of [3][Li] revealed cluster **1** in ~ 50% yield upon warm-up; no other carbonyl containing material was observed in this reaction. This observation suggests that the presence of cluster **1** in decomposed solutions of $[2^-]$ and $[3^-]$ is derived from the latter anionic cluster.

The stability of the new anionic clusters was examined under acidic conditions at −78 °C. THF solutions of $[2^-]$ and $[3^-]$ regenerated cluster **1** in quantitative yield upon treatment with trifluoroacetic acid, as did a THF solution containing [3][Li]. This acid promoted decomposition of clusters $[2^-]$ and $[3^-]$ has been noted in other mono- and polynuclear hydroxycarbonyl and methoxycarbonyl complexes [36–43]. Scheme 2 illustrates the proposed sequence of events that is triggered upon protonation of the hydroxy or methoxy oxygen group.

Addition of Et_3N (excess) to a solution of $[2^-]$ and $[3^-]$ at −78 °C led to no perceptible change in the IR spectrum (vide supra). This was somewhat surprising since we expected to observe the dianionic cluster $[Co_4(CO)_9(\mu_4\text{-PPh})_2(CO_2)^{-2}]$ as a result of acid deprotonation. While some hydroxycarbonyl complexes are deprotonated by Et_3N [44–46], many are not [26,27,41,42]. Such insensitivity to Et_3N suggests that a comparison between $[2^-]$ and organic carboxylic acids is inappropriate. Organic carboxylic acids RCO_2H (where R = alkyl) are sufficiently acidic ($pKa \approx 4$–5) and readily enter into the expected acid-base reaction with Et_3N as shown in Eq. 4 [47]. On the basis of no observable reaction between $[2^-]$ and Et_3N and the knowledge of the p*K*a (as $[Et_3NH^+]$) value of Et_3N reported as ca. 11 [48], we conclude that the hydroxycarbonyl moiety in $[2^-]$ must possess a p*K*a value in excess of 11. Future studies involving the preparation of $[2^-]$ in aprotic solvents are



Scheme 2

clearly required in order to facilitate deprotonation reactions with stronger bases (i.e., LDA or alkyllithium reagents).

$$\text{R–CO}_2\text{H} + \text{Et}_3\text{N} \rightleftharpoons [\text{RCO}_2^-] + [\text{Et}_3\text{NH}^+] \qquad (4)$$

The stability of a kinetic mixture of [**2**][Et_4N] and [**3**][Et_4N] (vide infra) was probed for its response toward added [Li^+] based on reports of metal ion promoted catalysis in acid and ester hydrolysis reactions [49–51]. Treatment of [**2**$^-$] and [**3**$^-$] (77:23 ratio) in THF at −78 °C with 10 equiv. of [Li^+] (as [CF_3SO_3][Li]) led immediately to [**3**][Li] in quantitative yield as determined by low-temperature IR analysis. This dramatic [Li^+]-induced effect was also verified for the reaction between cluster **1** and [Li][OH] (1.3 *M* in MeOH). Here only [**3**][Li] was observed in accordance with the above experiment using [CF_3SO_3][Li].

The ability of metal formyl complexes to function as hydride transfer agents is well known [52–54]. Of relevance to this study is the formyl cluster [$Co_4(CO)_9(\mu_4\text{-PPh})_2(CHO)^-$] which has been shown to transfer hydride to $Fe(CO)_5$ to give [$Fe(CO)_4(CHO)^-$] and $Co_4(CO)_{10}(\mu_4\text{-PPh})_2$ in near quantitative yield [21]. The small amount of the anionic hydride cluster [$Co_4(CO)_9(\mu_4\text{-PPh})_2(\mu_2\text{-H})^-$] observed (< 10%) indicates that hydride transfer from the formyl cluster [**4**$^-$] to $Fe(CO)_5$ is more favorable compared to the formyl deinsertion process which affords the hydride cluster [**6**$^-$]. On the basis of this reported transformylation activity, the hydroxycarbonyl and methoxycarbonyl clusters were examined for their propensity to function in transhydroxylation and methoxylation reactions, respectively, with $Fe(CO)_5$. No noticeable reaction between $Fe(CO)_5$ (1.1 mol equiv.) and the anionic clusters [**2**$^-$] and [**3**$^-$] was observed at −78 °C. However, evidence for the formal transhydroxylation of $Fe(CO)_5$ was obtained from solutions that were allowed to warm to room temperature. Besides the presence of regenerated **1**, unreacted $Fe(CO)_5$, cluster [**6**$^-$], and [$Co(CO)_4^-$] in the final solution, the presence of the iron hydride [$HFe(CO)_4^-$] [55], the decomposition product from [$Fe(CO)_4(CO_2H)^-$] [19], was also detected. Whether the transhydroxylation reaction involves [**2**$^-$] and/or free [OH^-] is not immediately clear. An independent variable-temperature IR study of [**2**$^-$] and [**3**$^-$] revealed that at ca. 0 °C the parent cluster was regenerated (< 10%) as a result of [OH^-] and [MeO^-] dissociation. This observation suggests that the [$HFe(CO)_4^-$] detected in the reaction between $Fe(CO)_5$ and [**2**$^-$] and [**3**$^-$] may arise, in part, from the attack of free [OH^-] on $Fe(CO)_5$. No attempt was made to quantify the decomposition products associated with these reactions due to extensive overlapping of the various ν(CO) bands.

