J. Am. Chem. Soc. 1995, 117, 4607−4622

Kinetics and Mechanism of the Formation of the Bis(ethylidyne) Tricobalt Cluster $Cp^*_3Co_3(\mu_3\text{-}CCH_3)_2$ from Reaction of Acetylene with $Cp^*_3Co_3(\mu_2\text{-}H)_3(\mu_3\text{-}H)$

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Received September 12, 1994®

Abstract: The paramagnetic tetrahydride cluster $Cp^*_3Co_3(\mu_2\text{-}H)_3(\mu_3\text{-}H)$ (**1**) reacts with acetylene to ultimately form the bis(ethylidyne) cluster $Cp^*_3Co_3(\mu_3\text{-}CCH_3)_2$ (**2**). Two kinetically formed intermediates were isolated from the reaction: the diamagnetic mono(ethylidyne) trihydride cluster $Cp^*_3Co_3(\mu_2\text{-}H)_3(\mu_3\text{-}CCH_3)$ (**3**) and the paramagnetic mono(ethylidyne) monohydride cluster $Cp^*_3Co_3(\mu_3\text{-}H)(\mu_3\text{-}CCH_3)$ (**4**). Cluster **3** loses H_2 at 80 °C [$\Delta G^\ddagger = 29.5(1)$ kcal mol^{-1}] to generate **4**, and **4** reacts with H_2 at 80 °C [$\Delta G^\ddagger = 23.8(1)$ kcal mol^{-1}] to regenerate **3**. A third intermediate in the reaction of **1** with acetylene, the bridging acetylene dihydride cluster $Cp^*_3Co_3(\mu\text{-}H)_2(\mu_3\text{-}\eta^2\text{-}HCCH)$ (**5**), was detected by ^1H NMR spectroscopy at 23 °C and rearranges to form exclusively cluster **4**. Cluster **1** reacts with $DC{\equiv}CD$ at 80 °C to form $Cp^*_3Co_3(\mu_2\text{-}H)_2(\mu_2\text{-}D)(\mu_3\text{-}CCH_2D)$ (**3-CH₂D**) as the exclusive diamagnetic product. The formation of **3-CH₂D** is consistent with the presence of the ethylidene dihydride intermediate $Cp^*_3Co_3(\mu_2\text{-}H)_2(\mu_2\text{-}CDCH_2D)$ (**III**).

Introduction

The chemisorption and rearrangement of acetylene on the Pt(111) surface has been extensively studied typically under ultrahigh-vacuum conditions.[1] These studies reveal that at low temperature, acetylene coordinates to three surface metal atoms by a $2\sigma-\pi$ interaction (Scheme 1). Upon warming, the initially formed adduct rearranges to a μ-vinylidene species, which is stable in the absence of H_2. In the presence of H_2 or surface-bound hydrides generated from the formation of μ-acetylide intermediates,[2] the μ-vinylidene rearranges to a μ_3-ethylidyne ligand, which is the most stable surface species. Exchange of surface hydrides with μ_3-ethylidyne hydrogen atoms has been proposed to involve both μ-vinyl[3] and μ-ethylidene intermediates.[4]

Much of the interest in cluster chemistry has resulted from the potential of clusters to mimic some of the reactivity of heterogeneous systems and the ability of metal clusters to bind organic fragments in orientations not accessible by a single metal center.[5] The reactions of acetylene with metal clusters have provided examples of all intermediates proposed in the conversion of acetylene to an ethylidyne ligand on the Pt(111) surface.[6] For example, Puddephatt has observed μ_3-η^2-acetylene, μ-vinyl, and μ-vinylidene intermediates in the reactions of acetylene with the triplatinum phosphine clusters $[Pt_3(\mu_3\text{-}CO)(\mu\text{-}dppm)_3]^{2+}$ and $[Pt_3(\mu_3\text{-}H)(\mu\text{-}dppm)_3]^+$ (dppm = $Ph_2PCH_2PPh_2$).[7] The direct conversion of acetylene to a μ_3-ethylidyne ligand on a homogenous metal cluster has been observed in several systems.[8−10]

In collaboration with Theopold and co-workers, we recently reported the synthesis of the unusual tricobalt tetrahydride cluster $Cp^*_3Co_3(\mu_2\text{-}H)_3(\mu_3\text{-}H)$ (**1**).[11] Complex **1** is a reactive cluster due to its paramagnetic, 46-electron configuration and lack of bridging ligands other than hydrogen.[12−15]

Here we report that tetrahydride **1** reacts with acetylene to ultimately form the bis(ethylidyne) cluster $Cp^*_3Co_3(\mu_3\text{-}CCH_3)_2$ (**2**). Two kinetically formed intermediates were isolated from the reaction: the diamagnetic mono(ethylidyne) trihydride cluster $Cp^*_3Co_3(\mu_2\text{-}H)_3(\mu_3\text{-}CCH_3)$ (**3**) and the paramagnetic mono(ethylidyne) monohydride cluster $Cp^*_3Co_3(\mu_3\text{-}H)(\mu_3\text{-}CCH_3)$ (**4**).[14] A third intermediate, the bridging acetylene dihydride cluster $Cp^*_3Co_3(\mu\text{-}H)_2(\mu_3\text{-}\eta^2\text{-}HCCH)$ (**5**), was observed by ^1H NMR spectroscopy at 23 °C and found to rearrange exclusively to cluster **4**. Due to the importance of the rearrangement of acetylene to a μ_3-ethylidyne ligand, we

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® Abstract published in *Advance ACS Abstracts*, April 1, 1995.

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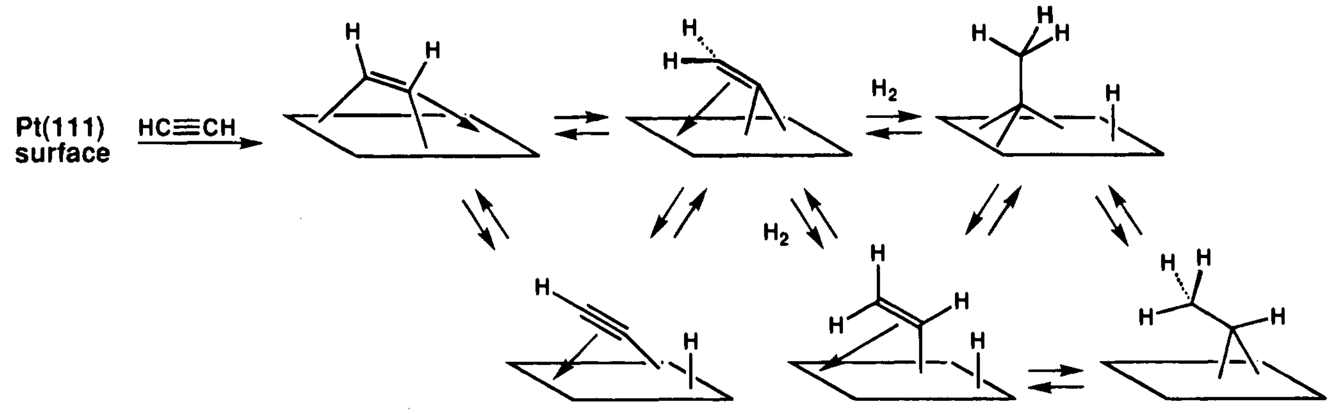
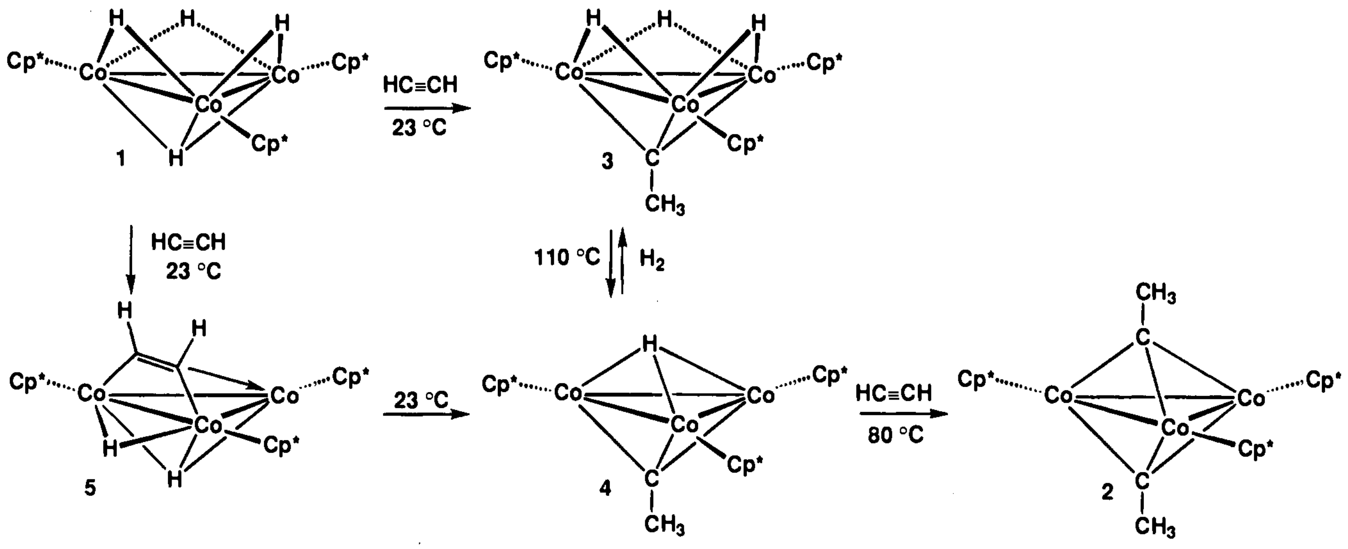
Scheme 1



Scheme 2



undertook a detailed kinetic and isotopic labeling study of the conversion of **1** to clusters **2**–**5**. Deuterium labeling studies indicate that the mechanism for formation of the trihydride cluster **3** from **1** and acetylene involves sequential formation of μ-vinyl and μ-ethylidene intermediates. Interestingly, deuterium labeling studies require a very different mechanism for formation of monohydride cluster **4** via the intermediate **5**.

Results

Formation of Bis(ethylidyne) Cluster $Cp^*_3Co_3(\mu_3\text{-}CCH_3)_2$ (2) from Reaction of Acetylene with $Cp^*_3Co_3(\mu_2\text{-}H)_3(\mu_3\text{-}H)$ (1). Reaction of a black benzene solution of $Cp^*_3Co_3(\mu_2\text{-}H)_3(\mu_3\text{-}H)$ (**1**) with excess acetylene at 100 °C for 2 days in a sealed tube produced the purple bis(ethylidyne) cluster $Cp^*_3Co_3(\mu_3\text{-}CCH_3)_2$ (**2**), which precipitated from solution and was isolated in 88% yield (Scheme 2). The 48-electron diamagnetic cluster **2** was characterized by spectroscopy and by X-ray crystallography. In the ^1H NMR spectrum, resonances at δ 1.67 and 4.48 confirmed the 3:2 ratio of Cp*Co:CCH_3 groups. In the $^{13}C\{^1H\}$ NMR spectrum of $Cp^*_3Co_3(\mu_3\text{-}^{13}C^{13}CH_3)_2$ (**2**-$^{13}C_2$), a doublet at δ 336 (J_{CC} = 27 Hz) was assigned to the apical carbon atom and a doublet at δ 44.3 was assigned to the ethylidyne methyl group. The X-ray crystal structure of **2** revealed an equilateral triangle of cobalt atoms symmetrically capped on each face by a μ_3-ethylidyne ligand.[15]

Mono(ethylidyne) Tricobalt Intermediates $Cp^*_3Co_3(\mu_2\text{-}H)_3(\mu_3\text{-}CCH_3)$ (3) and $Cp^*_3Co_3(\mu_3\text{-}H)(\mu_3\text{-}CCH_3)$ (4). Two mono(ethylidyne) intermediates were observed in the conversion of tetrahydride **1** to bis(ethylidyne) tricobalt cluster **2**. The reaction of **1** with 3 atm of acetylene at 80 °C in C_6D_6 was monitored periodically by ^1H NMR spectroscopy using C_6Me_6 as an internal standard. After 1 h the Cp* resonance of tetrahydride **1** could no longer be detected and the resonance of the bis(ethylidyne) cluster **2** accounted for ~5% of the Cp* resonances. The majority of the material consisted of a 44:56 ratio of two mono(ethylidyne) clusters, $Cp^*_3Co_3(\mu_2\text{-}H)_3(\mu_3\text{-}CCH_3)$ (**3**) and $Cp^*_3Co_3(\mu_3\text{-}H)(\mu_3\text{-}CCH_3)$ (**4**) (Scheme 2);[16] the ratio of **3**:**4** was constant throughout the complete disappearance of **1**.

