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Nucleophilic Discrimination in a Mixed-Metal Phosphinidene-Capped Cluster. Formation of Phosphido and Cobalt–Acyl Derivatives

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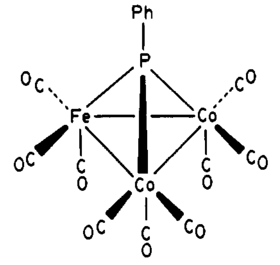
The reaction of the mixed-metal tetrahedrane cluster $FeCo_2(CO)_9(\mu_3\text{-}PPh)$ (**1**) with various reducing agents has been examined in THF. $[Et_3BH][Li]$ and $[(s\text{-}Bu)_3BH][K]$ react with **1** at −78 °C to give the thermally unstable cluster $[FeCo_2(CO)_9(\mu_2\text{-}PPhH)^-]$ (**2**$^-$) as a result of hydride attack at the μ_3-phosphinidene capping ligand and heterolytic scission of a Co–P bond. At −90 °C, ^{13}C NMR analysis of **2**$^-$ reveals a static structure with no intermetallic exchange of the ancillary CO groups. Whereas the $Co(CO)_3$ groups display a single CO resonances due to rapid 3-fold carbonyl scrambling, the $Fe(CO)_3$ group bound by the μ_2-phosphido ligand exhibits three resolvable carbonyl resonances, indicating hindered 3-fold carbonyl scrambling about the iron center. Reduction of **1** with MeLi is suggested to proceed at a cobalt-bound CO group, giving the acyl cluster $[FeCo_2(CO)_8\{C(O)Me\}(\mu_3\text{-}PPh)^-]$ (**3**$^-$). IR analysis reveals a 51:49 mixture of solvent-separated and acyl oxygen–$[Li^+]$ contact ion pairs, respectively at −70 °C. Use of the Grignard reagents *t*-BuMgCl or MeMgBr gives the 49-electron cluster $[FeCo_2(CO)_9(\mu_3\text{-}PPh)^{\bullet-}]$. [MeO][Li] reacts with **1** at a cobalt-bound CO group at −78 °C to furnish the methoxycarbonyl cluster $[FeCo_2(CO)_8\{C(O)OMe\}(\mu_3\text{-}PPh)^-]$ (**5**$^-$), which is shown by IR analysis to exist exclusively as an ester oxygen–$[Li^+]$ contact ion pair. ^{31}P NMR analysis suggests that **5**$^-$ rearranges to the μ_2-methoxyphosphido cluster $[FeCo_2(CO)_9(\mu_2\text{-}PPhOMe)^-]$ (**8**$^-$) at ambient temperature as the major product. Treatment of **1** with methanolic $[Et_4N][OH]$ in THF at −70 °C gives the corresponding methoxycarbonyl and hydroxycarbonyl clusters in a 55:45 ratio, respectively, as determined by IR band-shape analysis. The reactivity and stability of these new anionic clusters are discussed.

Introduction

Synthetic routes and reactivity patterns of polynuclear metal clusters are not as well understood in comparison to mononuclear organometallic complexes.[1] Interest in polynuclear metal clusters derives from their ability to function as working models for metal-containing proteins and nitrogenases,[2] redox transfer catalysts,[3] theoretical calculations related to band structure,[4] and multisite substrate activation as related to heterogeneous metal catalysis.[6]

Of the many diverse types of polynuclear compounds known, mixed-metal phosphinidene-capped clusters represent a cluster subclass that has received much recent attention.[7] The low symmetry associated with these clusters facilitates mechanistic studies that deal with heterometallic metal–metal bond reactivity and site selectivity in ligand substitution processes.[8,9] For example, Huttner and co-workers were the first to demonstrate that P-ligands reversibly add to the iron center in the tetrahedral cluster $MnFe_2(CO)_8Cp(\mu_3\text{-}PPh)$, via cleavage of the Mn–Fe bond, to give the corresponding arachno cluster $MnFe_2(CO)_8(PR_3)Cp(\mu_3\text{-}PPh)$.[10] Similar addition/elimination reactions have been reported by Vahrenkamp et al. for the clusters $FeCo_2(CO)_9(\mu_3\text{-}PMe)$ and $FeCoW(CO)_8Cp(\mu_3\text{-}PMe)$.[11,12] Site-specific substitutions need not involve heterometallic bond cleavage, as shown by the work of Ohst and Kochi using the six-vertex closo cluster $Fe_3Rh(CO)_8Cp^*(\mu_4\text{-}PPh)_2$.[13] In that study, the unique iron opposite the Cp*Rh center was shown to reversibly add and eliminate CO depending on the cluster's redox state.

Here we report results on the reduction pathways available to the phosphinidene-capped cluster $FeCo_2(CO)_9(\mu_3\text{-}PPh)$ (**1**).[14] To



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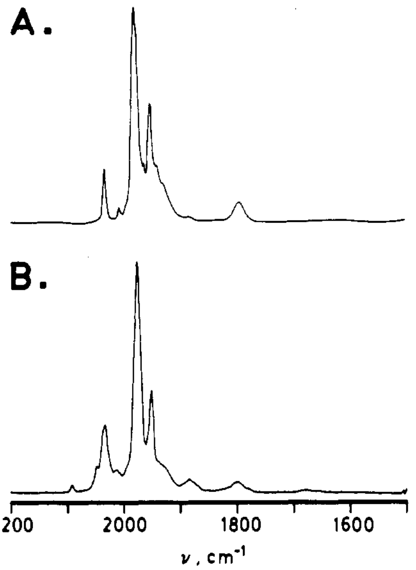


Figure 1. Infrared spectra of the carbonyl region for (A) $[FeCo_2(CO)_9(\mu_2\text{-}PPhH)^-]$ at −78 °C and (B) $[FeCo_2(CO)_9(\mu_2\text{-}PPhOMe)^-]$ at −5 °C. Both spectra were recorded in THF.

our knowledge, these results provide the first detailed study on the reactivity of a tetrahedrane cluster toward anionic two-electron donor ligands. The impetus for this study stems from an earlier report describing the catalytic activity of **1** in 1-pentene and styrene hydroformylations[15] along with a recent paper dealing with the reactivity and stability of the structurally similar cluster $[Co_3(CO)_8(CHO)(\mu_3\text{-}CPh)^-]$, the product of hydride attack at a terminal cobalt–carbonyl group.[16] Besides reactivity comparisons made between **1** and the tricobalt clusters $Co_3(CO)_9(\mu_3\text{-}CR)$, the chemistry of **1** is also contrasted with the mixed-metal cluster $Fe_2Co_2(CO)_{11}(\mu_4\text{-}PPh)_2$, which has been shown to react with anionic nucleophiles exclusively at a terminal cobalt–carbonyl group.[17]

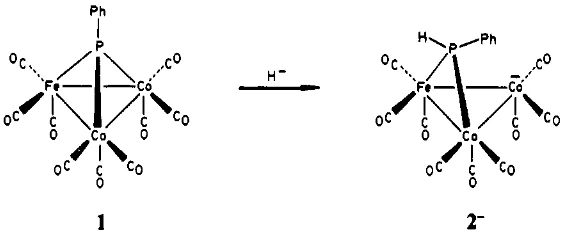
Results

The reactivity of the tetrahedrane cluster $FeCo_2(CO)_9(\mu_3\text{-}PPh)$ with various anionic nucleophiles is summarized in eqs 1–4 with spectroscopic data presented in Table I and Figures 1–3. Studies dealing with the reactivity and attempted functionalization of the new phosphide and CO-reduced clusters derived from **1** are discussed. These results are presented in the appropriate sections that follow.