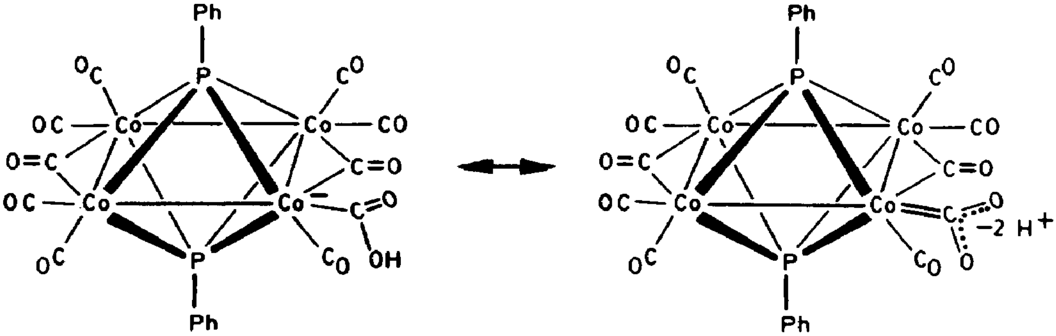
Discussion

I. Hydroxycarbonyl and methoxycarbonyl product distribution and gegencation influence

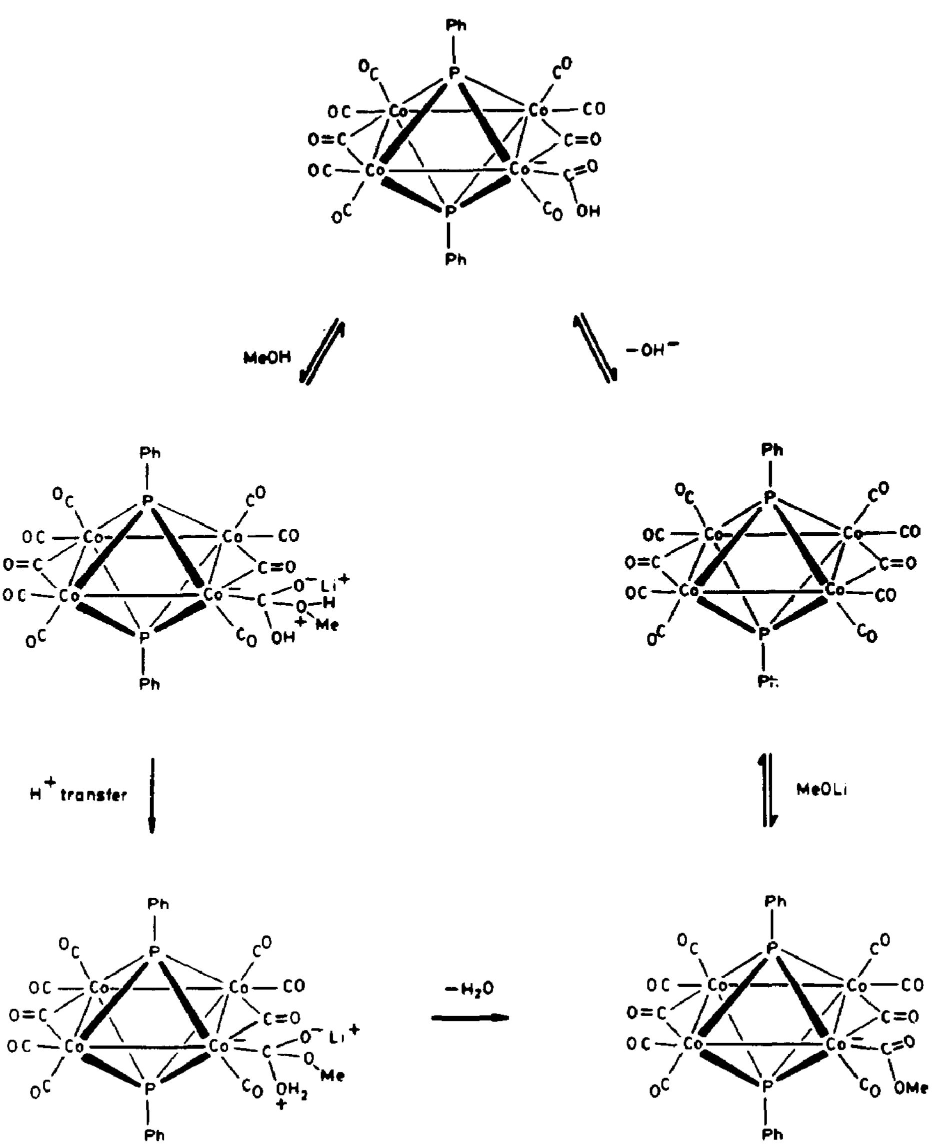
The reaction of methanolic [Et_4N][OH] with $Co_4(CO)_{10}(\mu_4\text{-PPh})_2$ leads to cluster reduction and formation of [$Co_4(CO)_9(\mu_4\text{-PPh})_2(CO_2H)^-$] and [$Co_4(CO)_9(\mu_4\text{-PPh})_2(CO_2Me)^-$] as a result of [$OH^-$] and [$MeO^-$] attack on a terminal carbonyl group. The identity of the anionic clusters was ascertained by low-temperature IR and ^{13}C NMR measurements. IR analysis revealed a 77:23 ratio of clusters [**2**$^-$] and [**3**$^-$], respectively, at −72 °C which remained unchanged for up to two weeks at this temperature. The observation of [**2**$^-$] as the major product could be interpreted as proceeding by a thermodynamically controlled sequence [56]. However, the ratio of [2^-] to [3^-] was observed to remain unchanged over the temperature range -70 to $-25\,°C$, supporting a kinetically controlled reaction [56]. Further proof for kinetic product control stems from the spectral invariance of [2^-] and [3^-] to the addition of small amounts of [Et_4N][OH] and MeOH. Such a kinetic effect is best viewed by considering the magnitude of the [MeO^-]/[OH^-] equilibrium in Eq. 5 which has a $K_{eq} \approx 7.7$ in aqueous MeOH [57]. Since the 1.3 M methanolic [Et_4N][OH] solution used exists in $>99\%$ as [MeO^-] ion, [3][Et_4N] would have been predicted as the major product given the greater nucleophilicity of [MeO^-] relative to [OH^-] [58]. Unfortunately, the