Pure trihydride **3** was obtained from reaction of **1** with acetylene under 4 atm of H_2. A black benzene solution of **1** and excess acetylene were heated at 80 °C under 4 atm of H_2 for 3 h to form a green solution of **3**. By ^1H NMR spectroscopy, only trihydride **3** and none of monohydride **4** was observed. Evaporation of solvent and crystallization from toluene gave the 48-electron mono(ethylidyne) trihydride cluster $Cp^*_3Co_3(\mu_2\text{-}H)_3(\mu_3\text{-}CCH_3)$ (**3**) in 53% yield. In the ^1H NMR spectrum, resonances were observed at δ 5.12 (μ-CCH_3), 1.67 (Cp*), and −32.24 (Co-μ-H). In the $^{13}C\{^1H\}$ NMR spectrum of $Cp^*_3Co_3(\mu_2\text{-}H)_3(\mu_3\text{-}^{13}C^{13}CH_3)$ (**3**-$^{13}C_2$), a pair of doublets δ 316.1 and δ 45.7 (J_{CC} = 27 Hz) were assigned to the bridging carbon and the methyl carbon, respectively. Both the chemical shifts

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[16] The observed ^1H NMR ratio of **3**:**4** is 60:40; the broad paramagnetic resonance for **4** consistently integrates to ~75% of its actual intensity.[25] The true ratio **3**:**4** was obtained by heating the two clusters under 4 atm of H_2 at 80 °C in the absence of acetylene and measuring the increase in intensity of the Cp* resonance for **3** at δ 1.67 relative to an internal standard (C_6Me_6).

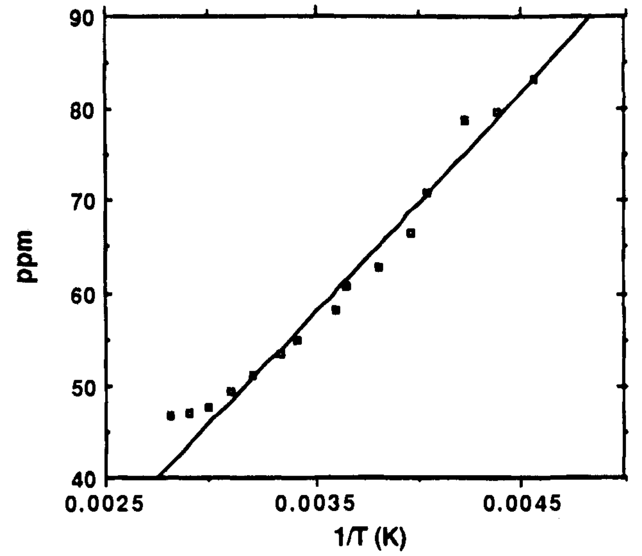

Figure 1. Temperature dependence of the ^1H NMR chemical shift of **4**.

and J_{CC} of the ethylidyne carbon atoms of **3**-$^{13}C_2$ are similar to the values observed for **2**-$^{13}C_2$.

Pure monohydride **4** was obtained by thermolysis of trihydride **3**. When a green toluene solution of **3** was refluxed for 3 days, the solution turned brown. Filtration and evaporation of solvent gave the paramagnetic 46-electron mono(ethylidyne) monohydride cluster $Cp^*_3Co_3(\mu_3\text{-}H)(\mu_3\text{-}CCH_3)$ (**4**) in 75% yield as a brown microcrystalline solid. The X-ray crystal structure of **4** revealed a triangular core of cobalt atoms capped on a single face by a μ_3-ethylidyne ligand.[15] The molecular formula of **4** was established by high-resolution mass spectrometry (m/z = 610). In the ^1H NMR spectrum of paramagnetic **4**, a single broad resonance at δ 53.6 ($w_{1/2}$ = 1330 Hz) was assigned to the three equivalent Cp* ligands; resonances corresponding to the ethylidyne methyl group and the hydride ligand were not observed.

The ^1H NMR chemical shift of **4** in toluene-d_8 displayed a linear dependence on inverse temperature over the range −54 to 60 °C but deviated slightly from linearity at higher temperatures (Figure 1; Supplementary Table 1). The effective magnetic moment (μ_{eff}) of **3** determined by the Evans NMR method[17] was 3.8 ± 0.3 μ_B at 23 °C in C_6D_6. The paramagnetism of the 46-electron cluster **4** is in accord with molecular orbital calculations performed on the related 46-electron clusters $Cp_3Co_3(\mu_3\text{-}CO)_2$[18] and $Cp_3Rh_3(\mu_3\text{-}CO)_2$;[19] the HOMO of these clusters is a pair of half-filled degenerate e″ orbitals. The effective magnetic moment obtained for **4** is considerably larger than the predicted spin-only value for a ground-state triplet (2.83 μ_B) and suggests that the unpaired electrons in cluster **4** possess considerable angular momentum.[17b] Unexpectedly high values for μ_{eff} have been observed for the 46-electron clusters **1** and $Cp_2Co_2Cp^*Ir(\mu_3\text{-}CO)_2$.[20]

NMR Observation of a Bridging Acetylene Intermediate $Cp^*_3Co_3(\mu\text{-}H)_2(\mu_3\text{-}\eta^2\text{-}HCCH)$ (5). In an effort to detect additional intermediates in the conversion of tetrahydride **1** to the mono(ethylidyne) clusters **3** and **4**, the reaction of **1** with excess acetylene (3.6 atm) and at lower temperature (23 °C) was monitored by ^1H NMR spectroscopy in C_6D_6 (Figure 2). After 25 h (33% remaining **1**), 27% of trihydride cluster **3** and 26% of monohydride cluster **4** had formed; in addition, resonances assigned to 14% of an intermediate bridging acetylene dihydride cluster, $Cp^*_3Co_3(\mu\text{-}H)_2(\mu_3\text{-}\eta^2\text{-}HCCH)$ (**5**), were also observed. The amount of **5** reached a maximum of 14% and then gradually decreased with predominant production of monohydride cluster **4**. At long times, **1** and **5** disappeared and a 56:44 ratio of monohydride cluster **4**:trihydride cluster **3** was seen. The ratio of (**5** + **4**):**3** remained constant throughout the reaction.

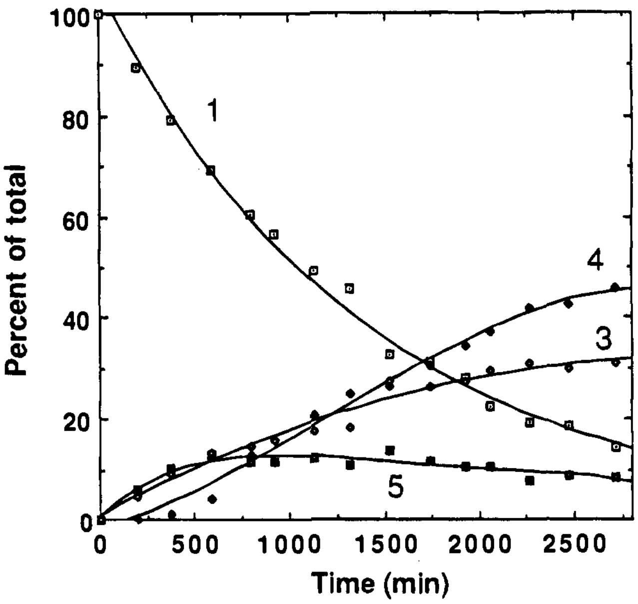

Figure 2. Conversion of **1** to clusters **3**, **4**, and **5** under 3.6 atm of acetylene at 23 °C.

Cluster **5** is thermally unstable and was characterized without isolation by ^1H and ^{13}C NMR spectroscopy. In the ^1H NMR spectrum in C_6D_6, a single Cp* resonance was observed at δ 1.84. In addition, a two-proton resonance at δ 7.50 was assigned to the equivalent acetylenic protons, and a two-proton resonance at δ −23.45 was assigned to the bridging hydride ligands. In the $^{13}C\{^1H\}$ NMR spectrum of $Cp^*_3Co_3(\mu\text{-}H)_2(\mu_3\text{-}\eta^2\text{-}H^{13}C^{13}CH)$ (**5**-$^{13}C_2$), an intense singlet at δ 151.3 was assigned to the equivalent acetylenic carbon atoms. In the ^1H NMR spectrum of **5**-$^{13}C_2$ in THF-d_8, the acetylenic protons appeared as an AA′XX′ pattern centered at δ 7.21 with $^1J_{CC}$ = 20 Hz and $^1J_{CH}$ = 150 Hz. The chemical shifts and coupling constants observed in the ^1H and ^{13}C NMR spectra of **5** and **5**-$^{13}C_2$ are consistent with the values observed for other μ_3-η^2-alkyne clusters.[21]

Cluster **5** is an intermediate in the formation of the monohydride cluster **4** but is not an intermediate in the formation of trihydride cluster **3** (Scheme 2). A mixture of clusters **1**, **3**, **4**, and **5** was generated from the reaction of **1** under 5 atm of acetylene at 23 °C. Acetylene was then removed under vacuum and the mixture was monitored periodically by ^1H NMR spectroscopy at 23 °C. Cluster **5** disappeared slowly to form **4**

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in 86 ± 10% NMR yield. Throughout the complete conversion of **5** to **4**, the concentration of clusters **1** (106 ± 10% of original intensity) and **3** (96 ± 5% of original intensity) remained essentially unchanged. The first-order rate constant for the conversion of **5** to **4** was found to be $2.3 \pm 0.2 \times 10^{-5}$ s^{-1} ($\Delta G^{\ddagger} = 23.6 \pm 0.2$ kcal mol^{-1} at 23 °C), which corresponds to a half-life of 8.4 h.

The maximum 14% buildup of intermediate **5** under 3.6 atm of acetylene is consistent with the rate of conversion of **5** being 4.7 times faster than its formation from **1** and acetylene (the reaction is first order in acetylene, see below).[22] Under these conditions, $k_{obs} = 6.6 \times 10^{-6}$ s^{-1} for disappearance of **1** and $k_{obs} = 3.7 \times 10^{-6}$ s^{-1} for the appearance of **5**. The rate of disappearance of **5** is calculated to be 1.7×10^{-5} s^{-1}, which corresponds to a half-life of 11 h in fair agreement with the observed half-life for direct measurement of the disappearance of **5**.

In a related experiment under even higher acetylene pressure (5 atm), after 11.5 h (40% remaining **1**), 30% of trihydride **3**, 5% of monohydride cluster **4**, and 25% of intermediate **5** were observed. Intermediate **5** reached a maximum of 29% under 5 atm of acetylene which is consistent with the rate of conversion of **5** being 1.6 times faster than its formation from **1** and acetylene.[22] Under 5 atm, $k_{obs} = 2 \times 10^{-5}$ s^{-1} for disappearance of **1** and $k_{obs} = 1.1 \times 10^{-5}$ s^{-1} for the appearance of **5**. The rate of disappearance of **5** is calculated to be 1.8×10^{-5} s^{-1}, which corresponds to a half-life of 11 h in fair agreement with the observed half-life for direct measurement of the disappearance of **5**.

The ability to detect additional intermediates in a reaction sequence upon lowering the temperature is not unusual, particularly when a second-order reaction is followed by a first-order reaction. If second-order and first-order reactions occur at the same rate at a given temperature ($\Delta G_2^{\ddagger} = \Delta G_1^{\ddagger}$), then because $\Delta S_2^{\ddagger}$ normally has a substantial negative value (unfavorable) compared with $\Delta S_1^{\ddagger}$, $\Delta H_2^{\ddagger}$ will be substantially smaller (less unfavorable) than $\Delta H_1^{\ddagger}$. As a consequence, the second-order reaction will show a smaller temperature dependence than the first-order reaction, and when the temperature is lowered, the first-order reaction which depletes the intermediate will be slowed more than the second-order reaction that generates the intermediate. As a result, it often becomes possible to directly observe an intermediate formed in a second-order reaction and further transformed in a first-order process by simply lowering the reaction temperature.

Kinetics of the Reaction of 1 with Acetylene. The kinetics of the reaction of **1** with a greater than 10-fold excess of acetylene were followed by ^{1}H NMR spectroscopy. Plots of ln[**1**] vs time were reasonably linear indicating a first-order dependence on [**1**] (Supplementary Figure 1). However, the measured concentration of acetylene in solution dropped by ~25% after 4 half-lives due to concurrent cyclotrimerization of acetylene. When the reaction was carried out in toluene-d_8, the formation of benzene was confirmed by ^{1}H NMR spectroscopy (δ 7.14) and by gas chromatographic comparison with an authentic sample. Due to the continuous depletion of acetylene during the conversion of tetrahydride **1** to the ethylidyne clusters **2**−**5**, the dependence of acetylene concentration on the rate of disappearance of **1** was determined by single-point kinetics (28−46% conversion) as a function of initial acetylene concentration (1−7 atm, 0.05−0.29 M) (Supplementary Table 2; Supplementary Figure 2). This compromise allowed measurement of a significant drop in [**1**] while minimizing the drop in acetylene concentration. A plot of rate constants versus initial acetylene concentration established a first-order rate dependence on acetylene and the second-order rate law: rate = k_2[**1**][HC≡CH]. The second-order rate constant was calculated to be $9.2 \pm 0.9 \times 10^{-3}$ M^{-1} s^{-1} at 80 °C, which corresponds to a half-life of 30 min under 1 atm of acetylene.

