

SITE SELECTIVITY IN CARBONYL REDUCTION OF MIXED Fe_2Co_2 CLUSTERS. FORMYL INTERMEDIATES IN THE FORMATION OF HYDRIDO DERIVATIVES

M.G. RICHMOND and J.K. KOCHI

Department of Chemistry, University of Houston, University Park, Houston, Texas 77004 (U.S.A.)

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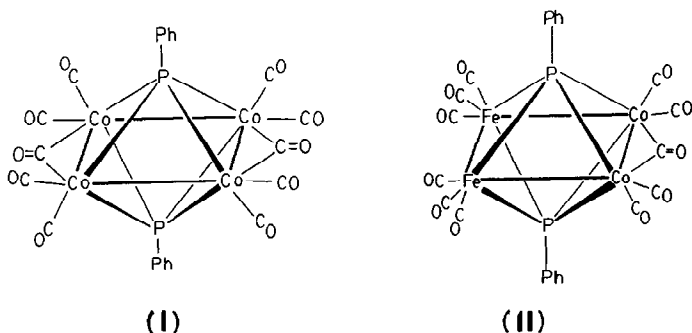
Summary

The mixed metal cluster $\text{Co}_2\text{Fe}_2(\text{CO})_{11}(\mu_4\text{-PPh})_2$ (II) undergoes a site-selective reduction of one of the carbonyl ligands by triethylborohydride reagent to afford a single formyl derivative $\text{Co}_2\text{Fe}_2(\text{CO})_{10}(\text{PPh})_2\text{CHO}^-$ (III) in excellent yields at -78°C . The same terminal CO bound to cobalt also selectively undergoes addition of methyllithium to afford the corresponding acetyl derivative (V). Whereas V is thermally robust at room temperature, the formyl derivative III is a transient species which readily loses carbon monoxide at -30°C to afford the μ_2 -hydride $\text{Co}_2\text{Fe}_2(\text{CO})_{10}(\text{PPh})_2\text{H}^-$ in quantitative yields. All of these site-selective reactions are compared to the corresponding transformations which were previously observed in the homonuclear analogue $\text{Co}_4(\text{CO})_{10}(\mu_4\text{-PPh})_2$ (I). The structural similarities of homo- and heteronuclear clusters I and II, respectively, are considered in the context of the fluxional behavior of their bound carbonyl ligands. The comparisons are extended to the IR, ^1H and ^{13}C NMR properties of their formyl, hydrido, and acetyl derivatives.

Introduction

Mixed-metal clusters offer the possibility of inducing a unique chemical reactivity mediated by adjacent dissimilar metals [1]. Such hetero-polynuclear systems are particularly attractive as models of mixed-metal surfaces representing bimetallic and alloy catalysts of known stoichiometry and composition [2,3]. The asymmetry inherent in mixed-metal clusters provide a ready definition of the site of reaction [1g]. Indeed such site-specific activity has been observed for various ligand substitutions and substrate activations [4]. Examples of the latter suggest that cooperative heterometallic interactions may afford chemistry that is otherwise unavailable in homonuclear clusters and mononuclear organometallic complexes.

Our recent study [5] of the reduction of carbonyl ligands in the bicapped tetracobalt cluster $\text{Co}_4(\text{CO})_{10}(\mu_4\text{-PPh}_2)$ (I) provides a useful backdrop for the mixed-metal system. Thus the analogous cobalt-iron system $\text{Co}_2\text{Fe}_2(\text{CO})_{11}(\mu_4\text{-PPh})_2$ (II) represents the hybrid of the homonuclear tetracobalt cluster I and the tetrairon clusters $\text{Fe}_4(\text{CO})_{11}(\mu_4\text{-PPh})_2$ and $\text{Fe}_4(\text{CO})_{12}(\mu_4\text{-PPh})_2$ [6,7]. Indeed, the X-ray crystallographic examinations point to the close structural similarity of the pseudo-octahedral Co_4P_2 and $\text{Co}_2\text{Fe}_2\text{P}_2$ cores in I and II [7,8]. In each case, the pair of



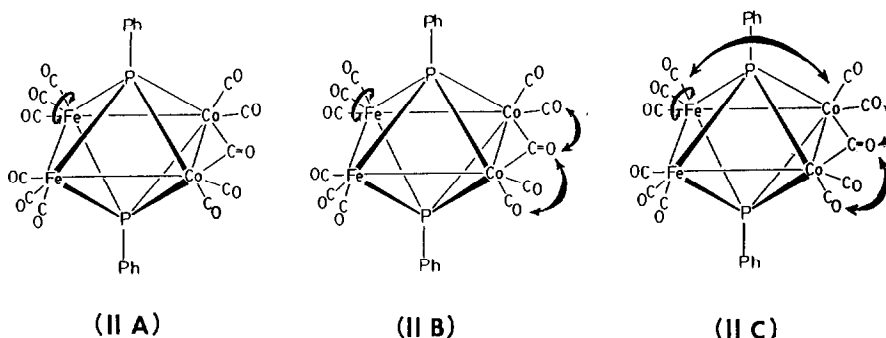
μ_4 -phenylphosphinidene caps preserves the integrity of the pseudo-octahedral cluster under reductive conditions in which simple binary carbonyl clusters fragment and decompose [9]. We focus in this study on the comparative reductive behavior of the carbonyl ligands in the mixed Co_2Fe_2 cluster II relative to the homonuclear Co_4 cluster I.