Discussion

I. Reaction of 1 with Hydrides. Formation of the Phosphido-Bridged Cluster $[FeCo_2(CO)_9(\mu_2\text{-}PPhH)^-]$. Treatment of a red-brown solution of **1** in THF with 1.0 mol equiv of $[Et_3BH][Li]$ at −70 °C immediately affords a dark brown solution containing $[FeCo_2(CO)_9(\mu_2\text{-}PPhH)^-]$ ($\mathbf{2}^-$) as the sole product on the basis of in situ IR and NMR analyses. The low-temperature IR spectrum of $\mathbf{2}^-$ revealed carbonyl stretching bands at 2037 (m), 2011 (w), 1985 (vs), 1967 (m), 1955 (s), 1944 (m), 1930 (sh), and 1799 cm⁻¹ (w, br) (see Figure 1A). These ν(CO) bands are shifted to lower frequency in comparison to the parent cluster, supporting the ascription of $\mathbf{2}^-$ as an anionic cluster. No formyl ν(CO) band was observed in the 1520–1630-cm⁻¹ region of the IR spectrum,[18] which strongly suggests that hydride attack on a terminal CO group is an unimportant pathway. Use of $[(s\text{-}Bu)_3BH][K]$ as the reducing agent yielded an IR spectrum that was identical with that obtained with $[Et_3BH][Li]$. The IR spectral similarity of $\mathbf{2}^-$ using these two different trialkylborohydrides indicates that $\mathbf{2}^-$ exists as a solvent-separated ion pair (SSIP), a feature easily confirmed through the addition of HMPA to a THF solution of $\mathbf{2}^-$.[19]

The unequivocal identity of $\mathbf{2}^-$ was ascertained by using low-temperature $^{31}P\{^1H\}$ NMR spectroscopy. The $^{31}P\{^1H\}$ resonance at **1** at −80 °C in THF/benzene-d_6 (5:1, v/v) appears as a singlet at δ 429.3, consistent with a μ_3-PPh group ligating the triangular face of the $FeCo_2$ cluster. This resonance is replaced by a singlet at δ 143.2 (d, J_{P-H} = 356 Hz) when treated with $[Et_3BH][Li]$. The observed ^{31}P doublet, which was obtained from a gated-decoupled spectrum, clearly establishes the attachment of the hydride at the μ_3-phosphinidene group in **1**, with further support derived from the high-field shift of the ^{31}P resonance that is typical for μ_2-phosphido moieties.[20-24] Equation 1 depicts the proposed course of this reaction.



(1)

1 $\mathbf{2}^-$

Hydride accession in **1** is depicted to occur anti with respect to the heterolytically cleaved Co–P bond. This stereochemistry is consistent with the course of hydride addition reported for the nido cluster $Fe_3(CO)_9(\mu_3\text{-}PPh)_2$.[20] At low temperature hydride addition was shown to give $[Fe_3(CO)_9(\mu_3\text{-}PPh)(\mu_2\text{-}PPhH)^-]$, as a result of cleavage of the Fe_{bas}–P bond (bas = basal). These reactions bear resemblance to S_N2 reactions, where the entering and leaving groups are oriented anti or trans to each other. A formal inversion of the phosphorus center requires the phenyl group to adopt a position directly over the face of the cluster.[23h] It is now well documented that phosphido and phosphinidene tethering ligands are not, as a rule, chemically inert, especially under reducing conditions. In contrast to the many reports involving anion-induced cleavage of μ_2-phosphido–metal bonds,[22,23] compounds possessing μ_3-phosphinidene ligands have remained relatively unexplored. With the exception of two reports dealing with the transformation of a phosphinidene → phosphido linkage in homonuclear clusters,[20,24] we believe this study represents the first example of a hydride-induced μ_3-PPh → μ_2-PPhH conversion in a heterometallic cluster.

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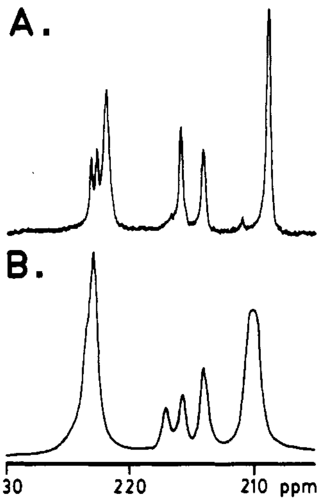

Figure 2. $^{13}C\{^1H\}$ NMR spectra of (A) $[FeCo_2(CO)_9(\mu_2\text{-}PPhH)^-]$ and (B) $[FeCo_2(CO)_8\{C(O)OMe\}(\mu_3\text{-}PPh)^-]$. Both spectra were recorded in 2-MeTHF/benzene-d_6 (5:1) at −90 °C.

The slow-exchange ^{13}C NMR spectrum of a ^{13}CO-enriched sample of **1** (−80 °C; toluene-d_8) exhibits three carbonyl resonances at δ 218.7, 211.6, and 201.0 in an integral ratio of 1:2:6, respectively. Rapid 3-fold carbonyl scrambling renders all the Co–CO groups equivalent and readily assignable to the highest field resonance, while frozen Fe–CO motion allows for the observation of distinct axial and equatorial CO groups.[25] The $^{13}C\{^1H\}$ NMR spectrum of $\mathbf{2}^-$, prepared from ^{13}CO-enriched **1**, reveals five carbonyl resonances at −90 °C in agreement with the proposed structure of $\mathbf{2}^-$. Figure 2 shows the low-temperature ^{13}C NMR spectrum of $\mathbf{2}^-$. The resonances at δ 208.6 and 221.8, both of which integrate for three CO groups, are assigned to the neutral and anionic $Co(CO)_3$ centers, respectively. Localized $Co(CO)_3$ rotation is rapid at both cobalt centers, as observed in all structurally similar tetrahedrane clusters containing $Co(CO)_3$ vertices.[25,26] Two one-carbon resonances at δ 214.0 and 215.8 derive from the unique equatorial CO groups of the $Fe(CO)_3$ moiety. No attempt has been made to specifically assign these resonances. The doublet resonance (1 CO) centered at δ 222.9 (J_{P-C} = 18.5 Hz) is ascribed to the axial Fe–CO group, on the basis of the near trans diaxial relationship that is expected for the μ_2-phosphido and axial Fe–CO groups.[20]