effect of the THF on the [MeO^-]/[OH^-] equilibrium has not been determined; however, Ford and coworkers have suggested that the K_{eq} should, if anything, increase upon the addition of THF [59]. The deviation in the product distribution from the equilibrium concentrations of [MeO^-] and [OH^-] reflects both the nature of the gegencation and the initial carbonyl complex.

$$MeOH + OH^- \rightleftharpoons MeO^- + H_2O \qquad (5)$$

The preference for [2][Et_4N] using [Et_4N][OH] is also driven by maximum delocalization of the anionic charge which, in turn, is strongly influenced by the gegencation. Use of [Et_4N][OH] leads to anions that exist in an unperturbed, symmetrical environment as the [Et_4N^+] ion is a nonspecific, charge-delocalized cation [28]. The IR frequencies of [2][Et_4N] and [3][Et_4N] are not affected upon the addition of 15-crown-5 or HMPA, supporting the absence of [Et_4N^+] ion pairing [30]. [3][Et_4N] is expected to exhibit high charge density on the ester/cobalt center relative to [2][Et_4N] which can delocalize the anionic charge more effectively through the carboxylate-like resonance structure shown below. Unlike the reaction using $Fe(CO)_5$ [26] and $Cr(CO)_6$ [27] which affords the corresponding hydroxycarbonyl compound in 95 and 98% yield, respectively, the cobalt cluster shows a substantially greater amount of ester product presumably due to the electron reservoir properties inherent with the cluster polyhedron which facilitates greater anionic charge delocalization relative to the mononuclear complexes [60].