Results and discussion

The mixed cluster $\text{Co}_2\text{Fe}_2(\text{CO})_{11}(\text{PPh})_2$ (II) was prepared from the exposure of dicobalt octacarbonyl to the phenylphosphido-bridged diiron hexacarbonyl in hexane for 3 weeks at room temperature [6]. It was isolated as dark red-brown crystals in 15–20% yield. The exchange of the carbonyl groups was effected with an atmosphere of labelled carbon monoxide (99% ^{13}C) over a benzene solution of II for 3 d at 25°C. It is noteworthy that the tetracobalt analog I underwent no significant carbonyl exchange under the same conditions. Indeed the dynamic properties of the coordinated CO's could be examined from the temperature-dependent behavior of the ^{13}C NMR spectrum of $\text{Co}_2\text{Fe}_2(\text{CO})_{11}(\text{PPh})_2$ as first described below.

I. Structural dynamics of the heteronuclear Co_2Fe_2 cluster II

The eleven carbonyl ligands in the mixed Co_2Fe_2 cluster II were separated into three distinct sets by the examination of the ^{13}C { ^1H } NMR spectrum at low temperatures. Thus at -100°C , three ^{13}C resonances were cleanly resolved into singlets at δ 239, 212, and 198 in an integral ratio of 1/6/4, respectively. The low-field resonance at δ 239 was readily assigned to that of the bridging CO between the cobalt centers, and the high field resonance at δ 198 to the terminal CO's bound to the cobalt atoms. By comparison, the homonuclear tetracobalt



SCHEME 1

analog I at the same temperature showed two resonances at δ 238 and 204 with relative intensities of 1/4 for the pair of bridging CO's and the eight equivalent terminal CO's, respectively, for the cluster core possessing idealized D_{2h} symmetry [10]. Moreover the resonance at δ 212 for the carbonyls bound to iron in II compared with those previously observed at δ 215 and 210 in $\text{Fe}_4(\text{CO})_{11}(\text{PPh})_2$ and $\text{Fe}_2(\text{CO})_{12}(\text{PPh})_2$, respectively [11].

The temperature-dependent behavior of the ^{13}C NMR spectrum revealed that these carbonyl ligands undergo three distinct dynamic processes, as schematically illustrated in Scheme 1.

In order to accommodate the large range of temperature variation, a change of solvent was necessitated from 2-methyltetrahydrofuran/benzene- d_6 (4/1 vol/vol) at $T < 273$ K to toluene- d_8 at $T > 303$ K. All the temperature-dependent spectral changes described below were completely reversible.

(a) The ^{13}C resonance at δ 212 associated with the iron tricarbonyl moiety was unchanged between 173 and 218 K, which indicated that the rapid, localized equilibration of the three axial and radical CO's associated with the iron centers remained fast on the NMR time scale [12]. A similar phenomenon has been observed with both $\text{Fe}_4(\text{CO})_{11}(\text{PPh})_2$ and $\text{Fe}_4(\text{CO})_{12}(\text{PPh})_2$ in which the singlet resonances (vide supra) persisted down to 143 K. The facile three-fold scrambling within the $\text{Fe}(\text{CO})_3$ group has been observed in other systems [12,13]. The low-energy intramolecular process depicted by IIA in Scheme 1 was estimated to have an activation energy of no more than ~ 8 kcal mol $^{-1}$ (see Experimental section).

(b) As the temperature was raised from 200 K, the ^{13}C resonances at δ 239 and 198 in Fig. 1a began to broaden (Fig. 1b). At 273 K, the rapid terminal \leftrightarrow bridge exchange of the carbonyl groups on cobalt was observed as a broadened resonance at $\delta \sim 205$ (Fig. 1c), which coincided with the weighted-average of the chemical shifts of the ^{13}C resonances at δ 239 and 198. From the coalescence temperature T_c 273 K and the relevant chemical shifts, we estimated the activation energy for the exchange process to be ≈ 11.7 kcal mol $^{-1}$ (see Experimental section). This barrier was essentially the same as that recently measured for the terminal \leftrightarrow bridge carbonyl exchange in the analogous homonuclear tetracobalt cluster I [10]. Such a temperature-dependent behavior of the ^{13}C NMR spectra of both II and I was characteristic of a rapid interchange via a mutual exchange mechanism [14]. The