Kinetics and Thermodynamics of the Interconversion of 3 and 4. Trihydride cluster **3** and monohydride cluster **4** interconvert quantitatively by reversible loss of H_2, but at a rate much slower than they are formed from **1** and acetylene. When a C_6D_6 solution of **3** was heated at 110 °C for 35 h in an open tube, 97% of **3** disappeared and **4** was the only observed product. Determination of the NMR yield for conversion of **3** to **4** was complicated by the consistently low integration of the paramagnetic resonance for **4**; the apparent yield was 75%. However, when this solution was heated at 80 °C under H_2 for 23 h, trihydride **3** was regenerated nearly quantitatively (94 ± 5% by ^{1}H NMR).

The equilibrium constant for the interconversion of **3** and **4** plus H_2 was determined by ^{1}H NMR spectroscopy. When a solution of **3** in C_6D_6 was heated at 80 °C in a sealed NMR tube a 48:52 equilibrium mixture of **3**:**4** formed after 4 days. The H_2 pressure in the tube at equilibrium was calculated to be 0.09 atm (3.7×10^{-4} M), corresponding to $K_{eq} = [H_2][\mathbf{4}]/[\mathbf{3}] = 4.1 \times 10^{-4}$ M. The value of this equilibrium constant is in fair agreement with the equilibrium constant calculated from the forward and reverse rate constants (see below): $K_{eq} = k(3 \rightarrow 4)/k(4 \rightarrow 3) = (3.92 \times 10^{-6}\ \mathrm{s^{-1}})/(1.42 \times 10^{-2}\ \mathrm{M^{-1}\ s^{-1}}) = 2.8 \times 10^{-4}$ M.

The equilibrium constant was also measured at 90 °C (7.8×10^{-4} M) and 105 °C (2.1×10^{-3} M) (Supplementary Table 3). A van't Hoff plot of the data allowed calculation of the thermodynamic parameters: $\Delta G = 5.5$ kcal mol^{-1}, $\Delta H = 16.9$ kcal mol^{-1}, $\Delta S = 32$ eu at 80 ± 0.5 °C (Supplementary Figure 3). The large, positive entropy for the formation of **4** and H_2 is nearly identical to the standard entropy of formation for H_2 (31.6 eu),[23] which indicates that the standard entropy for clusters **3** and **4** is very similar.

$$\underset{\mathbf{3}}{\mathrm{Cp^*_3Co_3(\mu_3\text{-}CCH_3)(\mu_2\text{-}H)_3}} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \underset{\mathbf{4}}{\mathrm{Cp^*_3Co_3(\mu_3\text{-}CCH_3)(\mu_3\text{-}H)}} + \mathrm{H_2} \qquad K_{eq} = k_1/k_2$$

The kinetics of the hydrogenation of monohydride cluster **4** at 80 °C to form trihydride cluster **3** were analyzed by ^{1}H NMR spectroscopy. The rate of conversion of **4** to **3** was measured as a function of hydrogen pressure from 1.1 to 5.5 atm of H_2 (4.6×10^{-3} to 2.3×10^{-2} M). For each reaction, good pseudo-first-order rate plots for approach to equilibrium were obtained by plotting $\ln\{[\mathbf{3}]_{inf} - [\mathbf{3}]_t / [\mathbf{3}]_{inf}\}$ vs time (Supplementary Table 4). A plot of pseudo-first-order rate constants versus hydrogen concentration established a first-order dependence of the rate of conversion of **4** to **3** on H_2 concentration ($k_{obs} = k_2[H_2] + k_1$) (Supplementary Figure 4). The second-order rate constant was calculated to be $k_2 = k_{obs}/\{[H_2] + K_{eq}\} = 1.42 \pm 0.05 \times 10^{-2}$ M^{-1} s^{-1}, which corresponds to a half-life of 3.0 h at 80 °C under 1.1 atm (4.6×10^{-3} M) of H_2. The reaction rate was also determined at 90 and 100 °C; an Eyring plot of the data (Supplementary Figure 5) provided activation parameters: $\Delta G^{\ddagger} = 23.8$ kcal mol^{-1}, $\Delta H^{\ddagger} = 16.6$ kcal mol^{-1}, $\Delta S^{\ddagger} = -20$ eu at 80 ± 0.5 °C.

The kinetics of the loss of H_2 from trihydride cluster **3** in an open tube to form monohydride cluster **4** were analyzed by ^{1}H

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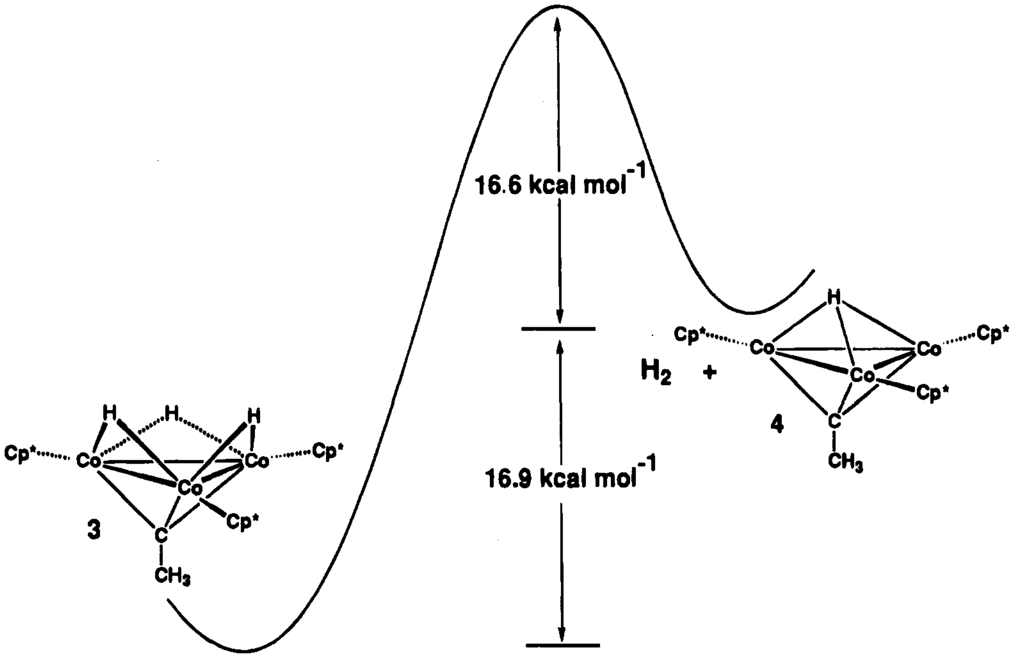

Figure 3. Enthalpy diagram for the conversion of **3** to **4** + H_2 at 80 °C.

NMR spectroscopy. A linear plot of ln[**3**] versus time established a first-order rate law for the disappearance of **3**. The rate constant for the disappearance of **3** was found to be 3.92 ± 0.09 × 10^{-6} s^{-1} ($\Delta G^{\ddagger} = 29.5$ kcal mol^{-1} at 80 ± 0.5 °C), which corresponds to a half-life of 49 h (Supplementary Figure 6).

Analysis of the enthalpy diagram for the conversion of trihydride **3** to monohydride **4** and H_2 (Figure 3) leads to the conclusion that the Co−(μ_2-H) bonds of **3** are considerably stronger than a terminal Co−H bond. Conversion of **3** to **4** + H_2 cleaves two Co−(μ_2-H) bonds, converts a Co−(μ_2-H) bond to a Co−(μ_3-H) bond, forms an H−H bond, and increases the number of Co−Co bonds from 3 to 4. Therefore, the enthalpy for the conversion of **3** to **4** + H_2 may be expressed as $\Delta H^\circ = 2E[\text{Co}-(\mu_2\text{-H})] - \{E[\text{Co}-(\mu_3\text{-H})] - E[\text{Co}-(\mu_2\text{-H})]\} - E(\text{H}-\text{H}) - E(\text{Co}-\text{Co})$, where E designates the energy of the respective bond. Because $E(\text{H}-\text{H}) = 105$ kcal mol^{-1} and $\Delta H^\circ = 17$ kcal mol^{-1}, the strength of the Co−(μ_2-H) bond is equal to 61 kcal mol^{-1} plus one-half the Co−Co bond energy plus one-half the difference in energy between a Co−(μ_3-H) bond and a Co−(μ_2-H) bond. The Co−(μ_2-H) bond of **3** is therefore estimated to be considerably stronger than a terminal Co−H bond (~60 kcal mol^{-1}).[24] This is consistent with energy barriers of 10−13 kcal mol^{-1} measured by variable-temperature ^1H NMR spectroscopy for the conversion of a bridging hydride ligand to a terminal hydride ligand in Co_3,[25] Os_3,[26] Ru_3,[27] and Ru_4[28] clusters. In addition, an Fe−(μ_2-H) bond energy of 81−85 kcal mol^{-1} was estimated from the equilibrium formation of $Fe_3(CO)_9(\mu_2\text{-H})_3(\mu_3\text{-CCH}_3)$ and CO from the reaction of $Fe_3(CO)_{10}(\mu_2\text{-H})(\mu_3\text{-CCH}_3)$ with H_2.[29]

The reversible addition of H_2 to a metal cluster such as mono(ethylidyne) monohydride tricobalt cluster **4** is interesting in relation to the reversible chemisorption of H_2 on a metal surface. The reversible addition of H_2 to the unsaturated 46-electron cluster **4** is unusual since it does not involve simultaneous loss of a ligand. The reversible addition of H_2 to a polynuclear metal complex is usually complicated by simultaneous dissociation or hydrogenation of an ancillary ligand.[10,29,30] We are aware of only four examples of the reversible addition of H_2 to metal clusters without ligand loss. Stone reported that the 46-electron mixed metal clusters $Cp^*_3Rh_2M(\mu_3\text{-CO})_2$ [M = Ir, Rh] add H_2 to form the 48-electron dihydride clusters $Cp^*_3Rh_2M(\mu_3\text{-CO})(\mu_2\text{-CO})(\mu_2\text{-H})_2$ [M = Ir, Rh] without ligand loss.[31] The tetranuclear dihydride cluster $Os_3Pt(\mu\text{-H})_2(CO)_{10}[P(C_6H_{11})_3]$ formed $Os_3Pt(\mu\text{-H})_4(CO)_{10}[P(C_6H_{11})_3]$ under 200 atm of H_2 and was regenerated under N_2 purge.[32] The 48-electron triruthenium dihydride cluster $Ru_3(CO)_8(\mu\text{-H})_2(\mu\text{-}t\text{-Bu}_2P)_2$ reacted reversibly with H_2 via cleavage of a Ru−Ru bond to form the 50-electron cluster $Ru_3(CO)_8(\mu\text{-H})_2(H)_2(\mu\text{-}t\text{-Bu}_2P)_2$.[33] We observed reversible H_2 addition to the 46-electron dicarbonyl cluster $Cp^*_3Co_3(\mu_3\text{-CO})_2$ to form the dicarbonyl dihydride cluster $Cp^*_3Co_3(\mu_3\text{-CO})(\mu_2\text{-CO})(\mu\text{-H})_2$.[12b]

Kinetics of the Reaction of 4 with Acetylene. Reaction of mono(ethylidyne) monohydride cluster **4** with excess acetylene at 100 °C for 8 h in benzene led to isolation of the bis(ethylidyne) cluster **2** in 90% yield [>95% pure by ^1H NMR]. The acetylene concentration dependence of the rate of conversion of **4** to **2** at 80 °C was determined by single point kinetics

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Chart 1

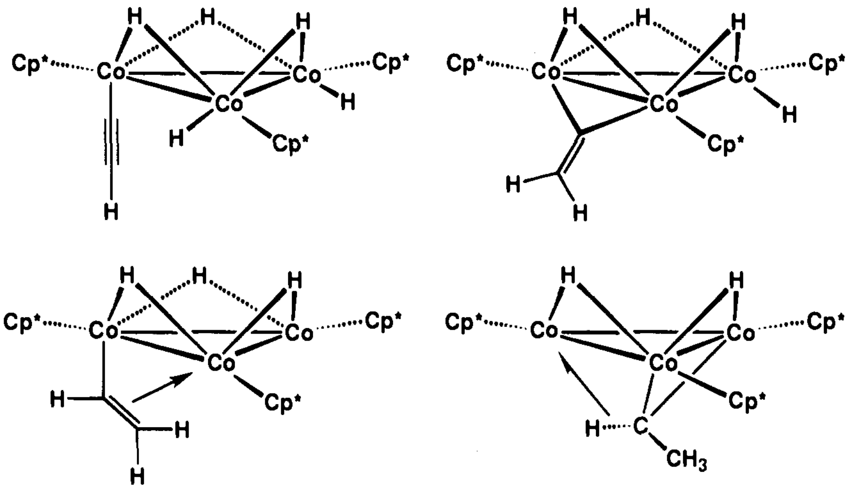

Table 1. ^1H NMR Data for Bridging Ligands in Isotopomers of Clusters **2**, **3**, and **5** in C_6D_6 at 23 °C

cluster	δ	cluster	δ
3		**2**	
μ_3-CCH$_3$	5.12	μ_3-CCH$_3$	4.48
μ_3-CCH$_2$D	5.10	μ_3-CCH$_2$D	4.46
μ_3-CCHD$_2$	5.08	μ_3-CCHD$_2$	4.44
Co$-$(μ_2-H)$_3$	-32.24	**5**	
Co$-$(μ_2-H)$_2$(μ_2-D)	-32.27	μ_3-η^2-HCCH	7.50
Co$-$(μ_2-H)(μ_2-D)$_2$	-32.30	μ_3-η^2-HCCD	7.47