The effect of added [Li^+] also confirms the importance of the gegencation in determining the ratio of [2^-] to [3^-]. Addition of [Li][O_3SCF_3] to [2][Et_4N] and [3][Et_4N] results in the immediate formation of the thermodynamically more stable



Scheme 3

cluster [3][Li] which exists exclusively as [Li^+]-ester oxygen contact ion pairs. Use of methanolic LiOH (1.3 *M* in MeOH) also furnishes [3][Li] without the spectroscopic observation of intermediates in agreement with the alkaline base being present in > 99% as [MeO^-].

The mechanism for the [Li^+]-induced transformation of [2][Et_4N] to [3][Li] is unknown at this time. A methanol addition/water elimination or a hydroxide dissociation/methoxide addition sequence represent the two most likely pathways as shown in Scheme 3. Given the low k^{-1} value associated with the equilibrium between $Co_4(CO)_{10}(\mu_4\text{-}PPh)_2$/[$Co_4(CO)_9(\mu_4\text{-}PPh)_2(CO_2H)^-$] and $Co_4(CO)_{10}(\mu_4\text{-}PPh)_2$/[$Co_4(CO)_9(\mu_4\text{-}PPh)_2(CO_2Me)^-$] at $-72°$ C, we favor the former pathway of the conversion of [2^-] → [3^-] in the presence of [Li^+]. [Li^+] coordination to the anionic oxygen in [2^-] should render the acid carbon more susceptible to MeOH attack as demonstrated in related organic ester/acid hydrolysis reactions. Furthermore, the addition of $H_2{}^{18}O$ to [2][Et_4N] and [3][Et_4N] at −72°C led to no incorporation of the ^{18}O label into the anionic clusters. This observation underscores the absence of a reversible equilibrium between [2^-] and **1** and hydroxide as free [$^{16}OH^-$] would surely afford [$^{18}OH^-$] via rapid proton transfer, ultimately producing ^{18}O enriched [2^-].

II. Structural and reactivity comparisons in the anionic [$Co_4(CO)_9(\mu_4\text{-}PPh)_2\{C(O)R\}^-$] clusters

$Co_4(CO)_{10}(\mu_4\text{-}PPh)_2$ reacts with a variety of nucleophiles to afford the corresponding anionic clusters [$Co_4(CO)_9(\mu_4\text{-}PPh)_2\{C(O)R\}^-$]. IR and ^{13}C NMR data for the anionic clusters are virtually identical except for small frequency differences ascribed to the unique R groups. Use of the oxyanions [OH^-] and [MeO^-] yields anionic clusters of limited stability at ambient temperature; extensive cluster decomposition is observed in each case. The anticipated loss of CO_2 from [2^-] represents a minor decomposition pathway given the low yield of the μ_2-hydride cluster, [6^-], observed (≈ 20%). In contrast, the formyl cluster decomposes cleanly via a decarbonylation pathway to give cluster [6^-] in near quantitative yield whereas the acetyl cluster is relatively stable at room temperature for several days [21]. Based on these observations it is clear that CO loss from the formyl cluster is faster than CO_2 loss from the hydroxycarbonyl cluster.

The intimate mechanism associated with the formation of [$Co_4(CO)_9(\mu_4\text{-}PPh)_2(CO_2H)^-$] using methanolic [$Et_4N$][OH] in addition to the reactivity displayed by other polynuclear hydroxycarbonyl complexes will be pursued using low-temperature stopped-flow techniques and reported in due course.

Experimental

General

$Co_4(CO)_{10}(\mu_4\text{-}PPh)_2$ was prepared according to the procedure given by Richmond and Kochi [60]. [Et_4N][OH] (20% aqueous solution) was obtained from Lancaster Synthesis and dried under high vacuum to give solid [Et_4N][OH]. 1.3 *M* methanolic solutions of [Et_4N][OH] were subsequently prepared under argon and transferred to Schlenk vessels for storage. $H_2{}^{18}O$ (98.8 atom % ^{18}O) and ^{13}CO (99% ^{13}C) were purchased from Isotec and used as received. THF and HMPA were distilled from sodium/benzophenone and CaH_2, respectively, and stored under argon in schlenk vessels. $Cr(acac)_3$ was used as a shiftless relaxation agent (~ 0.01 *M*) in the ^{13}C NMR study [61]. All reactions and manipulations were conducted under argon with Schlenk techniques [62].

Low-temperature infrared spectra were recorded on a Nicolet 20SXB FT-IR spectrometer with a Specac Model P/N 21.000 variable-temperature cell equipped with inner and outer CaF_2 windows. Solutions for analysis were transferred to the precooled IR cell via cannulation from an external Schlenk vessel maintained at −78°C. The transfer cannula was wrapped in dry ice to prevent undue warming. Dry ice/acetone was used as coolant, and the reported cell temperature, taken to be accurate to ±1°C, was determined with a copper-constantan thermocouple. The ^{13}C NMR spectrum was recorded at 75 MHz on a Varian 300-VXR spectrometer.