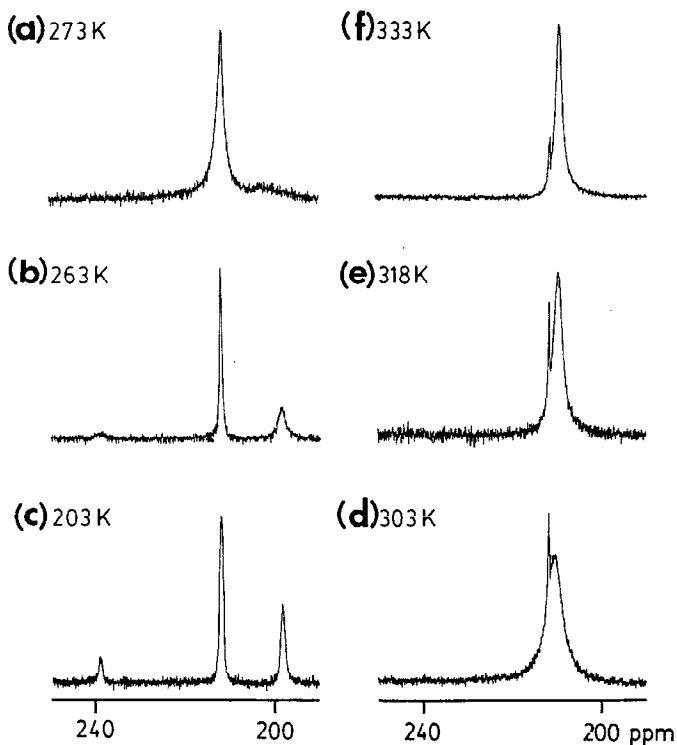


Fig. 1. Variable temperature $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Co}_2\text{Fe}_2(\text{CO})_{11}(\text{PPh})_2$ in 2-methyltetrahydrofuran/benzene- d_6 (203–273 K) and toluene- d_8 (303–333 K).

one-for-one, two center process of the type advocated by Lewis and coworkers for $\text{Cp}_2\text{Rh}_2(\text{CO})_3$ and $\text{Cp}_2\text{Rh}_2(\text{CO})_2[\text{P}(\text{O}^i\text{Pr})_3]$ [15] is included as IIB in Scheme 1.

(c) The carbonyl exchange process with highest energy (ΔG^\ddagger 15.7 kcal mol $^{-1}$) served to equilibrate all eleven carbons about the cluster polyhedron. Thus as the temperature was raised from 273 to 303 K, a new broad resonance appeared at δ 209 (Fig. 1d). It continued to sharpen and grow at the expense of the resonance at δ 212 as the temperature was raised to 318 K (Fig. 1e). Finally it became the dominant resonance at 333 K (Fig. 1f). The new resonance at δ 209 was in good agreement with the weighted-average of the chemical shifts obtained from the low-temperature ^{13}C NMR spectrum (vide supra). Owing to the slow decomposition of II at temperatures above 333 K, no attempt was made to examine the NMR spectra at higher temperatures. However from the trend observed in Figs. 1d–1f, we estimated T_c 348 K. This temperature-dependent behavior could arise from a rapid intramolecular carbonyl exchange among all the iron and cobalt centers, presumably by a series of bridge \leftrightarrow terminal exchanges including those between dissimilar metal centers (compare IIC in Scheme 1). However pending a quantitative kinetics study at high CO pressures, we cannot exclude the possibility of a dissociative mechanism for the exchange [16]. [Note that the ^{59}Co quadrupolar effects discourage a line-shape analysis [17].] Nonetheless these NMR studies have provided structural information of the mixed Co_2Fe_2 cluster relevant to the reductions described below.

TABLE 1

SPECTRAL PARAMETERS OF THE FORMYL DERIVATIVES $\text{Co}_2\text{Fe}_2(\text{CO})_{10}(\text{PPh})_2\text{CHO}^- \text{Li}^+$ AND $\text{Co}_4(\text{CO})_9(\text{PPh})_2\text{CHO}^- \text{Li}^+$

Spectrum	Co_2Fe_2 cluster	Co_4 cluster ^a
<i>¹H NMR</i> ^b		
formyl	11.24	13.40
aromatics	7.50	7.50
<i>¹³C{¹H} NMR</i> ^c		
formyl ($J(^{13}\text{C}-^1\text{H})$)	233 (161)	241 (150)
bridging carbonyl(s)	231	247, 220
terminal carbonyls		
Fe	216	-
Co	204, 202	206
<i>IR</i> ^d		
formyl	-	1575w
bridging carbonyl(s)	-	1847m
terminal carbonyls	2043m	2041s
	1999vs	2005vs
	1985vs	1991vs
	1955s	1980s
	1939s	-
	1887m	-

^a From ref. 5. ^b In THF/benzene-*d*₆ (4/1 vol/vol) with internal Me₄Si. ^c In 2-methyltetrahydrofuran/benzene-*d*₆, 4/1 vol/vol referenced to C₆D₆. ^d In THF.