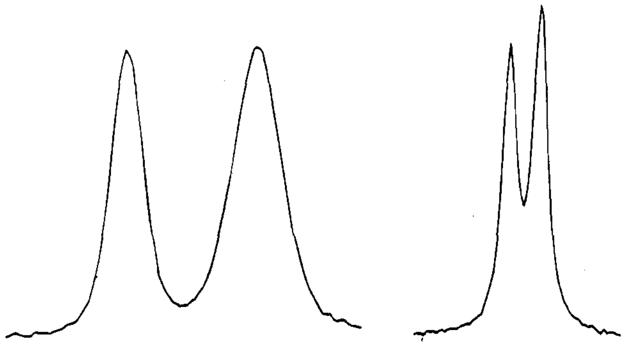

Figure 4. ^1H NMR spectrum of a 3:2 mixture of $Cp^*_3Co_3(\mu_2\text{-}H)_2(\mu_2\text{-}D)(\mu_3\text{-}CCH_2D)$ (**3-CH₂D**) and $Cp^*_3Co_3(\mu_2\text{-}H)_3(\mu_3\text{-}CCH_3)$ (**3**). The ethylidyne region (δ 5.12 and 5.10) is on the left and the hydride region (δ -32.24 and -32.27) is on the right.

as a function of initial acetylene concentration (1.1−5.7 atm, 0.07−0.29 M). A plot of the rate constants versus initial acetylene concentration established a first-order dependence of the reaction rate on acetylene concentration (Supplementary Figure 7, Supplementary Table 5). Overall, a second-order rate law was followed: rate = k_2[**4**][HC≡CH]. The second-order rate constant was calculated to be $1.1 \pm 0.2 \times 10^{-3}$ M^{-1} s^{-1} at 80 °C, which corresponds to a half-life of 4 h under 1 atm of acetylene. This rate is approximately 8 times slower than the reaction of tetrahydride **1** with acetylene.

Reaction of 1 with DC≡CD at 80 °C. There are a number of plausible mechanisms for the conversion of acetylene to μ-ethylidyne ligands including involvement of acetylide, μ-vinylidene, μ-vinyl, and μ-ethylidene intermediates (see Chart 1). Isotopic labeling experiments using DC≡CD or $Cp^*_3Co_3(\mu_2\text{-}D)_3(\mu_3\text{-}D)$ (**1-d_4**) are capable of distinguishing between such intermediates providing that prior scrambling between acetylenic hydrogens and cobalt hydrides does not occur.

The mechanism of the conversion of tetrahydride **1** to the mono(ethylidyne) clusters **3** and **4** was first probed through the analysis of the reaction of **1** with DC≡CD. An NMR tube containing **1** and 3 atm of DC≡CD in C_6D_6 was heated at 80 °C and monitored by ^1H NMR spectroscopy. After 30 min, the reaction had proceeded to 85% completion to produce a 44 ± 5:56 ± 5 mixture of deuterium labeled mono(ethylidyne) trihydride cluster **3** and mono(ethylidyne) monohydride cluster **4**. The ratio of diamagnetic **3** to paramagnetic **4** clusters in the reaction of **1** with DC≡CD was indistinguishable from the ratio of mono(ethylidyne) clusters obtained in the reaction of **1** with acetylene. Analysis of the gases over solution revealed the presence of H_2, HD, and D_2 in a 95:5:<0.5 ratio (~97.5% H) which indicated the predominant release of H_2 in the formation of the paramagnetic mono(ethylidyne) isotopomers.

Cluster **3** was shown to consist of the single isotopomer $Cp^*_3Co_3(\mu_2\text{-}H)_2(\mu_2\text{-}D)(\mu_3\text{-}CCH_2D)$ (**3-CH₂D**). It was possible to determine the isotopic composition of **3** unambiguously from ^1H NMR spectroscopy since deuterium isotope shifts on the ethylidyne methyl resonance gave rise to separate ^1H NMR resonances for **3** (δ 5.12), **3-CH₂D** (20 ppb lower frequency, 10 Hz at 500 MHz), and **3-CHD₂** (40 ppb lower frequency, 20 Hz at 500 MHz) (Table 1). Similarly, separate hydride resonances were observed for (μ_2-H)$_3$ (δ -32.24), (μ_2-H)$_2$(μ_2-D) (30 ppb lower frequency, 15 Hz at 500 MHz), and (μ_2-H)(μ_2-D)$_2$ (60 ppb lower frequency, 30 Hz at 500 MHz). In the ^1H NMR spectrum of **3** obtained from reaction of **1** with DC≡CD without isolation from the paramagnetic cluster **4**, a two-proton resonance at δ 5.10 was assigned to the μ-CCH$_2$D ligand and a two-proton resonance at δ -32.27 was assigned to (μ_2-H)$_2$(μ_2-D) cobalt hydrides. When a small amount of unlabeled **3** was added to the sample, separate ethylidyne resonances were observed for **3** (δ 5.12, $w_{1/2}$ = 2.5 Hz) and **3-CH₂D** (δ 5.10, $w_{1/2}$ = 5 Hz, broadened by deuterium coupling) (Figure 4; Table 1). Similarly, separate hydride resonances were observed for **3** (δ -32.24) and **3-CH₂D** (δ -32.27). The hydride resonances for both **3** and **3-CH₂D** were broadened ($w_{1/2}$ = 9 Hz) by the quadrupolar Co nuclei and no additional broadening of the hydride resonance of **3-CH₂D** due to deuterium coupling was detected.

To estimate the isotopic purity of cluster **3-CH₂D** obtained from the reaction of **1** with DC≡CD, the ethylidyne methyl region and the hydride region of the experimental ^1H NMR spectrum of **3-CH₂D** were compared to simulated spectra of mixtures of μ-CCH$_3$, μ-CCH$_2$D, and μ-CCHD$_2$ ligands employing the program RACCOON.[34] These simulations indicated that

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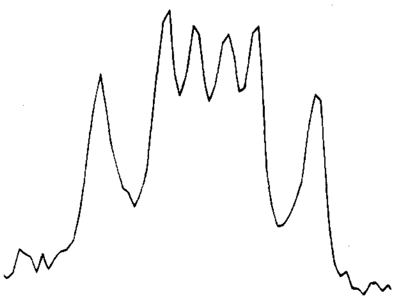

Figure 5. Ethylidyne methyl region of the $^{13}C\{^1H\}$ NMR spectrum of $Cp^*_3Co_3(\mu_2\text{-}H)_2(\mu_2\text{-}D)(\mu_3\text{-}{}^{13}C^{13}CH_2D)$ (**3-$^{13}C^{13}CH_2D$**).

>2% of a μ-CCH_3 species or >10% of a μ-$CCHD_2$ species would have been detectable and none were detected; similarly, >10% of a $(\mu_2\text{-}H)_3$ species and >20% of a $(\mu_2\text{-}H)(\mu_2\text{-}D)_2$ species would have been detectable and none were detected. Therefore, we conservatively estimate that $Cp^*_3Co_3(\mu_2\text{-}H)_2(\mu_2\text{-}D)(\mu_3\text{-}CCH_2D)$ (**3-CH_2D**) constituted >88% of **3** obtained from the reaction of **1** and DC≡CD.

Further support for the presence of a single deuterium atom in the ethylidyne methyl group of **3-CH_2D** was provided from the $^{13}C\{^1H\}$ NMR analysis of $Cp^*_3Co_3(\mu_2\text{-}H)_2(\mu_2\text{-}D)(\mu_3\text{-}{}^{13}C^{13}CH_2D)$ (**3-$^{13}C^{13}CH_2D$**), prepared from **1** and excess $D^{13}C{\equiv}^{13}CD$. The resonance for the ethylidyne methyl group at δ 45.4 (dt, J_{CC} = 27 Hz, J_{CD} = 20 Hz) was shifted 39 Hz upfield from the resonance for **3-$^{13}C_2$** which corresponds to an isotope shift of 31 ppb (Figure 5). The splitting pattern and the isotopic shift for the ethylidyne methyl carbon atom in the ^{13}C NMR spectrum are consistent with the presence of a single deuterium atom in the ethylidyne methyl group. If μ-^{13}C-$^{13}CH_3$ groups had been present, a sharp doublet shifted to higher frequency would have been superimposed on the observed spectrum. Similarly, the presence of μ-$^{13}C^{13}CHD_2$ groups would have led to the superposition of a more coupled multiplet at lower frequency.

The distribution of the deuterium atoms in **3-CH_2D** requires the migration of a single deuterium from carbon to cobalt and the transfer of two hydrides from cobalt to carbon. These transfers must occur without the intervention of an intermediate that would scramble hydrogen and deuterium.

Isotopic Composition of the Bridging Acetylene Intermediate 5 Formed in Reaction of 1 with DC≡CD at 23 °C. The reaction of **1** with excess DC≡CD in C_6D_6 (containing 1,4-bis(trimethylsilyl)benzene as an internal standard) at 23 °C was analyzed by ^1H NMR spectroscopy after 12 h, following removal of excess acetylene. Integration of the Cp* resonances indicated the presence of 40 ± 5% **1**, 30 ± 5% **3**, 10 ± 5% **4**, and 20 ± 5% **5**.

It was possible to determine the isotopic composition of the acetylene intermediate **5** since separate ^1H NMR resonances were seen for the acetylenic hydrogens of isotopomers of **5** (δ 7.50) and **5-HCCD** (δ 7.47, shifted 12 Hz to lower frequency, 25 ppb). The acetylenic hydrogen resonance for **5-HCCD** at δ 7.47 integrated for 0.5 H relative to the 45 H Cp* resonance at δ 1.84 and no resonance at δ 7.50 was seen for an unlabeled bridging acetylene ligand; the accuracy of this determination was greatly aided by comparing the integration of the δ 7.47 resonance to that of the aromatic hydrogens of 1,4-bis(trimethylsilyl)benzene and the integration of the δ 1.84 resonance to that of the trimethylsilyl hydrogens of the same compound. Therefore, the 45:0.5 ratio of the Cp* to acetylenic resonances corresponds to a ~1:1 ratio of $Cp^*_3Co_3(\mu_2\text{-}H)(\mu_2\text{-}D)(\mu_3\text{-}\eta^2\text{-}HCCD)$ (**5-HCCD**):$Cp^*_3Co_3(\mu_2\text{-}H)_2(\mu_3\text{-}\eta^2\text{-}DCCD)$ (**5-DCCD**) (Scheme 3). The resonance for the hydride ligands of **5** at δ −23.45 was too broad to be reliably integrated.

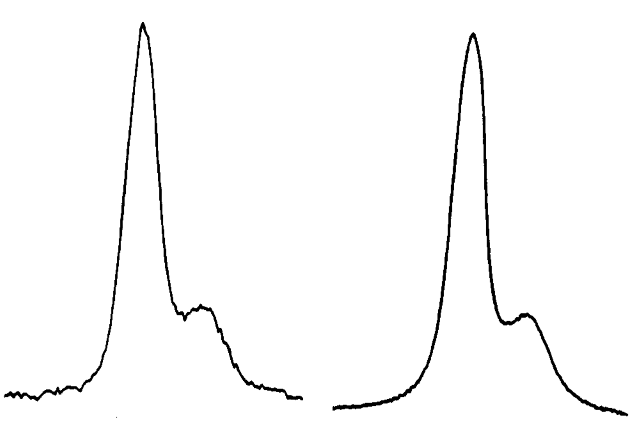

Figure 6. Ethylidyne methyl region of the ^1H NMR spectrum of a 57 ± 5:43 ± 5 mixture of $Cp^*_3Co_3(\mu_2\text{-}H)_2(\mu_2\text{-}D)(\mu_3\text{-}CCH_2D)$ (**3-CH_2D**) and $Cp^*_3Co_3(\mu_2\text{-}H)_3(\mu_3\text{-}CCHD_2)$ (**3-CHD_2**) formed from reaction of **1** with acetylene-d_2 at 23 °C followed by the hydrogenation of the mono(ethylidyne) clusters at 80 °C. The observed spectrum (δ 5.10 and 5.08) is on the left and the simulated spectrum is on the right.