II. Synthesis and Characterization of the Acyl Cluster $[FeCo_2(CO)_8\{C(O)Me\}(\mu_3\text{-}PPh)^-]$. **1** reacts with 1 equiv of MeLi in THF to give a black solution containing the acyl cluster $[FeCo_2(CO)_8\{C(O)Me\}(\mu_3\text{-}PPh)^-]$ ($\mathbf{3}^-$). At −70 °C the IR spectrum of $\mathbf{3}^-$ displayed terminal ν(CO) bands at 2043 (m), 2032 (w), 1976 (vs), 1966 (sh), 1949 (m), 1920 (b), and 1793 cm^{-1} (w) in addition two weak acyl ν(CO) bands at 1648 and 1595 cm^{-1}, as shown in Figure 3A. The ratio of these acyl bands was determined via IR band-shape analysis, which revealed a 51:49 ratio, respectively. When ~10 mol equiv of 12-crown-4 was added to $\mathbf{3}^-$, the latter acyl band disappeared completely while the former band grew in intensity. This behavior is indicative of an anionic metal–acyl moiety that exists as solvent-separated and acyl oxygen–$[Li^+]$ contact ion pairs (CIP).[7,27,28] Disruption of the acyl oxygen–$[Li^+]$ CIPs by 12-crown-4 is a well-established phenomen that allows for the unambiguous assignment of both types of ion pairs present in solution.[19] The observation of such ion pairs in polynuclear $\mathbf{3}^-$ is rare[29] in comparison to the many examples of ion pairing in mononuclear complexes.[19] Presumably, the dearth of data on cluster CIPs results from a greater electron delocalization of the anionic charge over the cluster's polyhedral core versus mononuclear complexes, which is in keeping with the electron reservoir properties of polynuclear clusters.[30] The IR data of the various clusters are summarized in Table I.

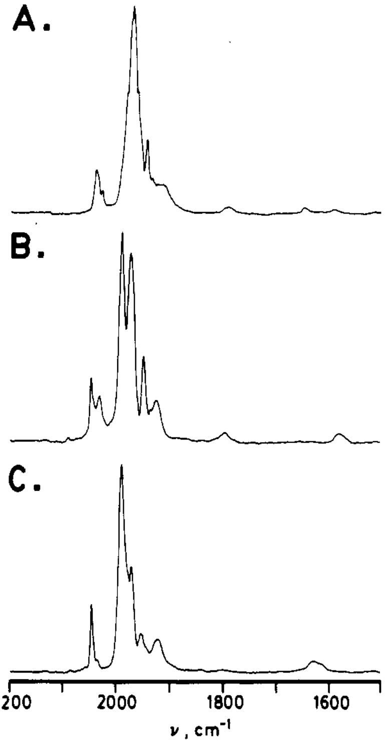

Figure 3. Infrared spectra of the carbonyl region for (A) $[FeCo_2(CO)_8\{C(O)Me\}(\mu_3\text{-}PPh)^-]$, (B) $[FeCo_2(CO)_8\{C(O)OMe\}(\mu_3\text{-}PPh)^-]$, and (C) $[FeCo_2(CO)_8\{C(O)OMe\}(\mu_3\text{-}PPh)^-]$ and $[FeCo_2(CO)_8(CO_2H)(\mu_3\text{-}PPh)^-]$. All spectra were recorded in THF at −70 °C.

A single broad $^{31}P\{^1H\}$ NMR resonance at δ 405.7 was observed for $\mathbf{3}^-$ at −78 °C, consistent with the presence of a μ_3-PPh group. In order to define the site of the acyl group, the $^{13}C\{^1H\}$ NMR spectrum of $\mathbf{3}^-$, prepared from ^{13}CO-enriched **1** and MeLi, was examined. Unfortunately, the carbonyl resonances were extremely broad at −90 °C, preventing a meaningful interpretation. This behavior most likely results from rapid carbonyl exchange about the cluster polyhedron, as has been observed with other $FeCo_2$ tetrahedrane clusters.[31] Support for this premise is found with the methoxycarbonyl cluster $\mathbf{5}^-$, which also displays very broad but discernible ^{13}C NMR resonances (vide infra).

At this time we cannot unambiguously assign the site of the acyl moiety on the basis of the spectroscopic data. However, we note that the bicapped cluster $Fe_2Co_2(CO)_{11}(\mu_4\text{-}PPh)_2$ has been shown to react with hydrides and MeLi, yielding anionic Co–CHO and Co–C(O)Me clusters, respectively.[17] These reports lead us to propose a cobalt-bound acyl group as shown in eq 2.[32]

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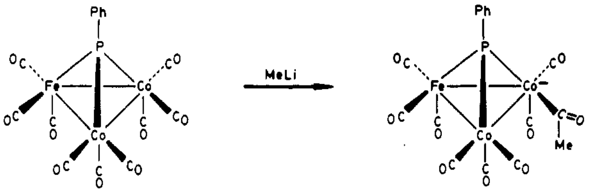
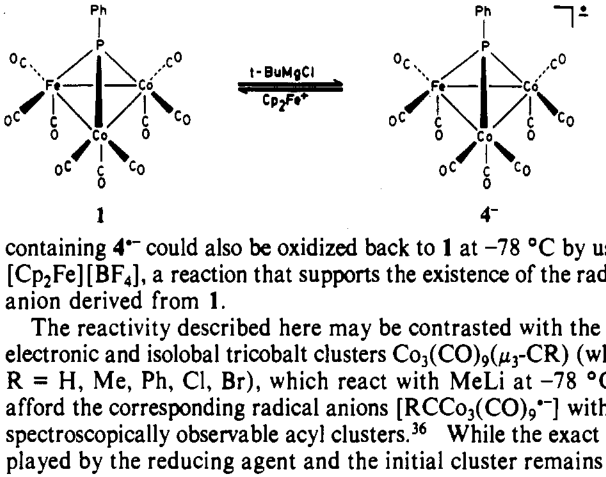
[32] We have depicted an equatorially disposed acyl group for convenience. The distinction between equatorial versus axial substitution is clouded due to the presumed presence of rapid, localized carbonyl scrambling at the anionic cobalt center.