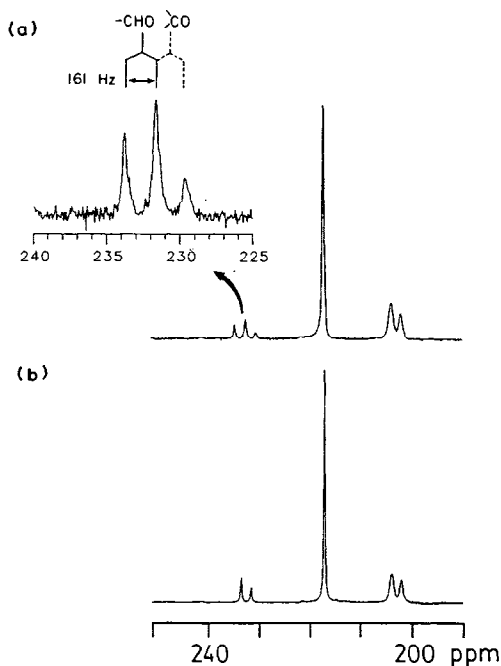
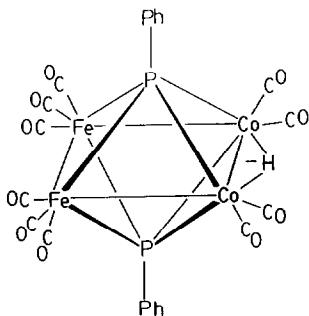


Fig. 2. (a) The ^{13}C {gated decoupled} NMR spectrum of $\text{Co}_2\text{Fe}_2(\text{CO})_{10}(\text{PPh})_2\text{CHO}^- \text{Li}^+$ in 2-methyltetrahydrofuran/benzene-*d*₆ at 183 K. The inset shows the low-field multiplet at higher gain ($\times 50$). (For assignment of the splitting pattern, see Experimental section.); (b) The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the same solution.

However above this temperature the solution darkened and the distinctive ^{13}C NMR spectrum in Fig. 2 began to disappear. It was completely replaced by a simple spectrum consisting of only two resonances at δ 220 and 206 in a 6/4 integral ratio at 183 K for the terminal CO's on iron and the terminal CO's on cobalt, respectively. The low-field resonance due to a bridging carbonyl was absent. In its place, the ^1H NMR spectrum showed a high-field resonance at δ -13.6 diagnostic of the presence of a bridging hydride [22]. The striking simplicity of the ^{13}C NMR spectrum suggested a Co_2Fe_2 cluster IV with mirror symmetry, as illustrated below.



(IV)

The observation of only three principal bands in the carbonyl stretching region ($1500\text{--}2000\text{ cm}^{-1}$) of the IR spectrum (Table 2) is consistent with the idealized C_{2v} symmetry of IV. As such, it is a close relative to the μ_2 -hydrido derivative of the homonuclear tetracobalt cluster, the structure of which has been established by X-ray crystallography [23]. Thus the comparison of the spectral parameters listed in Table 2 strongly supports the structure IV.

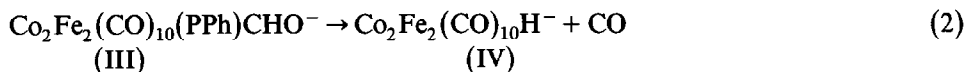
TABLE 2

SPECTRAL PARAMETERS OF THE μ_2 -HYDRIDE DERIVATIVES $\text{Co}_2\text{Fe}_2(\text{CO})_{10}(\text{PPh})_2\text{H}^- \text{Li}^+$ AND $\text{Co}_4(\text{CO})_9(\text{PPh})_2\text{H}^- \text{Li}^+$

Spectrum ^a	Co_2Fe_2 cluster	Co_4 cluster ^b
<i>¹H NMR</i>		
μ_2 -hydride	-13.63	-13.00
aromatics	7.52	7.40
<i>¹³C {¹H} NMR</i>		
bridging-carbonyl	-	256
terminal carbonyls		
Fe	221	-
Co	206	210
<i>IR</i>		
bridging carbonyl(s)		1831w
terminal carbonyls	1983vs	1988vs
	-	1973s
	1955s	1958s
	-	1936w
	1886m ^c	1887w

^a As in Table 1. ^b From ref. 5. ^c In addition to a very weak band at 2001 cm^{-1} .