Reaction of $Co_4(CO)_{10}(\mu_4\text{-}PPh)_2$ with [Et_4N][OH]

To 0.06 g (0.082 mmol) of $Co_4(CO)_{10}(\mu_4\text{-PPh})_2$ in 10 ml of THF at −78 °C was added 0.07 ml (slight excess) of a 1.3 *M* methanolic [Et_4N][OH] solution. The formation of [**2**][Et_4N] and [**3**][Et_4N] was instantaneous based on low-temperature IR analysis. IR (−72 °C, THF) ν(CO): 2037(m), 2002(vs), 1983(s), 1976(s), 1960(sh), 1848(sh, bridging), 1838(m, bridging), 1624(vw, ester), and 1606(w, acid) cm^{-1}. $^{13}C\{^1H\}$ NMR [−78 °C, THF/C_6D_6 (3 : 1 v/v)] δ: 247.8 (1C, bridging CO), 244.8 (1C, bridging CO), 211.1 and 210.7 (1C combined, ester and acid), and 207.5 (7C, terminal CO).

Reaction of $Co_4(CO)_{10}(\mu_4\text{-}PPh)_2$ with [MeO][Li]

To 0.06 g (0.082 mmol) of $Co_4(CO)_{10}(\mu_4\text{-PPh})_2$ in 10 ml of THF at −78 °C was added 0.11 ml (slight excess) of 1.3 *M* solution of [MeO][Li] in methanol. After the low-temperature IR spectrum of [**3**][Li] was recorded, 0.15 ml (~ 10 mol equiv.) of HMPA was added. The solution was stirred for 0.5 h and the IR spectrum of [$\mathbf{3}^-$] recorded. IR (−72 °C, THF) ν(CO) for [**3**][Li]: 2042(m), 2002(vs), 1988(s), 1979(s), 1842(m, bridging), and 1540(w, ester) cm^{-1}; ν(CO) for [**3**][Li · $(HMPA)_x$]: 2039(m), 2001(vs), 1982(s), 1974(s), 1847(sh, bridging), 1837(m, bridging), and 1624(w, ester) cm^{-1}.

Reaction of [2][Et_4N] and [3][Et_4N] with $H_2{}^{18}O$

To 0.06 g (0.082 mmol) of $Co_4(CO)_{10}(\mu_4\text{-PPh})_2$ in 10 ml of THF at −78 °C was added 0.07 ml (slight excess) of a 1.3 *M* methanolic [Et_4N][OH] solution. The solution was stirred for 0.5 h and then treated with 1.0 ml (~ 2.5 mmol) of a 2.5 *M* solution of $H_2{}^{18}O$ in THF. The solution was stirred for 4 h at −78 °C with monitoring by low-temperature IR spectroscopy. The IR spectra remained unchanged during this time period, suggesting no ^{18}O incorporation into [$\mathbf{2}^-$] or [$\mathbf{3}^-$].

Band-shape analysis

Since the acid and ester carbonyl stretching bands exhibit partial overlap, the infrared band shapes of these CO bands were calculated using a numerical procedure in order to determine the ratio of their areas. Absorbances were digitized from 1650 cm^{-1} to 1550 cm^{-1} at 1 cm^{-1} intervals and entered into files on the university VAX 11/85 computer. Following baseline correction, the spectra were fit by a model consisting of Lorentzian bandshapes, each characterized by a peak frequency (ν), maximum intensity (I), and halfwidth [FWHH] (δ). Since the instrument resolution (2 cm^{-1}) is far less than the observed bandwidths (~ 20 cm^{-1}), it was unnecessary to convolute the model spectrum with a resolution (slit) function. The parameters were varied to minimize the squared deviation between the experimental and calculated intensities using a non-linear regression procedure [63]. A representative experimental and calculated spectrum of [$\mathbf{2}^-$] and [$\mathbf{3}^-$] at −72 °C is shown in Fig. 2. Given that the are of a Lorentzian peak is proportional to the product of the bandwidth and the maximum intensity, the area ratio of the different anionic clusters is calculated easily as $A_2/A_1 = (I_2 \cdot \Delta_2/(I_1 \cdot \Delta_1)$.

Acknowledgment

We thank George Delong for NMR assistance and one of the reviewers for helpful comments. Financial support form the Robert A. Welch Foundation (B-1039) and the UNT faculty research program is gratefully acknowledged.

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