(2)

1 **3**$^-$

III. Reaction of 1 with Grignard Reagents. When **1** (in THF) is treated with a slight excess of *t*-BuMgCl at −78 °C, a green solution is immediately obtained. IR analysis at −70 °C reveals the complete conversion to a compound with ν(CO) bands that are shifted to lower frequency relative to the parent cluster, as shown in Table I. The same product was also seen when MeMgBr (>3.5 mol equiv) was used, whereas no reaction was discerned at −78 °C when Me_3SiCH_2MgCl was used (5.0 mol equiv). Moreover, added $[CF_3SO_3][Li]$ or $[Ph_4B][Na]$ did not affect the course of this reaction. The lack of an observable acyl band(s) and the grossly different symmetry associated with the ν(CO) bands of this green material compared to the spectra of **2**$^-$ and **3**$^-$ argue against the attack of the Grignard reagent at the μ_3-PPh capping ligand or a terminal CO group. Since Grignard and organolithium reagents have been reported to function as single-electron-transfer reagents in other organometallic complexes,[33,34] we independently synthesized $[FeCo_2(CO)_9(\mu_3\text{-PPh})^{\bullet -}]$ (**4**$^{\bullet-}$) from **1** and Cp_2Co and examined it by IR analysis.[35] All of these IR spectra were identical within experimental error, which serves to establish the course of the reaction as shown in eq 3. Samples containing **4**$^{\bullet-}$ could also be oxidized back to **1** at −78 °C by using $[Cp_2Fe][BF_4]$, a reaction that supports the existence of the radical anion derived from **1**.



(3)

1 **4**$^-$

The reactivity described here may be contrasted with the isoelectronic and isolobal tricobalt clusters $Co_3(CO)_9(\mu_3\text{-CR})$ (where R = H, Me, Ph, Cl, Br), which react with MeLi at −78 °C to afford the corresponding radical anions $[RCCo_3(CO)_9{}^{\bullet -}]$ without spectroscopically observable acyl clusters.[36] While the exact role played by the reducing agent and the initial cluster remains unknown at this time, subtle differences in these two variables are undoubtedly responsible for determining the preference for the 1e$^-$ (set) or 2e$^-$ (polar) pathway.

The formation of **4**$^{\bullet-}$ from **1** and *t*-BuMgCl (or MeMgBr) may be viewed as arising from an either outer- or inner-sphere electron-transfer mechanism.[37] We favor the latter manifold, which presumably proceeds through the intimate complexation of **1** and RMgX in much the same fashion as reported for the reaction of ketones with Grignard reagents.[38] Here Grignard coordination at a carbonyl oxygen would be required prior to the formal electron-transfer step. Such a sequence is akin to the electron-transfer reactions reported for donor–acceptor complexes.[39] Alternatively, if the acyl cluster $[FeCo_2(CO)_8\{C(O)R\}(\mu_3\text{-PPh})^-]$ (where R = Me, *t*-Bu), formed by RMgX attack on a terminal CO group, underwent a homolytic C–C (acyl–R) bond cleavage, **4**$^{\bullet-}$ and R$^\bullet$ would be produced. Similar C–H formyl bond cleavages have been suggested as a route to paramagnetic clusters, provided that the accompanying R$^\bullet$ (or H$^\bullet$) is efficiently extricated from the reaction by common radical deactivation steps.[16,28,40] However, this pathway is considered umimportant given the characterization and stability (vide infra) of the acyl cluster **3**$^-$. Finally, the small scale of these reactions has prevented the characterization and assessment of the fate of the presumed organic radicals. Dimerization and/or hydrogen atom abstraction

Table I. Infrared Spectral Data for the Carbonyl Regions of **1** and Related Anionic Clusters[a]

$FeCo_2(CO)_9(\mu_3\text{-PPh})$ (**1**)[b]	2101 (s), 2059 (vs), 2048 (vs), 1981 (s), 1969 (s)
$FeCo_2(CO)_9(\mu_3\text{-PPh})$ (**1**)	2093 (s), 2050 (vs), 2038 (vs), 2030 (sh), 2014 (m), 1966 (m)
$[FeCo_2(CO)_9(\mu_2\text{-PPhH})^-]$ (**2**$^-$)	2037 (m), 2011 (w), 1985 (vs), 1967 (m), 1955 (s), 1944 (m), 1930 (sh), 1799 (w, br)
$[FeCo_2(CO)_9(\mu_2\text{-PPhH})^-]$ (**2**$^-$)[c]	2040 (m), 1985 (vs), 1956 (sh), 1778 (w, b), 1724 (vw, b)
$[FeCo_2(CO)_8\{C(O)Me\}(\mu_3\text{-PPh})^-]$ (**3**[Li])	2043 (m), 2032 (w), 1976 (vs), 1966 (sh), 1949 (m), 1920 (b), 1793 (w), 1648 (w, acyl-SSIP), 1595 (w, acyl-CIP)
$[FeCo_2(CO)_8\{C(O)Me\}(\mu_3\text{-PPh})^-]$ (**3**$^-$)[d]	2041 (m), 2032 (w), 1978 (vs), 1961 (sh), 1949 (m), 1920 (b), 1793 (w), 1648 (w, acyl-SSIP)
$[FeCo_2(CO)_9(\mu_3\text{-PPh})^{\bullet -}]$ (**4**[Cp_2Co])[e]	2038 (m), 1986 (vs), 1975 (vs), 1946 (m, sh), 1920 (m)
$[FeCo_2(CO)_9(\mu_3\text{-PPh})^{\bullet -}]$ (**4**[MgCl])	2044 (m), 1978 (vs), 1973 (s, sh), 1966 (s, sh), 1905 (w, br)
$[FeCo_2(CO)_9(\mu_3\text{-PPh})^{\bullet -}]$ (**4**[Cp_2Co])	2044 (m), 1976 (vs), 1972 (s, sh), 1966 (s, sh), 1901 (w, br)
$[FeCo_2(CO)_8\{C(O)OMe\}(\mu_3\text{-PPh})^-]$ (**5**[Li])	2051 (m), 2036 (m), 1994 (vs), 1977 (vs), 1952 (m), 1928 (m), 1797 (w, br), 1582 (w, ester-CIP)
$[FeCo_2(CO)_8\{C(O)OMe\}(\mu_3\text{-PPh})^-]$ (**5**$^-$)[d]	2046 (m), 2036 (m), 1990 (vs), 1978 (vs), 1952 (m), 1927 (m), 1627 (m, ester-SSIP)

[a] All spectra were recorded in THF at −70 °C unless otherwise noted. [b] Recorded in cyclohexane at room temperature. See ref 14. [c] Recorded in CH_2Cl_2 at −70 °C. [d] ~10 mol equiv of 12-crown-4 present. [e] Recorded in 1,2-dichloroethane at room temperature. See ref 35c.

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(33) (a) Don, M. J.; Richmond, M. G. *Inorg. Chim. Acta* **1990**, *173*, 61. (b) Aradi, A. A.; Grevels, F. W.; Kruger, C.; Raabe, E. *Organometallics* **1988**, *7*, 812 and references therein. (c) Bedard, R. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1986**, *108*, 5942.

(34) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic Press: New York, 1978.