Isotopic Composition of the Mono(ethylidyne) Monohydride Cluster 4 Formed in Reaction of 1 with DC≡CD. The product mixture generated from the reaction of **1** and DC≡CD at 23 °C was then heated at 80 °C for 15 min to convert the isotopomers of **5** into isotopomers of the paramagnetic mono(ethylidyne) cluster **4**. At this point, a mixture of 40% **1**, 26% **3-CH_2D**, and 34% **4** was present. The isotopic composition of the mono(ethylidyne) monohydride cluster **4** could not be determined directly because only a broad Cp* resonance at δ 54 is observed in its ^1H NMR spectrum. Consequently, this mixture was hydrogenated under 4.5 atm of H_2 at 80 °C to convert **4** to additional **3**. (Under these conditions, a control experiment demonstrated that there is no exchange of H_2 with μ-CCH_2D units.)[35] The ^1H NMR spectrum of the resulting **3** displayed a pair of ethylidyne resonances at δ 5.10 for **3-CH_2D** and at 5.08 (shifted 20 Hz to lower frequency, 40 ppb) for **3-CHD_2** in a 73 ± 5:27 ± 5 area ratio, which corresponds to a 57 ± 5:43 ± 5 ratio of **3-CH_2D**:**3-CHD_2** (Figure 6). Because **3-CH_2D** formed directly from **1** and DC≡CD accounts for 44 ± 5% of the total **3**, hydrogenation of paramagnetic cluster **4** produced 13 ± 5% additional **3-CH_2D** and 43 ± 5% **3-CHD_2**. Therefore, **4** formed from DC≡CD and **1** is a 23 ± 5:77 ± 5 ratio of $Cp^*_3Co_3(\mu_3\text{-}D)(\mu_3\text{-}CCH_2D)$ (**4-CH_2D**):$Cp^*_3Co_3(\mu_3\text{-}H)(\mu_3\text{-}CCHD_2)$ (**4-CHD_2**) (Scheme 3).

The isotopic composition of the mono(ethylidyne) monohydride cluster **4** formed directly at 80 °C was similar to that seen above. A 40 ± 5:60 ± 5 mixture of **3-CH_2D**:**4** obtained from reaction of **1** with DC≡CD at 80 °C was heated overnight under 4.5 atm of H_2 at 80 °C to convert **4** to additional **3**. The ^1H NMR spectrum of the resulting pure **3** displayed a pair of ethylidyne resonances of δ 5.10 for **3-CH_2D** and at δ 5.08 for **3-CHD_2** in a 74 ± 5:26 ± 5 area ratio, which corresponds to a 59 ± 5:41 ± 5 ratio of **3-CH_2D**:**3-CHD_2**. Because **3-CH_2D** formed directly from **1** and DC≡CD accounts for 40 ± 5% of the total **3**, hydrogenation of paramagnetic cluster **4** produced 19 ± 5% additional **3-CH_2D** and 41 ± 5% **3-CHD_2**. Therefore, **4** formed from DC≡CD and **1** is a 32 ± 5:68 ± 5 ratio of $Cp^*_3Co_3(\mu_3\text{-}D)(\mu_3\text{-}CCH_2D)$ (**4-CH_2D**) and $Cp^*_3Co_3(\mu_3\text{-}H)(\mu_3\text{-}CCHD_2)$ (**4-CHD_2**).

Reaction of a 1:1 Mixture of HC≡CH and DC≡CD with 1. The reaction of **1** with a 1:1 mixture of HC≡CH:DC≡CD

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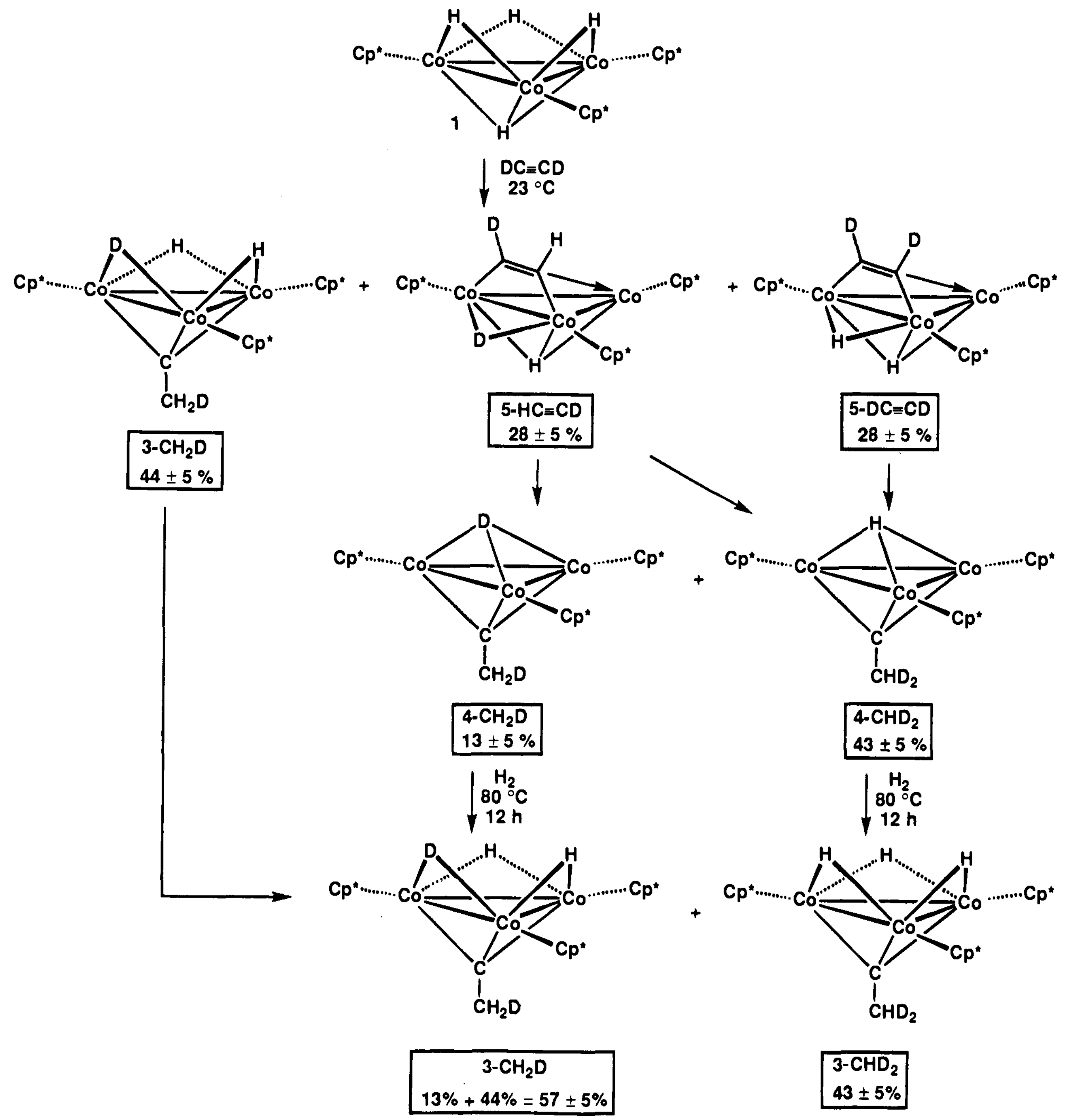
[35] Slow exchange was observed at higher temperatures. A solution of **3** (3 mg, 0.005 mmol) in C_6D_6 (0.5 mL) was heated at 110 °C under 5 atm of D_2 and monitored periodically by ^1H NMR. After 10 days, the intensity of the ethylidyne methyl resonance (δ 5.12) had dropped from 3.0 H to 2.1 H relative to the Cp* resonance (δ 1.67).

Scheme 3



(3 atm total) at 80 °C formed nearly the same 44 ± 5:56 ± 5 ratio of **3**:**4** as obtained from either pure HC≡CH or pure DC≡CD. The diamagnetic mono(ethylidyne) cluster was obtained as a 1:1 ratio of the isotopomers **3**:**3-CH$_2$D** (Supplementary Figure 8). At the end of the reaction, some H/D exchange of recovered acetylene had occurred to give an approximate 32:25:43 ratio of HC≡CH:HC≡CD:DC≡CD. This complicates interpretation of the data. Nevertheless, it is clear that there is little isotope effect on the partitioning between **3** and **4**, little isotope effect on the reaction of acetylene with **1**, and probably little isotope effect on the partitioning of HC≡CD between **3** and **3-CH$_2$D**.

Reaction of 4 with DC≡CD. The reaction of **4** with excess DC≡CD at 80 °C for 24 h formed $Cp^*_3Co_3(\mu_3\text{-}CCH_3)(\mu_3\text{-}CCHD_2)$ (**2-CHD$_2$**). In the ^{1}H NMR spectrum of **2-CHD$_2$**, ethylidyne resonances were observed in a 3:1 area ratio for μ_3-CCH$_3$ at δ 4.48 (unshifted relative to unlabeled **2**) and for μ_3-CCHD$_2$ at δ 4.44 ($w_{1/2}$ = 7 Hz, shifted 18 Hz to lower frequency, 37 ppb) (Supplementary Figure 9).

Synthesis of $Cp^*_3Co_3(\mu_2\text{-}D)_3(\mu_3\text{-}D)$ (1-d_4). The tetradeuteride cluster **1-d_4** was prepared by the reaction of $[Cp^*CoCl]_2$ with LiAlD$_4$ in ether at room temperature followed by quenching with CD$_3$OD. The extent of deuteration of **1-d_4** was determined by reaction with CO which forms $Cp^*Co(CO)_2$[11] and releases hydrogen gas which was analyzed by mass spectrometry. The 60:30:10 ratio of D$_2$:HD:H$_2$ observed by mass spectrometry corresponds to 75% deuteration of **1-d_4**. Assuming a statistical distribution of deuterium, "**1-d_4**" would consist of 32% $Cp^*_3Co_3(\mu\text{-}D)_4$, 42% $Cp^*_3Co_3(\mu\text{-}H)(\mu\text{-}D)_3$, 21% $Cp^*_3Co_3(\mu\text{-}H)_2(\mu\text{-}D)_2$, 5% $Cp^*_3Co_3(\mu\text{-}H)_3(\mu\text{-}D)$, and <1% $Cp^*_3Co_3(\mu\text{-}H)_4$.[36,37]

Reaction of 1-d_4 with Acetylene at 80 °C. The reaction of **1-d_4** with acetylene at 80 °C was 70% complete after 20 min and gave a significantly lower 32 ± 5:68 ± 5 ratio of diamagnetic trihydride cluster **3**:paramagnetic monohydride cluster **4** than the reaction of **1** with either HC≡CH or DC≡CD, which gave 44 ± 5:56 ± 5 ratios. The different ratios obtained from **1** and **1-*d*$_4$** indicate a cobalt hydride isotope effect on the partitioning between **3** and **4**.

The isotopic composition of the diamagnetic trihydride cluster was shown by ^{1}H NMR to be a 73 ± 5:21 ± 5:6 ratio of **3-CHD$_2$** (δ 5.08):**3-CH$_2$D** (δ 5.10):**3** (δ 5.12) (Supplementary Figure 10).[38] The exclusive formation of **3-CH$_2$D** from reaction of **1** with DC≡CD indicated that two hydrides were transferred from cobalt to carbon. The statistical transfer of two hydrides from **1-*d*$_4$** during the formation of **3** would have produced a 56:38:6 ratio of labeled ethylidyne ligands μ_3-CCHD$_2$:μ_3-CCH$_2$D:μ_3-CCH$_3$. The excess μ_3-CCHD$_2$ ligand observed in the reaction of **1-*d*$_4$** with acetylene (73%) is consistent with an inverse kinetic isotope effect of $k_H/k_D \approx 0.5$ favoring transfer of Co−D over Co−H to the ethylidyne ligand.

The ratio of paramagnetic mono(ethylidyne) isotopomers of **4** was obtained by hydrogenating the initially formed mixture to pure **3**, analyzing the ratio of isotopomers of **3**, and then subtracting the amount of initially formed isotopomers of **3**. ^{1}H NMR analysis following hydrogenation indicated the presence of a 67 ± 5:28 ± 5:5 ratio of **3-CHD$_2$** (δ 5.08), **3-CH$_2$D** (δ 5.10), and **3** (δ 5.12) (Supplementary Figure 11). After subtracting the 32% of the initially formed 73:21:6 ratio of isotopomers, the 68% of **3** obtained from hydrogenation of **4** was calculated to result from a 65 ± 5:35 ± 5:<5 ratio of the paramagnetic isotopomers **4-CHD$_2$**:**4-CH$_2$D**:**4**. This 65:35:<5 ratio of paramagnetic mono(ethylidyne) isotopomers is similar to the 72 ± 5:28 ± 5:~0 ratio of **4-CHD$_2$**:**4-CH$_2$D**:**4** obtained in the reaction of **1** with DC≡CD. The similarity of these ratios indicates that essentially complete scrambling of label between cobalt hydride and acetylenic hydrogen sources occurred prior to formation of **4**.