The spectral changes accompanying the conversion of the formyl derivative $\text{Co}_2\text{Fe}_2(\text{CO})_{10}(\text{PPh})_2\text{CHO}^-$ (III) to the μ_2 -hydride IV indicated that the spontaneous decarbonylation occurred with complete conversion, i.e.,

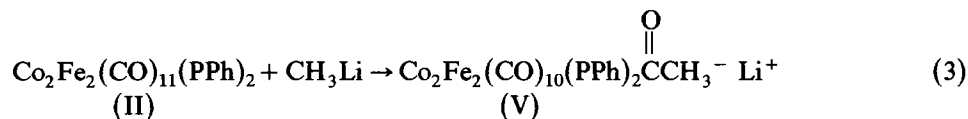


The same transformation of a formyl ligand to a μ_2 -hydride occurred in the homonuclear tetracobalt cluster. Although a quantitative comparison was not performed, we judged that the apparent half-life of III was approximately three times shorter than that of the tetracobalt analogue. The pathway by which this facile decarbonylation occurred was discussed separately [5].

IV. Interaction of the mixed Co_2Fe_2 cluster II with alkyllithium. Formation of the acyl derivative

The formyl derivative III represents the product of nucleophilic addition of an hydridic moiety to a carbonyl ligand of the mixed Co_2Fe_2 cluster II. Accordingly we examined the reactivity of II toward methyl lithium as a prototypical carbon-centered nucleophile.

The heteronuclear Co_2Fe_2 cluster II reacted readily with one equiv. of methyl lithium under an argon atmosphere at -78°C in much the same manner as it did with borohydride in eq. 1. The analogous acetyl derivative V formed by the nucleophilic addition of the methyl group to a coordinated CO, i.e.



was considerably more stable than the formyl analogue III. Thus the brown THF solutions of V persisted unchanged for days even at room temperature. The presence of the acetyl ligand was determined by the characteristic band at 1566 cm^{-1} . Otherwise the carbonyl stretching bands of II disappeared completely, and they

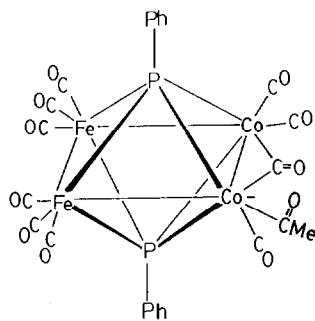
TABLE 3

SPECTRAL PARAMETERS OF THE ACETYL DERIVATIVES $\text{Co}_2\text{Fe}_2(\text{CO})_{10}(\text{PPh})_2\text{COCH}_3^- \text{Li}^+$ AND $\text{Co}_4(\text{CO})_9(\text{PPh})_2\text{COCH}_3^- \text{Li}^+$

Spectrum ^a	Co_2Fe_2 cluster	Co_4 cluster ^b
<i>¹³C {¹H} NMR</i>		
acetyl	254	291
bridging carbonyl(s)	238	247, 237
terminal carbonyls		
Fe	217	—
Co	205, 202	205
<i>IR</i>		
acetyl	1566vw	1574w
bridging carbonyl(s)	1835w	1840m
terminal carbonyls	2041m, 2000vs, 1970vs, 1928m, 1909m	2039m, 2000vs, 1988s, 1979s, 1961sh

^a As in Table 1. ^b From ref. 5.

were replaced by a different set which was consistently shifted to lower energy (see Table 3), as expected for an anionic cluster [18]. The ^{13}C $\{^1\text{H}\}$ NMR spectrum of V displayed a low-field resonance at δ 254 which was also diagnostic of an acetyl ligand [24]. The other ^{13}C resonances at δ 238, 217, 205 and 202 in an integral ratio of 1/6/2/1, respectively, were reminiscent of those in the acetyl derivative of the tetracobalt cluster, i.e. $\text{Co}_4(\text{CO})_9(\text{PPh})_2\text{COCH}_3\text{Li}^+$ (see Table 3). Accordingly they were assigned a seriatim to the $\mu_2\text{-CO}$, the terminal CO's on iron, the pair of terminal CO's on cobalt, and the lone terminal CO on the acetyl-substituted cobalt center as illustrated for V.



(V)

Indeed the similarity of the ^{13}C resonances in the NMR spectra and the carbonyl stretching pattern in the IR spectra of the formyl and acetyl derivatives III and V respectively, in Tables 1 and 3 support the general structural core which is common to both clusters. The persistence of the acetyl cluster V toward carbonyl de-insertion compared to its formyl analogue was presumed to be derived from its greater thermodynamic stability [19].