(35) (a) Beurich, H.; Madach, T.; Richter, F.; Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 690. (b) Lindsay, P. N.; Peake, B. M.; Robinson, B. H.; Simpson, J.; Honrath, U.; Vahrenkamp, H.; Bond, A. M. *Organometallics* **1984**, *3*, 413. (c) Honrath, U.; Vahrenkamp, H. *Z. Naturforsch.* **1984**, *39B*, 555.

(36) Hwang, S.; Richmond, M. G. Unpublished results.

(37) For reviews of electron-transfer mechanisms, see: (a) Taube, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 329. (b) Taube, H. *J. Chem. Educ.* **1968**, *45*, 452. (c) Sutin, N. *Acc. Chem. Res.* **1982**, *15*, 275. (d) Pross, A. *Acc. Chem. Res.* **1985**, *18*, 212. (e) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155. (f) Eberson, L. *Adv. Phys. Org. Chem.* **1982**, *18*, 79. (g) See also: Purcell, K. F.; Kotz, J. C. *Inorganic Chemistry*; W. B. Saunders Co.: Philadelphia, PA, 1977; Chapter 12.

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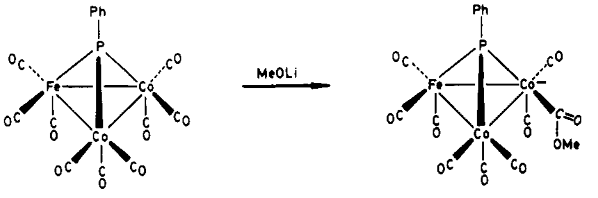
(39) (a) Bockman, T. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1989**, *111*, 4669 and references therein. (b) Kochi, J. K. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1227 and references therein.

(40) For examples of the microscopic reverse of this principle, see: Narayanan, B. A.; Amatore, C.; Kochi, J. K. *Organometallics* **1986**, *5*, 926; **1987**, *6*, 129.

from the THF solvent represent the most likely consumption reactions for these radicals.[41]

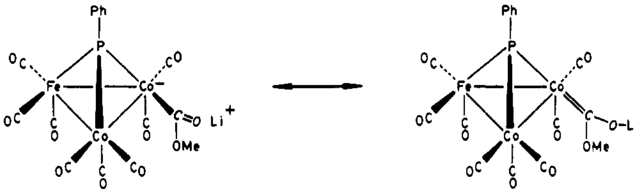
IV. Methoxy- and Hydroxycarbonyl Derivatives. The reaction of **1** in THF with 1 mol equiv of [MeO][Li] (1.3 M in MeOH) yields the purple methoxycarbonyl cluster $[FeCo_2(CO)_8\{C(O)OMe\}(\mu_3\text{-PPh})^-]$ (5^-) in quantitative yield at −78 °C. Qualitatively, the low-temperature IR spectrum of 5^- mirrors that of 3^- as seen by the similar ν(CO) data in Table I and comparison of the IR spectra in Figure 3A,B. This suggests that methoxide attack occurs at a Co–CO group to give a cobalt-bound methoxycarbonyl moiety. Equation 4 illustrates the course of this reaction.



(4)

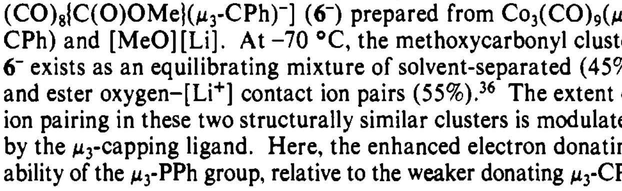
1 5^-

The observation of only one low-frequency ν(CO) band at 1582 cm^{-1} and its shift to 1627 cm^{-1} upon the addition of 12-crown-4 reveals that the initial cluster exists exclusively as a CIP within the limits of IR detection.[19,42] A significant contribution from the alkoxy–carbene resonance structure



is important in determining the ground-state structure of **5**[Li]. Table I lists the frequency of the C–O stretching bands of **5**[Li] and 5^-.

That **5**[Li] exists entirely as a CIP reflects the fact that the methoxycarbonyl cluster is extremely electron rich and dissipates charge density by effectively competing with a THF solvent molecule in the ion-pair equilibrium shown in eq 5.[43] At −70 °C,

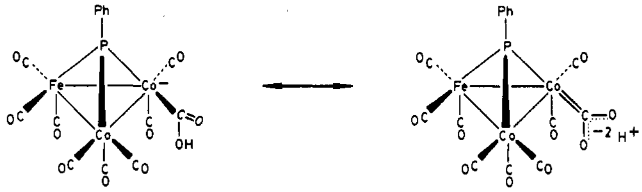


(5)

we estimate that this reaction has a $K_{eq} \geq 19$, which places an upper limit of SSIPs of 5^- at 5%. A clear degree of the electron richness in **5**[Li] is also seen when these results are compared to those obtained from the corresponding tricobalt cluster $[Co_3(CO)_8\{C(O)OMe\}(\mu_3\text{-CPh})^-]$ (6^-) prepared from $Co_3(CO)_9(\mu_3\text{-CPh})$ and [MeO][Li]. At −70 °C, the methoxycarbonyl cluster 6^- exists as an equilibrating mixture of solvent-separated (45%) and ester oxygen–[Li$^+$] contact ion pairs (55%).[36] The extent of ion pairing in these two structurally similar clusters is modulated by the μ_3-capping ligand. Here, the enhanced electron donating ability of the μ_3-PPh group, relative to the weaker donating μ_3-CPh group, manifests itself in an increased concentration of carbonyl oxygen–[Li$^+$] contact ion pairs. An analogous trend is also reflected by the location of highest frequency ν(CO) band of these anionic methoxycarbonyl clusters. This ν(CO) band has also been shown to function as a sensitive probe for the electron density associated with tetrahedrane clusters.[35b,44]

The identity of **5**[Li] was further established by NMR spectroscopy. **5**[Li] exhibited a single low-field ^{31}P resonance at δ 336.0, which is in keeping with the presence of a μ_3-PPh capping ligand. The ^{13}C{^{1}H} NMR spectrum of **5**[Li] recorded at −90 °C (Figure 2B) provides the crucial evidence relating to the site of [MeO$^-$] attack in **1**. Despite the fact that the slow-exchange spectrum has not been fully reached, five broad carbonyl resonances were observed at δ 210.0, 214.0, 215.7, 217.1, and 222.9 with a relative integration ratio of nearly 3:1:1:1:3, respectively. The highest field resonance is readily assigned to the neutral $Co(CO)_3$ unit. As in the phosphido-bridged cluster 2^-, the equatorial carbonyls belonging to the $Fe(CO)_3$ moiety appear as distinct, one-carbonyl resonances tentatively assigned as δ 214.0 and 215.7. The ester moiety accounts for the remaining one carbon at δ 217.5.[42] These last three assignments are by no means unequivocal; however, this uncertainty will not negate the premise of [MeO$^-$] attack at a terminal Co–CO group in **1**. The remaining resonance at δ 223.0 consists of a superposition of the axial Fe–CO group and the two CO groups associated with the anionic ester-substituted cobalt center. Of the other possible structure alternatives, [MeO$^-$] attack at the μ_3-PPh group can be immediately ruled out when the IR data are considered (vide supra), while the existence of an anionic $Fe(CO)_2(CO_2Me)$ moiety is dismissed on the basis of the absence of two equivalent $Co(CO)_3$ groups.