Analysis of the gases over solution revealed the presence of D$_2$:HD:H$_2$ in a 66:25:9 ratio, which corresponds to 79% D released from the cluster. This is a higher percentage of D$_2$ than observed in the fragmentation reaction of **1-*d*$_4$** with CO (60 D$_2$:30 HD:10 H$_2$, 75% D).[37] The excess D$_2$ observed in the reaction of **1-*d*$_4$** with acetylene is consistent with an inverse kinetic isotope effect of $k_{HD}/k_{DD} \approx 0.4$ favoring loss of D$_2$.

Inverse kinetic isotope effects in organometallics systems have been observed for hydrogen transfer from the metal atom to a coordinated ligand, and for the reductive elimination of C−H[39,40] and H−H[41] bonds. For example, inverse kinetic isotope effects were observed in the stoichiometric hydrogenation of α-methylstyrene employing the mononuclear hydride complexes HCo(CO)$_4$,[42] HMn(CO)$_5$,[43] CpMo(H)(CO)$_3$, and CpW(H)(CO)$_3$.[44] An inverse isotope effect of $k_H/k_D = 0.8$ was measured for the reductive elimination of methane from the rhenocene cations Cp$_2$Re(H)CH$_3$$^+$ and Cp$_2$Re(D)CD$_3$$^+$.[39] A similar isotope effect of $k_H/k_D = 0.7$ was determined for methane elimination from the tungsten hydride complex Cp*$_2$W(H)CH$_3$ and the tungsten deuteride compound Cp*$_2$W(D)CD$_3$.[40d] An inverse isotope effect of $k_H/k_D = 0.4 \pm 0.2$ was reported for the reductive elimination of H$_2$ from the iridium dihydride complex (norbornadiene)(PPh$_3$)$_2$Ir(H)$_2$$^+$.[41a]

Inverse kinetic deuterium isotope effects for the transfer of a hydrogen atom from a transition metal to a carbon or hydrogen atom have been attributed to reversible formation of a σ-bound intermediate prior to alkane or H$_2$ dissociation.[45] There is a greater zero point energy difference between C−H and C−D bonds than between M−H and M−D bonds due to the substantially greater force constant of the σ-HH or σ-CH complex compared with that of the M−H bond of the reactant. Because of the substantial thermodynamic preference for deuterium to concentrate in the site with the strongest bond and the highest vibrational frequency,[46] the σ-D intermediate will have a greater equilibrium concentration than will the corresponding σ-H complex. Assuming a negligible isotope effect on the dissociation of the σ-complex, the greater concentration of the σ-D intermediate results in a faster overall rate for D elimination and an inverse isotope effect is observed. Inverse kinetic deuterium isotope effects would also be observed if no intermediate were involved but the reaction coordinate in the neighborhood of the transition state resembled a σ-complex dissociating from the metal center.[47]

Isotopic Composition of the Bridging Acetylene Intermediate 5 Formed in Reaction of 1-*d*$_4$ with Acetylene at 23 °C. ^{1}H NMR analysis of the reaction of **1-*d*$_4$** with excess acetylene in C$_6$D$_6$ (containing 1,4-bis(trimethylsilyl)benzene as an internal standard) at 23 °C after 12 h showed 40% **1-*d*$_4$**, 30% **3**, 5% **4**, and 25% **5**. The acetylenic hydrogen resonance for **5-HCCD** at δ 7.47 integrated for 0.5 H relative to the 45 H Cp* resonance at δ 1.84 and only a trace (<5%) of the perprotio **5** was detected at δ 7.50. The resonance for the hydride ligands of **5** at δ −23.5 was too broad to be reliably integrated. These spectra are

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(36) We have not been able to determine the source of the residual protons in **1-*d*$_4$**. All glassware was flame dried, washed with D$_2$O, and flame dried a second time under vacuum. LiAlD$_4$ was obtained from two independent sources (Aldrich, 98% D; Cambridge Isotope Laboratories, 98% D) and was transferred under N$_2$ directly into an inert-atmosphere glovebox where it was either used as received or purified by extraction with dry ether. Likewise, CD$_3$OD (Cambridge Isotope Laboratories, 99.8% D) was transferred under N$_2$ into glass tubes with Teflon valves, degassed, and transferred into an inert-atmosphere glovebox; separate bottles of CD$_3$OD were employed for each synthesis of **1-*d*$_4$**. None of the above variations resulted in a detectable change in the yield or deuterium content of **1-*d*$_4$**. Attempted use of EtOD from either Aldrich (99% D) or Isotech (99% D) as the quenching agent led to very low yields of **1-*d*$_4$** (<5%).

(37) An isotope effect for release of hydrogen in the reaction of **1** with CO can be approximated from these data if several assumptions are made. Assuming a statistical distribution of D, if each molecule of **1** releases two molecules of hydrogen gas without any intermolecular scrambling, then the ratio of D$_2$:HD:H$_2$ is determined by the isotopic composition of all the isotopomers except for **1-*d*$_2$**. The ratio of D$_2$:HD:H$_2$ released from **1-*d*$_2$** is influenced by the isotope effect on the release of the first molecule of hydrogen. To obtain the observed 60:30:10 ratio of D$_2$:HD:H$_2$, the 21% **1-*d*$_2$** would need to produce 7.0% D$_2$, 6.5% HD, and 7.5% H$_2$. The statistical ratio expected for **1-*d*$_2$** is 3.5% D$_2$, 14% HD, and 3.5% H$_2$. Thus, an isotope effect results in preferential formation of the symmetric species D$_2$ and H$_2$ relative to HD. This is consistent with an inverse isotope effect of $k_{HD}/k_{DD} = 0.25$ (or with a normal isotope effect of $k_{HH}/k_{HD} = 4$). In a separate experiment, **1-*d*$_4$** was reacted with just enough CO to produce Cp*$_3$Co$_3$(μ-H)$_2$(μ-CO)$_2$ and hydrogen gas.[12] Mass spectrometry showed a 82:14:4 ratio of D$_2$:HD:H$_2$. The greater proportion of D$_2$ formed compared with the reaction with excess CO is consistent only with an inverse isotope effect.

(38) Due to the mixture of isotopomers present in **1-*d*$_4$**, we were unable to determine the exact isotopic composition of the clusters **2**−**5** formed from the reaction of **1-*d*$_4$** and acetylene. While the methyl ethylidyne and acetylenic resonances were sufficiently resolved to determine the relative composition of the bridging hydrocarbon ligands, the ratio of the hydride isotopomers could not be determined due to the low intensity of the broad resonances ($w_{1/2}$ = 9 Hz).

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consistent with formation of a 50:50:<5 ratio of **5-DCCD**:**5-HCCD**:**5** isotopomers. This is very similar to the ratio of isotopomers obtained from the reaction of **1** with $DC{\equiv}CD$. The generation of the same 1:1 mixtures of **5-DCCD**:**5-HCCD** from both the reaction of **1**-d_4 with acetylene and the reaction of **1** with $DC{\equiv}CD$ requires complete isotopic scrambling between cobalt hydride and acetylenic hydrogen sources in the formation of intermediate **5**.

Reaction of both **1** and $DC{\equiv}CD$ or **1**-d_4 and $HC{\equiv}CH$ formed an equilibrium mixture of the isotopomers of **5-DCCD**:**5-HCCD**:**5** after ~6 h as determined by ^{1}H NMR spectroscopy; the low intensity of the acetylenic resonances of **5** precluded ^{1}H NMR analysis before 6 h. In an effort to determine whether the scrambling observed in the isotopomers of **5** had occurred prior to or after the formation of **5**, we searched for ^{1}H NMR magnetization exchange between the acetylenic hydrogens and the hydride ligands of perprotio **5** by selective inversion of the acetylenic protons. Delay times ranging from 10 μs to 100 ms were employed; the relaxation time for the acetylenic resonance (T_1 = 0.4 s) limited the delay time allowed to $\leq$100 ms. At a delay time of 100 ms, no magnetization transfer was observed which indicates that $\leq$~20% of the acetylenic protons and hydride ligands had undergone chemical exchange within 100 ms. As a result, if chemical exchange of the acetylenic protons and hydride ligands of **5** occurs at all, the rate must be slower than 10 s^{-1}.

Statistically, a 16:65:16 ratio of **5-DCCD**:**5-HCCD**:**5** would have been expected for a scrambled intermediate. The greater than statistical amount of deuterium found in the bridging acetylene unit is consistent with an equilibrium isotope effect favoring each C$-$D bond over a Co$-$D bond by a factor of 3.5.

Equilibrium deuterium isotope effects previously have been observed to concentrate deuterium in C$-$D bonds over M$-$D bonds. For example, an equilibrium constant of $K_{eq} = 1.0 \pm 0.1$ was reported for the equilibration of the rhenocene hydride methyl-d_3 complex $Cp_2Re(H)CD_3^+$ and $Cp_2Re(D)(CHD_2)^+$, which is considerably less than the equilibrium constant of $K_{eq} = 3$ predicted on a statistical basis.[36] Similarly, an equilibrium constant of $K_{eq} = 1.4$ was measured for the equilibration of the tungsten hydride methyl isotopomers $Cp_2W(H)CD_3$ and $Cp_2W(D)(CHD_2)$.[48] Reaction of CH_2N_2 with the triosmium dideuteride cluster $Os_3(CO)_{10}D_2$ generated a mixture of dideuteride isotopomers of the hydride methyl cluster $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}CH_3)$ and the dihydride methylene cluster $Os_3(CO)_{10}(\mu\text{-}H)_2(\mu\text{-}CH_2)$. Neutron diffraction and ^{1}H NMR spectroscopy revealed a preference for deuterium in the carbon-bound sites for both the methyl ($K_{eq} = 1.74$) and methylene tautomers ($K_{eq} = 1.58$).[49]

Discussion

Formation of μ_3-Ethylidyne Ligands. The reaction of **1** with acetylene that produces μ-ethylidyne complexes **2**, **3**, and **4** is closely related to processes occurring on metal surfaces and to reactions of other metal cluster compounds. μ_3-Ethylidyne ligands can be generated on a clean metal surface such as Pt(111) either from reaction with acetylene[1] via a surface-bound μ-vinylidene intermediate or from reaction with ethylene[1b,50] via a μ-vinyl intermediate.

The direct or stepwise rearrangement of ethylene to a μ_3-CCH_3 ligand on a homogeneous metal cluster has also been demonstrated. For example, the tetrahydride tetraruthenium cluster $Ru_4H_4(CO)_{12}$ reacted with ethylene at 65 °C to form the mono(ethylidyne) trihydride cluster $Ru_3H_3(CO)_9(\mu_3\text{-}CCH_3)$ in 12% yield.[51] Likewise, the hexaosmium cluster $Os_6(CO)_{18}$ reacted with ethylene at 165 °C to form the bis(ethylidyne) cluster $Os_6(CO)_{16}(\mu_3\text{-}CCH_3)_2$.[52] Ethylene reacted readily with the tricobalt monohydride cluster $Co_3(CO)_9H$ to form the mono(ethylidyne) derivative $Co_3(CO)_9(\mu_3\text{-}CCH_3)$.[53] The triruthenium trihydride cluster $Cp_3Ru_3(\mu_2\text{-}H)_3(CO)_3$ reacted with ethylene in boiling toluene to give the tricarbonyl ethylidyne cluster $Cp_3Ru_3(\mu_2\text{-}CO)_3(\mu_3\text{-}CCH_3)$.[10] The triosmium cluster $Os_3(CO)_{12}$ reacted with ethylene to initially form the μ-vinylidene cluster $Os_3(CO)_9(\mu\text{-}CCH_2)$ which reacted with H_2 in refluxing heptane to form the mono(ethylidyne) trihydride cluster $Os_3(CO)_9(\mu_3\text{-}CCH_3)(H)_3$.[54]

The thermal rearrangement of mononuclear complexes which possess a coordinated ethylene ligand has also led to the formation of μ_3-ethylidyne clusters. For example, thermolysis of the bis(ethylene) cobalt complex $CpCo(H_2C{=}CH_2)_2$ (**6**) formed the tetranuclear mono(ethylidyne) monohydride cluster $Cp_4Co_4(\mu_3\text{-}CCH_3)(\mu_3\text{-}H)$ (**7**).[55] Decomposition of **6** under H_2 formed **7** along with the tetracobalt bis(ethylidyne) cluster $Cp_4Co_4(\mu_3\text{-}CCH_3)_2$ and the tricobalt bis(ethylidyne) cluster $Cp_3Co_3(\mu_3\text{-}CCH_3)_2$.[56] Thermolysis of $Cp^*Co(H_2C{=}CH_2)_2$ at 120 °C was initially reported to form the bis(ethylidyne) cluster **2**.[57] However, a reinvestigation of the reaction revealed that thermolysis of $Cp^*Co(H_2C{=}CH_2)_2$ actually forms the mono(ethylidyne) monohydride cluster **4** as the exclusive product.[15]

The direct conversion of acetylene to a μ_3-CCH_3 ligand is less common than the analogous transformation involving ethylene but has been observed in several instances. Acetylene reacted with the anionic triiron cluster $[Fe_3(CO)_{11}H]^-$ at room temperature to form a mixture of clusters including the mono(ethylidyne) decacarbonyl cluster $[Fe_3(CO)_{10}(\mu_3\text{-}CCH_3)]^-$.[8] Acetylene reacted rapidly with the tricobalt monohydride cluster $Co_3(CO)_9H$ to form the ethylidyne cluster $Co_3(CO)_9(\mu_3\text{-}CCH_3)$ as the exclusive product.[9] $Cp_3Ru_3(\mu_2\text{-}H)_3(CO)_3$ reacted with acetylene in boiling toluene to initially form the μ-vinyl cluster $Cp_3Ru_3(\mu_3\text{-}CO)(\mu_2\text{-}CO)(\mu\text{-}CH{=}CH_2)$ which underwent 1,2 hydrogen migration to afford the ethylidyne cluster $Cp_3Ru_3(\mu_2\text{-}CO)_3(\mu_3\text{-}CCH_3)$.[10] In addition, *tert*-butyl acetylene reacted with the triruthenium cluster $Ru_3(CO)_{12}$ to form the μ_3-acetylide monohydride cluster $HRu_3(CO)_9(\mu_3\text{-}C_2CMe_3)$ which reacted with H_2 to form the trihydride μ_3-alkylidyne cluster $H_3Ru_3(CO)_9(\mu_3\text{-}CCH_2CMe_3)$.[58] Thermolysis of $CpCo(CO)_2$ in the presence of substituted alkynes[59] or thermolysis of cobalt acetylene complexes[60] results in cleavage of the $C{\equiv}C$ triple bond and formation of the corresponding bis(ethylidyne) tricobalt cluster.