V. Comments on the structure and reactivity of the mixed Co_2Fe_2 cluster II

The members of the family of bicapped tetranuclear clusters containing cobalt and iron which include I and II bear strong structural similarity to each other. However such a resemblance could belie their unique chemical reactivities. For this reason, the mixed-metal cluster $\text{Co}_2\text{Fe}_2(\text{CO})_{11}(\text{PPh})_2$, which is simply the structural composite of the two halves of the homonuclear clusters $\text{Co}_4(\text{CO})_{10}(\text{PPh})_2$ and $\text{Fe}_4(\text{CO})_{12}(\text{PPh})_2$, provides an especially invaluable basis for intramolecular comparisons. For example, consider the fluxional behavior of the carbonyl ligands in these clusters by an examination of the temperature-dependent ^{13}C NMR spectra. The results in Fig. 1 show that the carbonyl groups in the two halves of the cluster, i.e., $\text{Fe}_2(\text{CO})_6$ and $\text{Co}_2(\text{CO})_5$, behave essentially independent of each other. Thus the low-energy interchanges described in Scheme 1 are first of $\text{Fe}_2(\text{CO})_6$ above (see IIA with $\Delta G_1^\ddagger < 8 \text{ kcal mol}^{-1}$) and then of $\text{Co}_2(\text{CO})_5$ alone (see IIB with $\Delta G_2^\ddagger \cong 12 \text{ kcal mol}^{-1}$). Only at relatively high temperatures (see IIC with $\Delta G^\ddagger \sim 16 \text{ kcal mol}^{-1}$) is there any indication of communication between the $\text{Fe}_2(\text{CO})_6$ and $\text{Co}_2(\text{CO})_5$ moieties in the mixed clusters II.

The chemical behavior of the mixed-metal cluster $\text{Co}_2\text{Fe}_2(\text{CO})_{11}(\text{PPh})_2$ (II) supports this dichotomy. Thus the reduction of only one of the carbonyl groups in II by borohydride underscores an highly site-selective nucleophilic attack on the

mixed metal cluster. Furthermore the lability of the resultant formyl derivative III leads selectively to a single μ_2 -hydride IV. The same site-selectivity is observed during nucleophilic addition of methyllithium to form the acetyl derivative V as the single adduct. The reasons for the specific choice of the terminal CO bound to a cobalt for site selectivity with both reagents remains to be established. Indeed the possibility of the reactivity of the other CO's by different types of reagents also remains for further explorations.

Experimental section

Materials

Dicobalt octacarbonyl and iron pentacarbonyl (Pressure Chemical) were used as received. Phenylphosphine was prepared from dichlorophenylphosphine (Pressure Chemical) [25]. $\text{Co}_2\text{Fe}_2(\text{CO})_{11}(\text{PPh})_2$ was prepared according to the procedure described by Vahrenkamp and Wucherer [6]. Lithium triethylborohydride (1.0 M in THF from Aldrich) was used as received. Methyllithium (1.2 M in Et_2O from Aldrich) was assayed by titration with diphenylacetic acid prior to use [26].

All the reactions were conducted under an atmosphere of dry argon using Schlenk techniques [27]. 2-Methyltetrahydrofuran, THF, benzene, and hexane were distilled from sodiobenzophenone and stored under an argon atmosphere. The deuterated solvents for use in the NMR studies were used as received (Merck) and degassed by repeated freeze-pump-thaw cycles. Chromium(III) acetylacetonate was added as a shiftless relaxation agent in ~ 0.03 M concentration for all ^{13}C NMR studies [28]. The isotopically enriched carbon monoxide (99% ^{13}C) was obtained from Mound Laboratory, Monsanto Research Corp.

Formation of $\text{Co}_2\text{Fe}_2(\text{CO})_{10}(\text{PPh})_2\text{CHO}^- \text{Li}^+$

To 0.075 g (0.10 mmol) of $\text{Co}_2\text{Fe}_2(\text{CO})_{11}(\text{PPh})_2$ in 6 ml of THF at -78°C was added 0.1 ml of a 1.0 M solution of LiEt_3BH in THF. The suspension became homogeneous, and the color changed from brown-red to brown as the formyl cluster formed. The formyl cluster was not isolated, but characterized spectroscopically as follows. IR (THF, sampled rapidly at -78°C): $\nu(\text{CO})$ 2043m, 1999.0vs, 1985vs, 1955s, 1939s, 1887m cm^{-1} . ^{13}C NMR [2-methyltetrahydrofuran/benzene- d_6 (4/1 vol/vol) -90°C] δ : 232.8 (1, s, formyl, $J(\text{H}-\text{C})$ 161 Hz), 229.9 (1C, s, μ_2 -CO), 216.4 (6C, s, terminal Fe(CO)), 203.6 (2C, s, terminal Co(CO)), 201.9 (1C, s, terminal Co(CO)). ^1H NMR [THF/benzene- d_6 (4/1 vol/vol) -55°C] δ : 11.24 (1H, formyl), 7.50 (10H, b, aromatic).