The reaction between **1** and methanolic [Et$_4$N][OH] was next examined as part of our interest in the generation of hydroxycarbonyl complexes.[45,46] When **1** in THF was treated with 1 mol equiv of [Et$_4$N][OH] (1.3 M in MeOH) at −78 °C, immediate and quantitative conversion to 5^- and the hydroxycarbonyl cluster $[FeCo_2(CO)_8(CO_2H)(\mu_3\text{-PPh})^-]$ (7^-) was observed by IR analysis. The IR spectrum recorded at −70 °C revealed ν(CO) bands at 2046 (s), 2036 (w), 1990 (vs), 1972 (s), 1954 (m), 1912 (m), 1798 (vw), 1626 (w), and 1617 cm^{-1} (w). The IR spectrum is shown in Figure 3C. The terminal ν(CO) bands of this mixture are virtually identical with those given in Table I for the solvent-separated ions of 5^-. This is the result expected for the superposition of the closely related derivatives. Disparate perturbations in the terminal C–O stretching bands of clusters 5^- and 7^- are not anticipated, since the ester and acid functionalities possess similar electronic and steric properties. The ester C–O stretch at 1626 cm^{-1} is readily assigned to the solvent-separated ions of 5^-, on the basis of its prior characterization (vide supra). Accordingly, the remaining low-frequency C–O stretch at 1617 cm^{-1} is attributed to the acid moiety of 7^-. That the acid moiety is 9 cm^{-1} lower in energy than the ester group reflects the greater charge delocalization present in 7^-. This phenomenon is directly attributable to the carboxylate-like resonance structure.



The regioselectivity associated with this reaction is assumed to proceed through a kinetically controlled pathway involving [MeO$^-$] and [HO$^-$] attack at a terminal Co–CO group (see eq 4).[46]

The ratio of 5^- to 7^- at −70 °C was determined by measuring the area under the overlapping low-frequency ester and acid C–O

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[41] (a) Ingold, K. U. *Pure Appl. Chem.* **1984**, *56*, 1767 and references therein. (b) Jordan, R. F. *J. Chem. Educ.* **1988**, *65*, 285. (c) See also: Bates, R. B.; Kroposki, L. M.; Potter, D. E. *J. Org. Chem.* **1972**, *37*, 560.

[42] Ford, P. C.; Rokicki, A. *Adv. Organomet. Chem.* **1988**, *28*, 139 and references therein.

[43] For reports dealing with the THF coordination numbers of [Li$^+$] and [Na$^+$], see: (a) Darensbourg, M. Y.; Jimenez, P.; Sackett, J. R.; Hanckel, J. M.; Kump, R. L. *J. Am. Chem. Soc.* **1982**, *104*, 1521. (b) Schaschel, E.; Day, M. C. *J. Am. Chem. Soc.* **1968**, *90*, 503. (c) Hammonds, C. N.; Day, M. C. *J. Phys. Chem.* **1969**, *73*, 1151. (d) Setzer, W. N.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985**, *24*, 353 and references therein.

[44] Penfold, B. R.; Robinson, B. H. *Acc. Chem. Res.* **1973**, *6*, 73.

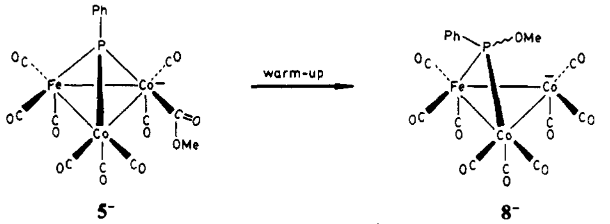
[45] Lee, S. W.; Tucker, W. D.; Richmond, M. G. *Inorg. Chem.* **1990**, *29*, 3053.

[46] Partin, J. A.; Richmond, M. G. *J. Organomet. Chem.* **1990**, *396*, 339.

stretching bands. IR band-shape analysis yielded a 55:45 ratio of $\mathbf{5}^-$ to $\mathbf{7}^-$. This ratio is of interest when compared to the results obtained by using other metal carbonyl complexes. For example, the mononuclear carbonyls $Fe(CO)_5$ and $Cr(CO)_6$ afford ester:acid ratios of 5:95[45] and 2:98,[47] respectively, while the polynuclear clusters $Co_4(CO)_{10}(\mu_4\text{-}PPh)_2$ and $Co_3(CO)_9(\mu_3\text{-}CPh)$ give ester:acid ratios of 23:77[46] and 51:48,[36] respectively. While it appears that these results suggest that polynuclear complexes favor higher yields of the corresponding methoxycarbonyl clusters, we note that additional examples are required before any generalizations can confidently be made. The subtle balance involving the nature of the initial carbonyl complex, gegencation, and anion solvation includes but some of the factors that determine the observed ester:acid ratio.[45,46]

V. Reactivity and Stability Studies. All of the new anionic clusters were observed to be stable for a period of at least 1 week when maintained at −78 °C. Extensive cluster decomposition accompanied all reactions that were warmed to room temperature. Besides the presence of varying amounts of regenerated **1** (<20%), the only other carbonyl-containing material observed was $[Co(CO)_4^-]$.[48] Yields of $[Co(CO)_4^-]$ ranged from 16% to 37%, as determined by quantitative IR spectroscopy. No perceptible stabilization was noticed when clusters $\mathbf{3}^-$ and $\mathbf{5}^-$ were allowed to warm-up in the presence of 12-crown-4 or [PPN][Cl]. Variable-temperature IR studies revealed that $\mathbf{3}^-$ and $\mathbf{5}^-$ decomposed to $[Co(CO)_4^-]$ at rates virtually identical with those of solutions without these additives. The relative instability of these mixed-metal anionic clusters may be contrasted to that of $[Co_3(CO)_9(\mu_3\text{-}CPh)^{\bullet -}]$. Enhanced cluster stabilization and retardation of electron-transfer processes have been reported for $[Co(CO)_9(\mu_3\text{-}CPh)^{\bullet -}]$ in the presence of nonspecific, charge-delocalized cations such as $[PPN^+]$ and $[Na(15\text{-}crown\text{-}5)^+]$.[49] However, recent reports have shown that in the case of $[Co_3(CO)_9(\mu_3\text{-}CMe)^{\bullet -}]$ decomposition is preceded by dissociative CO loss and that this destructive process is concentration dependent.[50] Finally, the growth of crystals suitable for X-ray diffraction analysis was thwarted due to poor crystal quality and competing cluster decomposition.