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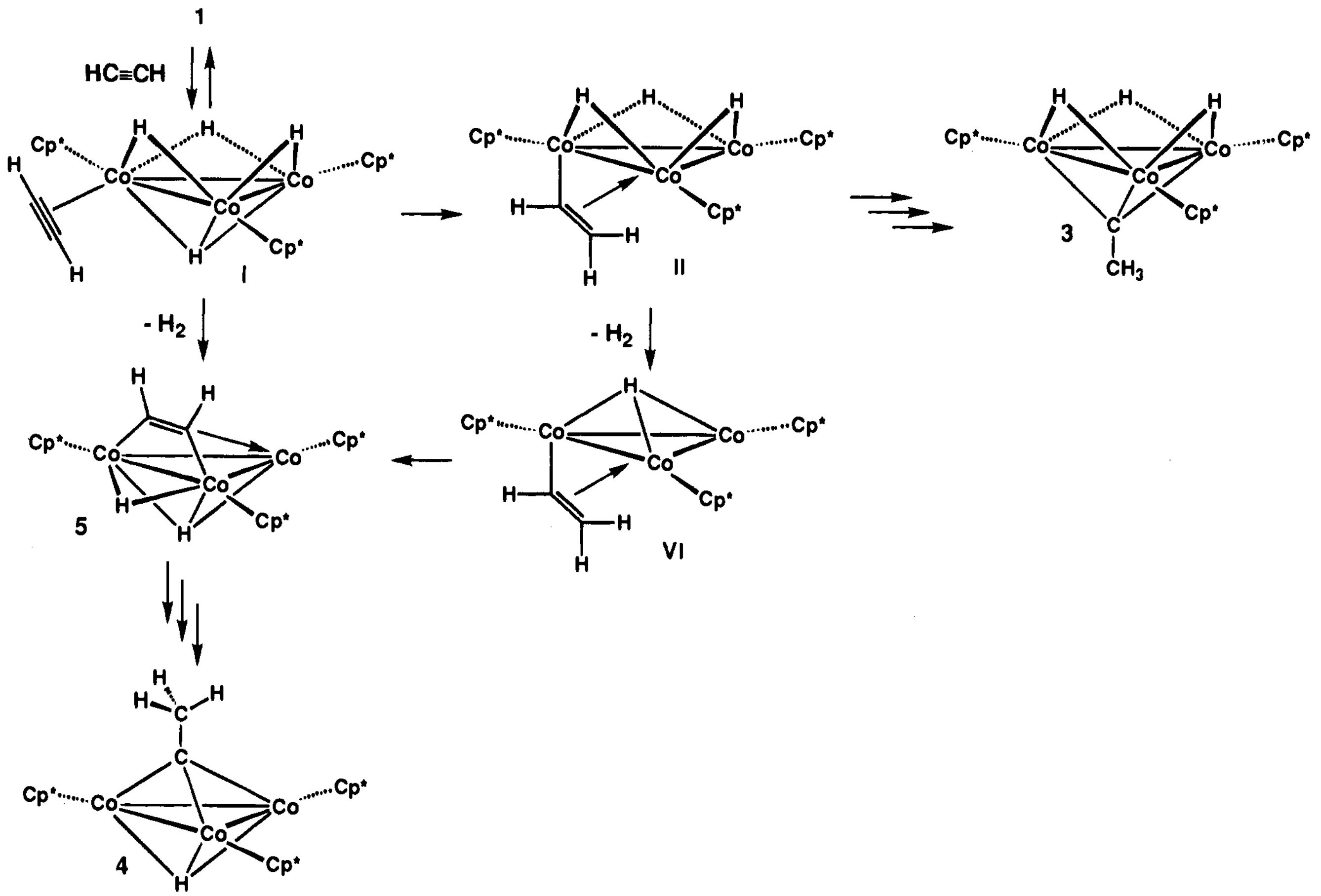
Scheme 4



Kinetics of the Formation and Interconversion of Mono(ethylidyne) Clusters 3 and 4. The mechanism of conversion of **1** to mono(ethylidyne) clusters **3** and **4** depicted in Scheme 4 is consistent with all of our kinetic measurements. Because tetrahydride **1** is coordinatively unsaturated (46 electrons), acetylene can coordinate to **1** to form the 48-electron acetylene adduct **I** without prior loss of H_2. The second-order rate law observed for the reaction of **1** and acetylene is consistent with either rate determining formation of **I** followed by rapid rearrangement to clusters **3** and **5** or rapid and reversible formation of **I** followed by rate-limiting rearrangement to clusters **3** and **5**.

Tetrahydride cluster **1** reacts with 3 atm of acetylene at 80 °C to form a 44:56 ratio of the mono(ethylidyne) clusters **3** and **4** with a half-life of ~6 min. This rate is much faster than either the conversion of **3** to **4** with loss of H_2 ($t_{1/2} = 49$ h) or the addition of H_2 to **3** to form **4** ($t_{1/2} = 36$ h calculated for a H_2 pressure of ≤ 0.1 atm). Since the rate of formation of **3** and **4** from reaction of **1** with acetylene is greater than 100 times faster than the interconversion of **3** and **4**, independent formation of mono(ethylidyne) clusters **3** and **4** is required. The formation of **3** and **4** as kinetic products is consistent with the detection of the μ-acetylene intermediate **5** at lower temperature and the observation that **5** is converted exclusively to monohydride **4**.

Formation of $Cp^*_3Co_3(\mu_2\text{-}H)_2(\mu_2\text{-}D)(\mu_3\text{-}CCH_2D)$ (3-CH₂D) from the Reaction of 1 with DC≡CD. The exclusive formation of the single isotopomer $Cp^*_3Co_3(\mu_2\text{-}H)_2(\mu_2\text{-}D)(\mu_3\text{-}CCH_2D)$ (**3-CH₂D**) from the reaction of **1** and DC≡CD requires that two hydrides be transferred from cobalt to carbon while one deuterium is transferred from carbon to cobalt without any scrambling of label. Since rapid scrambling of any cobalt-bound hydrogen and deuterium can be confidently assumed,[26-28,61] transfer of both cobalt hydride atoms to carbon must occur prior to transfer of deuterium from carbon to cobalt.

The mechanism for the formation of **3-CH₂D** from **1** and DC≡CD shown in Scheme 5 is consistent with these observations. Initial coordination of DC≡CD to the 46-electron tetrahydride cluster **1** would produce the 48-electron adduct **I**. Hydride addition across the coordinated acetylene C≡C bond would generate the μ-η^1,η^2-vinyl intermediate **II**. Metal hydride addition across a coordinated alkyne to form a bridging alkenyl ligand has been observed in Os_3[62] and W_2[63] systems. Transfer of a second hydride from cobalt to the terminal μ-vinyl carbon atom would give the 46-electron ethylidene intermediate **III**. Although intramolecular hydride transfer to a μ-vinyl ligand to form an alkylidene ligand has not been previously observed, intermolecular addition of hydride and other nucleophiles to a μ-alkenyl ligand to form a μ-alkylidene ligand has been reported.[64] Transfer of deuterium from the bridging carbon to

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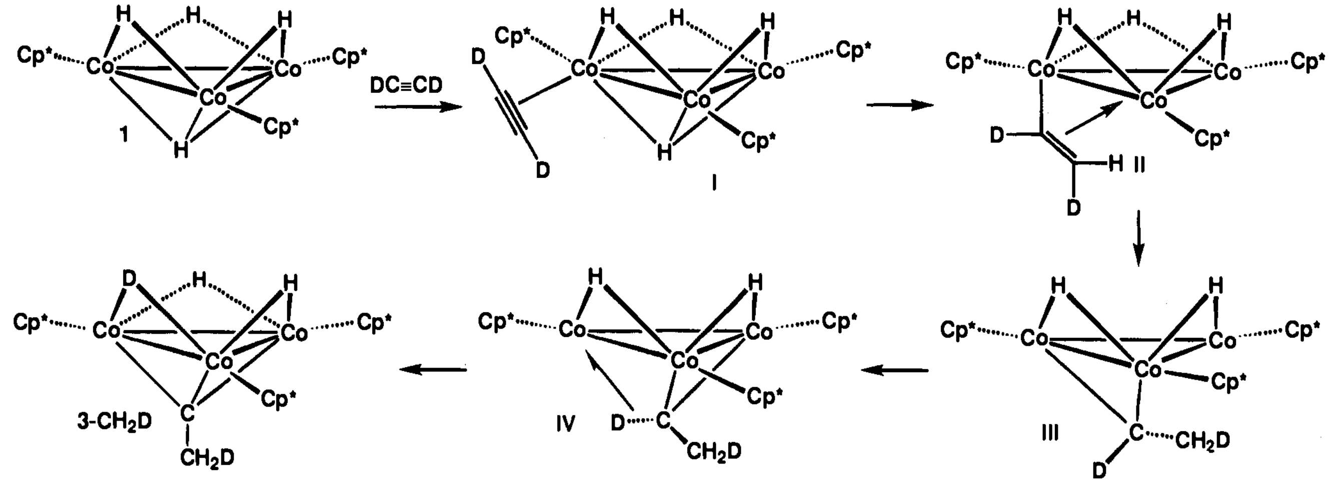
Scheme 5



cobalt appears difficult from the initially formed ethylidene intermediate **III**, but could readily occur if the ethylidene ligand first migrates to place the deuterium on the bridging carbon over the cobalt triangle. The resulting intermediate **IV** could be stabilized through formation of an α-agostic bond. The migration of a μ-alkylidene ligand has been observed in a diruthenium propylidene complex[65] and a Os_3W cluster.[66] Finally, transfer of the α-deuterium atom from carbon to cobalt would produce the observed product **3-CH₂D** as the sole isotopomer. The strong tendency of an alkylidene α-hydrogen atom to form an α-agostic bond and to undergo α-elimination to form an alkylidyne ligand has been well documented in electron deficient mononuclear complexes,[67] W_2 dimers,[68] and Os_3,[49,69] $FeCo_2$,[70] Ru_3,[71] and Ru_4[72] clusters. The predominant formation of $Cp^*_3Co_3(\mu_2\text{-}H)(\mu_2\text{-}D)_2(\mu_3\text{-}CCHD_2)$ (**3-CHD₂**) from the reaction of **1-*d*₄** and acetylene is also consistent with the presence of an ethylidene intermediate.

Formation of *μ*-Acetylene Intermediates 5-HCCD and 5-DCCD. Both the reaction of **1** with DC≡CD and the reaction of **1-*d*₄** with HC≡CH produced the *same* 1:1 mixture of **5-HCCD** and **5-DCCD**. This is consistent with an equilibration process which scrambles carbon and cobalt bound hydrogen atoms. On a statistical basis a 1:4:1 ratio of isotopomers **5**:**5-HCCD**:**5-CDCD** would have been expected; the observed ratio of isotopomers is consistent with an equilibrium isotope effect which favors each C−D bond over a Co−D bond by a factor of 3.5 ($K_H/K_D \approx 0.29$).

Several things are known about the timing of the scrambling. First, because the gas released in the reaction of **1** and DC≡CD was >97% H_2, the isotopic scrambling must occur after loss of H_2. Second, because **5** is fully scrambled when it first appears, scrambling must occur either before the formation of **5** or with a half-life of less than 3 h after its formation. Third, scrambling of **5** after its formation must be slower than the time scale for an NMR saturation transfer experiment.