Formation of $\text{Co}_2\text{Fe}_2(\text{CO})_{10}(\text{PPh})_2[\mu_2\text{-H}]^- \text{Li}^+$

The synthesis of the μ_2 -hydride cluster $\text{Co}_2\text{Fe}_2(\text{CO})_{10}(\text{PPh})_2(\mu_2\text{-H})^-$ was carried out either by (a) reduction of II at low temperature followed by warming the resultant solution to room temperature, or (b) direct reduction of II at room temperature. Both methods afforded the hydride cluster in essentially quantitative yields as determined from their ^1H NMR and IR spectra. The latter procedure is described in detail as follows. To 0.04 g (0.05 mmol) of $\text{Co}_2\text{Fe}_2(\text{CO})_{11}(\text{PPh})_2$ and 5 ml THF at room temperature was added 0.055 ml of a 1.0 M solution of LiEt_3BH in THF. The reduction was essentially instantaneous, as evidenced by the rapid gas evolution (CO) and the color change from red-brown to brown. The hydride cluster

appeared to be stable indefinitely at room temperature under an argon atmosphere. Single crystals of the hydride cluster were grown from a mixture of THF and hexane. Unfortunately they were either too small or of poor crystallographic quality for further X-ray study. The identity of the cluster was deduced from the following spectroscopic characterizations. IR(THF); $\nu(\text{CO})$ 2002s, sh, 1985vs, b, 1954vs, b, 1886vs, b. ^{13}C NMR [2-methyltetrahydrofuran/benzene- d_6 (4/1 vol/vol), -90°C] δ : 220.7 (6C, s, terminal Fe(CO)), 205.7 (4C, s, terminal Co(CO)). ^1H NMR [2-methyltetrahydrofuran/benzene- d_6 (4/1 vol/vol) 25°C] δ : -13.63 (1H, b, μ_2 -hydride), 7.52 (10H, b, aromatic). Since these properties of $\text{Co}_2\text{Fe}_2(\text{CO})_{10}(\text{PPh})_2[\mu_2\text{-H}]^- \text{Li}^+$ were entirely consistent with those of the tetracobalt analogue $\text{Co}_4(\text{CO})_9(\text{PPh})_2[\mu_2\text{-H}]^- \text{H}^+$ which has been thoroughly characterized [5], elemental analysis was not deemed necessary to establish its structure.

Decomposition of $\text{Co}_2\text{Fe}_2(\text{CO})_{10}(\text{PPh})_2\text{CHO}^- \text{Li}^+$

To 0.08 g (0.11 mol) of $\text{Fe}_2\text{Co}_2(\text{CO})_{11}(\text{PPh})_2$ in 10 ml of THF at -78°C was added a stoichiometric amount of a 1.0 M solution of LiEt_3BH in THF. The reaction turned brown indicative of formyl formation. The stability of the formyl cluster IV was evaluated by withdrawing an aliquot of the solution at -78°C and examining the IR spectrum of the solution as it warmed up to room temperature. The complete conversion to the μ_2 -hydride cluster $\text{Co}_2\text{Fe}_2(\text{CO})_{10}(\text{PPh})_2\text{CHO}^-$ occurred after approximately 5 min in the IR cavity. No other carbonyl bands for other organometallic products were observed in the IR spectrum.

Formation of $\text{Co}_2\text{Fe}_2(\text{CO})_{10}(\text{PPh})_2\text{COCH}_3^- \text{Li}^+$

To 0.075 g (0.1 mmol) of $\text{Co}_2\text{Fe}_2(\text{CO})_{11}(\text{PPh})_2$ in 6 ml of THF at -78°C was added 0.083 ml of a 1.2 M solution of MeLi in Et_2O . The reaction was instantaneous as judged by the change in color of the suspension from red-brown to brown. The acetyl derivative was thermally persistent at room temperature for at least a week under an argon atmosphere. It was characterized spectroscopically as follows. IR (THF, 25°C): $\nu(\text{CO})$ 2041m, 2000.4vs, 1970s, 1909w, 1835w,b, 1565 vw,b cm^{-1} . ^{13}C NMR [2-methyltetrahydrofuran/benzene- d_6 (4/1 vol/vol) -90°C] δ : 253.8 (1C, s, acetyl), 238.3 (1C, s, μ_2 -carbonyl), 216.6 (6C, s, terminal Fe(CO)), 205.4 (2C, s, terminal Co(CO)), 202.1 (1C, s, terminal Co(CO)). Since these properties of $\text{Co}_2\text{Fe}_2(\text{CO})_{10}(\text{PPh})_2\text{COCH}_3^- \text{Li}^+$ were entirely consistent with those of the tetracobalt analogue $\text{Co}_4(\text{CO})_9(\text{PPh})_2(\text{COCH}_3)^- \text{Li}^+$ which has been thoroughly characterized [5], elemental analysis was not deemed necessary to establish its structure.

Instrumentation

Infrared spectra were recorded in the linear absorbance mode on a Nicolet 10DX FT spectrometer in either 0.1 or 1.0 mm NaCl cells. ^1H NMR spectra were recorded on a JEOL FX-90Q spectrometer at 89.6 MHz. The ^{13}C NMR spectra were obtained at 75.5 MHz on a Nicolet NT-300 wide-bore spectrometer.