When monitored by IR spectroscopy, the decomposition of $\mathbf{2}^-$ and $\mathbf{3}^-$ was observed to occur without the spectroscopically observable intermediates. A different course of reaction was noted for $\mathbf{5}^-$. Starting at −25 °C, the solution acquired a brown color and the ester $\nu(CO)$ band at 1582 cm^{-1} and the terminal $\nu(CO)$ bands at 2051 and 1994 cm^{-1} diminished in intensity. This transformation is complete by ca. −5 °C, and the resulting spectrum (Figure 1B) closely resembles that of $\mathbf{2}^-$. Also evident in this warm-up process is the presence of a small amount of **1** and $[Co(CO)_4^-]$, which are estimated at <10% yield. The similarity of the IR spectra of $\mathbf{2}^-$ and $\mathbf{5}^-$ (recorded at −5 °C) strongly supports the ester → phosphido sequence shown in eq 6.



$\mathbf{5}^-$ $\mathbf{8}^-$ (6)

^{31}P NMR spectroscopy has also provided complementary data for the reaction shown in eq 6. When $\mathbf{5}^-$ was briefly warmed to −25 °C and then cooled back down to −78 °C,[51] ^{31}P NMR analysis revealed two major resonances at δ 336.0 and 320.0. The latter resonance is assigned to the methoxyphosphido cluster $[FeCo_2(CO)_9(\mu_2\text{-}PPhOMe)^-]$ ($\mathbf{8}^-$), while the former resonance belongs to $\mathbf{5}^-$. The chemical shift ascribed to the proposed μ_2-PPhOMe group is slightly outside the range expected for a μ_2-phosphido group (δ 300–50),[21] but we note that Bruce et al.[24] have also observed a low-field ^{31}P chemical shift for a μ_2-PPhOMe-bridged ruthenium cluster (i.e., δ 297.2). A ^{31}P gated-decoupled NMR spectrum of a mixture containing $\mathbf{5}^-$ and $\mathbf{8}^-$ failed to reveal any ^1H–^{31}P coupling, presumably due to the broadness associated with these resonances. The stereochemistry associated with the μ_2-PPhOMe ligand in $\mathbf{8}^-$ is unknown at this time, and no attempt has been made to determine it.

An analogous reaction involving the transformation of the formyl complexes $[Fe_2(CO)_5\{C(O)H\}(\mu_2\text{-}PR_2)_2^-]$ (where R = Me and Ph) to the corresponding phosphido/phosphines $[Fe_2(CO)_6(\mu_2\text{-}PR_2)(PR_2H)^-]$ has been demonstrated by Wojcicki and co-workers.[22d,52] The observation of the methoxyphosphido cluster $\mathbf{8}^-$ from $\mathbf{5}^-$ upon warm-up illustrates the critical role played by the reaction temperature. At −78 °C, $\mathbf{5}^-$ is formed via a kinetically controlled reaction, while at higher temperature (>−20 °C) $\mathbf{8}^-$ is derived as a result of thermodynamic product control.

Anion functionalization using methyl triflate and trifluoroacetic acid was also examined in an attempt to further characterize these new clusters.[53] Unfortunately, no reaction was observed by IR spectroscopy when either $\mathbf{2}^-$ or $\mathbf{3}^-$ was treated with methyl triflate at −78 °C. Extensive polymerization accompanied all reactions upon warm-up. Solvent polymerization and the absence of cluster alkylation indicate the O-alkylation of THF is favored.[54] The unreactive nature of $\mathbf{2}^-$ toward electrophiles was also demonstrated by changing the reaction solvent to CH_2Cl_2. CH_2Cl_2 solutions of $\mathbf{2}^-$ at −78 °C showed no noticeable reaction with methyl triflate (1–5 equiv) and trifluoroacetic acid (~5 equiv).[55] Warm-up of these solutions led to the regeneration of **1** in reduced yield (~ 20–50%). It is possible that $\mathbf{2}^-$ functions as a hydride-transfer agent much like that reported for metal formyls,[18] but this remains to be established. Finally, cluster **5**[Li] regenerates **1** in quantitative yield at −78 °C when treated with trifluoroacetic acid (~5 equiv), consistent with the many reports of acid-promoted ester decomposition.[45,46,56]

Experimental Section

$FeCo_2(CO)_9(\mu_3\text{-}PPh)$[14] and methyl triflate[57] were prepared according to known literature procedures. $[Et_3BH][Li]$ (1.0 M in THF), $[\{CH_3CH_2CH(CH_3)\}_3BH][K]$ (1.0 M in THF), t-BuMgCl (2.0 M in THF), MeLi (1.4 M in Et_2O), and trifluoroacetic acid were all purchased from Aldrich and used as received. MeLi was titrated against diphenylacetic acid prior to use.[58] $[Et_4N][OH]$ (20% aqueous solution) was obtained from Lancaster Synthesis and dried under high vacuum to give solid $[Et_4N][OH]$. The 1.3 M methanolic solutions of $[Et_4N][OH]$ were subsequently prepared under argon and transferred to Schlenk vessels for

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(47) Partin, J. A.; Richmond, M. G. Unpublished results.

(48) (a) Gladysz, J. A.; Williams, G. M.; Tam, W.; Johnson, D. L.; Parker, D. W.; Selover, J. C. *Inorg. Chem.* **1979**, *18*, 553. (b) Edgell, W. F.; Hedge, S.; Barbatta, A. *J. Am. Chem. Soc.* **1978**, *100*, 1406.

(49) Kirk, C. M.; Peake, B. M.; Robinson, B. H.; Simpson, J. *Aust. J. Chem.* **1983**, *36*, 441.

(50) (a) Hinkelmann, K.; Mahlendorf, F.; Heinze, J.; Schacht, H. T.; Field, J. S.; Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 353. (b) Hinkelmann, K.; Heinze, J.; Schacht, H. T.; Field, J. S.; Vahrenkamp, H. *J. Am. Chem. Soc.* **1989**, *111*, 5078.

(51) Warmed samples of $\mathbf{5}^-$ were cooled back to −78 °C for ^{31}P NMR analysis in order to reduce the cobalt-induced quadrupolar broadening of the ^{31}P nucleus. See: (a) Schulman, C. L.; Richmond, M. G.; Watson, W. H.; Nagl, A. *J. Organomet. Chem.* **1989**, *368*, 367. (b) Richmond, M. G.; Kochi, J. K. *Organometallics* **1987**, *6*, 254.

(52) See also: Wojcicki, A. In *Coordination Chemistry and Catalysis*; Ziolkowski, J. J., Ed.; World Scientific: Teaneck, NJ, 1988; pp 3–25.

(53) For example, see: (a) Richmond, M. G.; Kochi, J. K. *Organometallics* **1987**, *6*, 777 and references therein. (b) Jensen, C. M.; Knobler, C. B.; Kaesz, H. D. *J. Am. Chem. Soc.* **1984**, *106*, 5926 and references therein. (c) Adams, R. D. *Chem. Rev.* **1989**, *89*, 1703.

(54) (a) Howells, R. D.; McCown, J. D. *Chem. Rev.* **1977**, *77*, 69. (b) Matyjaszewski, K.; Penczeks, S. *J. Polym. Sci.* **1974**, *12*, 1905. (c) Wu, T. K.; Pruckmayr, G. *Macromolecules* **1978**, *11*, 77, 265. (d) Kobayaski, S.; Danda, H.; Saegusa, T. *Macromolecules* **1974**, *7*, 415.

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storage. ^{13}CO (99% ^{13}C) was purchased from Isotec. All reactions were conducted under argon with Schlenk techniques.[59] THF and 2-MeTHF were distilled from sodium/benzophenone ketyl and stored under argon in Schlenk vessels. CH_2Cl_2, HMPA, benzene-d_6, and toluene-d_8 were distilled from CaH_2 and stored under argon in Schlenk vessels. $Cr(acac)_3$ was used as a shiftless relaxation agent (~0.0001 M) in the ^{13}C NMR studies.[60]

Low-temperature IR spectra were recorded as previously described.[61] ^{13}C and ^{31}P NMR spectra were recorded at 75 and 121 MHz, respectively, on a Varian 300-VXR spectrometer.

Preparation of ^{13}CO-Enriched $FeCo_2(CO)_9(\mu_3\text{-}PPh)$. A 0.50-g (0.94-mmol) amount of $FeCo_2(CO)_9(\mu_3\text{-}PPh)$ in ~75 mL of benzene in a 500-mL Schlenk storage vessel was charged with ~1.0 atm of ^{13}CO. The solution was stirred at room temperature for 12 h and then at 50 °C for 3.0 h. IR analysis revealed negligible ^{13}CO incorporation in **1**. The flask was recharged with fresh ^{13}CO and irradiated for 6.0 h by using a medium-pressure Hg lamp. After the solution was cooled and vented, IR analysis indicated ~15–25% ^{13}CO enrichment had occurred. ^{13}CO-enriched **1** was purified by column chromatography under argon using Florisil and benzene as the eluant. Integration of the ^{13}C NMR resonance of the different carbonyl groups revealed that statistical ^{13}CO enrichment had occurred. Yield: 0.42 g (~84%). ^{13}C NMR (−80 °C; toluene-d_8): δ 218.7 (1 C, axial FeCO), 211.6 (2 C, equatorial FeCO), 201.0 (6 C, $Co(CO)_3$). ^{31}P NMR [−80 °C; THF/benzene-d_6 (5:1, v/v)]: δ 429.3.

Reaction of $FeCo_2(CO)_9(\mu_3\text{-}PPh)$ with Reducing Agents. Since all the reduction reactions were conducted under similar conditions, only reaction between $FeCo_2(CO)_9(\mu_3\text{-}PPh)$ and $[Et_3BH][Li]$ will be described in detail. To 20 mg (0.037 mmol) of $FeCo_2(CO)_9(\mu_3\text{-}PPh)$ in 25 mL of THF at −78 °C was added 0.037 mL (0.037 mmol) of 1.0 M $[Et_3BH][Li]$ solution. The reaction was instantaneous as judged by the immediate discharge of the red solution and low-temperature analysis, which revealed only the presence of **2**$^-$. ^{31}P NMR [−78 °C; 2-MeTHF/benzene-d_6 (4:1, v/v)]: δ 143.2. ^{13}C NMR [−90 °C; 2-MeTHF/benzene-d_6 (4:1, v/v)]: δ 222.9 (1 C, J_{P-C} = 18.5 Hz, axial FeCO), 221.8 (3 C, anionic $Co(CO)_3$), 215.8 (1 C, equatorial FeCO), 214.0 (1 C, equatorial FeCO), 208.6 (3 C, neutral $Co(CO)_3$).

Band-Shape Analysis. Since the acid and ester carbonyl stretching bands of **7**$^-$ and **5**$^-$ exhibit substantial overlap, the infrared band shapes of these CO bands were calculated by using a numerical procedure in order to determine the ratio of their areas. Absorbances were digitized from 1670 to 1560 cm^{-1} at 1-cm^{-1} intervals and entered into files of the university VAX 11/85 computer. Following baseline correction, the spectra were fit by a model consisting of Lorentzian band shapes, each characterized by a peak frequency (ν), maximum intensity (I), and half-width (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 by using a nonlinear regression procedure.[62] Given that the area 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 $A_2/A_1 = (I_2\Delta_2)/(I_1\Delta_1)$. The same procedure was also used in the area calculation of **3**$^-$ and **3**[Li].

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Low-Temperature ^{31}P NMR Studies of Metal Phosphine Clusters

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$[Au(PPh_3)(AuPPh_3)_7]^{2+}$, $[Pt(H)(PPh_3)(AuPPh_3)_7]^{2+}$, and $[Pt(Ag)(AuPPh_3)_8]^{3+}$ show sharp ^{31}P NMR resonances in solutions at room temperature although from the solid-state structure different phosphine sites are expected. This is due to fluxionality, the chemical exchange of different phosphorus sites. This process can be slowed by lowering the temperature, and in this slow-exchange regime the different phosphine sites can be assigned by means of ^{31}P homonuclear shift correlated spectroscopy methods. The tensor surface harmonics model, which is used for the description of the bonding in this type of clusters, offers a rationale for the trends in the observed magnitude of the coupling constants. Deviation of this model is observed for the toroidal clusters, in which the peripheral interactions are shown to be stronger than in the spheroidal clusters.

1. Introduction

Metal cluster compounds have attracted considerable interest for several years. They are considered to be compounds that can aid in understanding the behavior of small metal particles in solution. They are therefore important chemically in view of understanding catalytic behavior in which the ligands mimic the adsorbed species on a metal surface. From a physical point of view, they are important in investigating the breakdown of the macroscopic description of certain properties of metals, like conductivity, and electronic band structure as opposed to discrete molecular orbitals.

Bonding in metal phosphine clusters has been described in the past with a "porcupine" model.[1] This model stresses the importance of radial bonding in the cluster. The peripheral interactions are thought to be less important, which has been confirmed by Mingos et al. with the use of extended Hückel molecular orbital (EHMO) calculations.[2] For the total stabilization, the smaller peripheral interactions do contribute, since there are so many of them. The radial bonding model was confirmed by Mössbauer studies on homonuclear gold clusters showing that the data found for peripheral Au atoms are in the range that is found for linear mononuclear gold compounds.[3] Several years ago, Stone proposed the tensor surface harmonics theory (TSH), which provides us with a framework in which to describe molecular orbitals in terms of linear combinations of fragment orbitals of the peripheral metal–ligand groups.[4-6] Mingos et al. showed that the application of this theory to gold clusters is straightforward and enables us to predict the gross geometry in terms of prolate, oblate, and

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