Isotopic enrichment of $\text{Fe}_2\text{Co}_2(\text{CO})_{11}(\text{PPh})_2$ with ^{13}CO

To 0.2 g (0.26 mmol) of $\text{Fe}_2\text{Co}_2(\text{CO})_{11}(\text{PPh})_2$ contained in a 500 ml round bottom flask was added 20 ml of benzene. The solution was cooled to -78°C and the vessel evacuated on a gas manifold/vacuum line. Subsequently, an atmosphere

of ^{13}C O (150 mm) was introduced into the reaction vessel. The mixture was stirred for 72 h at room temperature. IR analysis indicated a statistical enrichment of ^{13}C O had occurred to the extent of 30%. The degree of ^{13}C O enrichment was easily assessed by comparing the relative area of the μ_2 -carbonyl band of the natural abundance cluster with that of the ^{13}C O enriched cluster.

Kinetic studies

The activation energies for carbonyl scrambling in $\text{Co}_2\text{Fe}_2(\text{CO})_{11}(\text{PPh})_2$ were calculated according to the procedure given by Shanani-Atidi and Bar-Eli [29,30]. The three-fold carbonyl scrambling about the $\text{Fe}(\text{CO})_3$ moieties was assumed to reflect intramolecular axial and radial carbonyl interchange. The coalescence temperature (T_c) was taken to be 173 K (the lowest temperature examined). The chemical shift difference of 75 Hz was assumed for the axial and radical iron carbonyls. The exchanging carbonyls were then treated as unequal doublet capable of undergoing intramolecular exchange. This led to an upper limit for the activation energy for exchange of $\sim 8 \text{ kcal mol}^{-1}$.

For the terminal-bridge carbonyl exchange involving the CO's bound to the two cobalt atoms, the resonances were treated as unequal doublets capable of undergoing intramolecular carbonyl exchange. The relative populations of the carbonyls were obtained from the integration of the limiting ^{13}C NMR spectrum. A variable-temperature ^{13}C NMR study established the temperature of coalescence (T_c) to be 273 K. At this temperature the observed chemical shift was in good agreement with the weighted-average chemical shifts obtained from the slow-exchange spectrum. We have assumed that this behavior represented complete, intramolecular carbonyl exchange about the two cobalt sites. Through the use of the relative populations of exchanging carbonyls and the coalescence temperature, the activation energy for intramolecular carbonyl scrambling was calculated with the aid of the modified Eyring equation [31].

The high-energy carbonyl exchange process involving all the cluster carbonyls was calculated by a similar procedure by assuming complete intramolecular carbonyl scrambling about the cluster polyhedron. Note the slight variation in the linewidths in Fig. 1 resulting from the change in solvent [32].

Temperature-dependent ^{13}C NMR for $\text{Co}_4(\text{CO})_{10}(\text{PPh})_2$

At the slow exchange limit of 173 K, $\text{Co}_4(\text{CO})_{10}(\text{PPh})_2$ displayed two ^{13}C carbonyl resonances at ~ 238 and 204 with a relative intensity of 1/4. These resonances have been assigned to the pair of bridging CO's and the eight terminal CO's respectively, as expected for $\text{Co}_4(\text{CO})_{10}(\text{PPh})_2$ which possesses idealized D_{2h} symmetry. As the temperature was raised, both resonances broadened more or less simultaneously and merged to afford a single resonance at 273 K. The observed chemical shift of the broadened resonance at $\delta 208$ was in good agreement with the weighted average chemical shift obtained from the slow exchange spectrum. The energy of activation for terminal-bridge carbonyl exchange in $\text{Co}_4(\text{CO})_{10}(\text{PPh})_2$ was calculated according to the procedure given by Shanani-Atidi and Bar-Eli [29]. Here the resonances due to bridging carbonyls and terminal carbonyls were treated as unequal doublets capable of undergoing intramolecular exchange. From the relative populations of the carbonyls obtained from the integration of the slow-exchange spectrum together with the knowledge of the coalescence temperature obtained from

a variable temperature ^{13}C NMR study, the energy of activation for terminal-bridge carbonyl exchange was readily calculated. We have assumed that this temperature-dependent behavior represented complete, intramolecular carbonyl scrambling about the cluster polyhedron.

Measurement of the ^1H coupling constant of the formyl ligand in III

To obtain the proton-carbon coupling constant for the formyl moiety in III, the ^{13}C NMR spectrum of $\text{Co}_2\text{Fe}_2(\text{CO})_{10}(\text{PPh})_2\text{CHO}^-\text{Li}^+$ (Fig. 2a) at 183 K was run in the gated decoupled mode using the available software program equipped with the NT-300 NMR spectrometer. Here the proton decoupler is gated off at the time of the initial observe pulse in the ^{13}C observation channel. This affords a proton-coupled ^{13}C NMR spectrum with all the signal intensity gain resulting from nuclear Overhauser enhancement [33]. This experiment yielded a $J(\text{C}-\text{H})$ value of 161 Hz for the formyl moiety in addition to the observation of a formyl-proton/bridge-carbonyl coupling. The magnitude of coupling appeared to be on the order of that observed for the formyl moiety (compare Fig. 2a).

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