There are at least three different types of intermediates that could explain the scrambling of label: a μ-acetylide, a μ-vinylidene, and a $\mu_3\text{-}\eta^1,\eta^2$-vinyl intermediate. In all these cases, scrambling might occur either before or after formation of **5** and more complex mechanisms involving more than one of these three types of intermediates are also possible. The scrambling could occur via the μ-acetylide intermediate **V** (Scheme 6); the interconversion of alkyne ligands with acetylides is well documented.[58,62a,73]

Alternatively, scrambling might occur via two pathways involving initial formation of a $\mu_3\text{-}\eta^1,\eta^2$-vinyl intermediate **VI** (Scheme 7). The first involves reversible formation of μ-vinylidene intermediate **VII**; the interconversion of μ-vinyl and μ-vinylidene ligands has been observed on metal clusters.[62d,74] The second involves reversible formation of the $\mu_3\text{-}\eta^1,\eta^2$-vinyl intermediate **VIII** which has a plane of symmetry passing through two vinyl carbons and one cobalt; $\mu_3\text{-}\eta^1,\eta^2$-vinyl complexes are known but rare.[75]

Conversion of 5-HCCD and 5-DCCD to Isotopomers of 4. Scrambling of the deuterium label in the bridging acetylene intermediate **5** precludes exact determination of the mechanistic pathway for the conversion of a 1:1 mixture of **5-HCCD** and **5-DCCD** to a 72 ± 5:28 ± 5 mixture of the mono(ethylidyne) monohydride isotopomers **4-CHD₂** and **4-CH₂D**. It is clear, however, that the mechanism is quite different from that seen for formation of trihydride mono(ethylidyne) cluster **3**. If no further scrambling of deuterium label occurs after formation of

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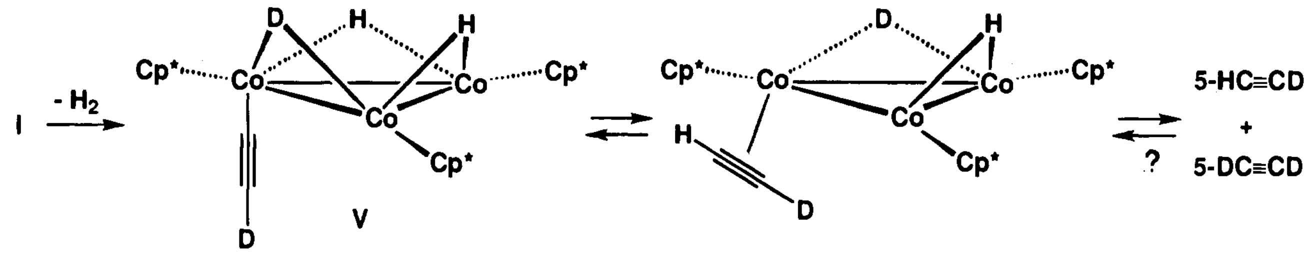
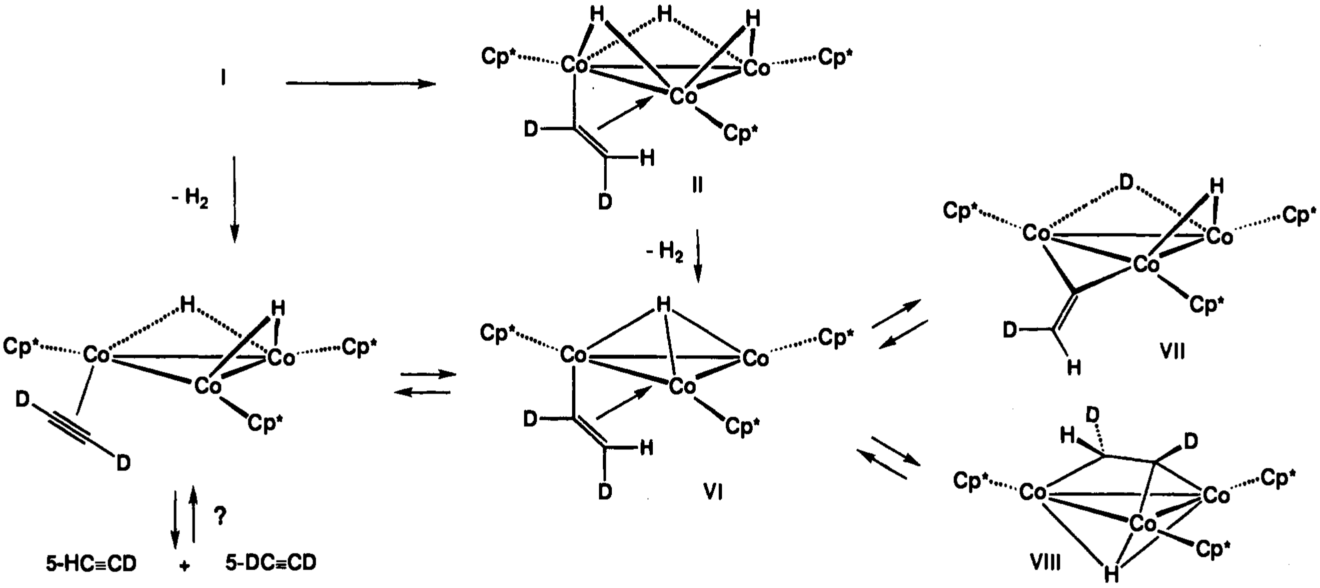
Scheme 6



Scheme 7



5 (questionable and untestable), then formation of **4** by transfer of two hydrogens from cobalt to carbon to form an ethylidene intermediate followed by back transfer of hydrogen from the bridging carbon to cobalt would have led to **4-CH$_2$D** as the major isotopomer, contrary to our observation.

The 72 ± 5:28 ± 5 ratio of clusters **4-CHD$_2$** and **4-CH$_2$D** is consistent with complete scrambling of the deuterium label prior to the irreversible formation of **4-CHD$_2$** and **4-CH$_2$D** with an equilibrium isotope effect favoring C−D over C−H by a factor of 2.6. Conversion of **5** to **4** could occur via a variety of intermediates including the μ-vinyl intermediate **VI**, the μ-vinylidene intermediate **VII**, or a combination of the two (Scheme 8). Conversion of an alkyne ligand to a μ_3-η^2-vinylidene ligand has been observed on Pt_3,[7d] Co_2Ru,[76] Fe_3,[77] and Os_6[78] clusters. Bridging alkyne ligands have also been proposed to convert to vinylidene ligands via acetylide intermediates.[79] The interconversion of μ-alkenyl and μ-alkylidyne complexes via 1,2-hydrogen migration has been observed in Fe_2 cations[80] and in neutral Ru_3[10] and Os_3[74] clusters.

Partitioning between Trihydride 3 and μ-Acetylene Intermediate 5. The partitioning between mono(ethylidyne) trihydride cluster **3** and μ-acetylene dihydride intermediate **5** involves a competition between hydride transfer from cobalt to carbon to form **3** and H_2 loss to produce **5** from a common intermediate. Because the gas evolved in the reaction of **1** with DC≡CD consisted of >97% H_2, the partitioning must occur before the transfer of any deuterium from acetylene to cobalt. There are two candidates for the partitioning intermediate. The first is the initial 48-electron acetylene adduct **I** (Scheme 4) which could either transfer hydride to an acetylenic carbon atom to produce the μ-vinyl complex **II** and ultimately cluster **3** or eliminate H_2 to produce the acetylene dihydride cluster **5**. The second possibility is the μ-vinyl trihydride intermediate **II** which could either transfer hydride to the μ-vinyl ligand to produce the ethylidene intermediate **III** and eventually cluster **3** or eliminate H_2 to form the monohydride vinyl cluster **VI** which could then back transfer hydrogen from carbon to cobalt and form **5**.

The reaction of **1** with either HC≡CH or DC≡CD formed the same 44:56 ratio of **3**:**4**, but the reaction of **1-d_4** with HC≡CH gave a 32:68 ratio of **3**:**4**. These isotope effects require that partitioning involve only Co−D and Co−H bonds. The ratio **3**:**4** observed in the reaction of **1** with HC≡CH corresponds to the ratio of the rate constant for H transfer versus the rate constant for H_2 elimination from a common intermediate, $k_{[\text{H-transfer}]}/k_{[\text{H-elim}]} = 44/56$. Similarly, the ratio of **3**:**4** observed in the reaction of **1-d_4** with HC≡CH corresponds to the ratio of the rate constant for D transfer versus the rate constant for D_2 elimination, or $k_{[\text{D-transfer}]}/k_{[\text{D-elim}]} = 32/68$. Because the ratio **3**:**4** depends on the ratio of two independent rate constants, the change in the ratio **3**:**4** observed upon substitution of **1-d_4** for **1** corresponds to a ratio of the isotope effects for H transfer ($k_{[\text{H-transfer}]}/k_{[\text{D-transfer}]}$) and for H_2 elimination ($k_{[\text{H-elim}]}/k_{[\text{D-elim}]}$), or

$$\frac{k_{[\text{H-transfer}]}/k_{[\text{D-transfer}]}}{k_{[\text{H-elim}]}/k_{[\text{D-elim}]}} = \frac{(44/56)}{(32/68)} = 1.8$$

An inverse isotope effect of $k_{[\text{H-transfer}]}/k_{[\text{D-transfer}]} \approx 0.5$ favoring the transfer of Co−D over Co−H was determined from the

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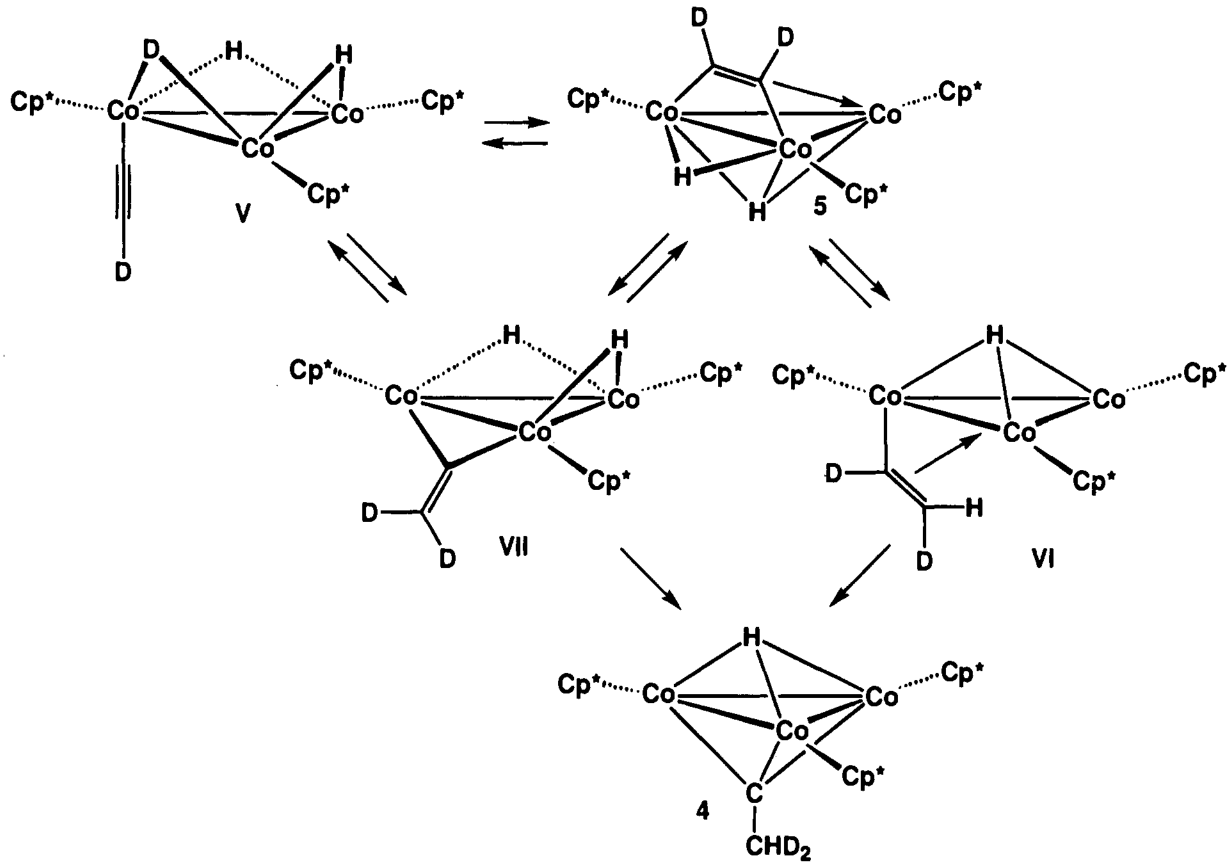
Scheme 8



excess deuterium incorporated into the ethylidyne ligand of 3 formed in the reaction of **1**-d_4 with acetylene. Therefore, we estimate an inverse isotope effect of $k_{HH}/k_{DD} \approx 0.3$ (0.5/1.8 = 0.3) for the elimination of H_2 from cobalt. We have confidence in the relative magnitude of these isotope effects, but because of the number of independent measurements of limited accuracy that go into their calculation, the absolute values of the isotope effects should be considered as very approximate.

Conclusion

These detailed kinetic and deuterium labeling studies of the reaction of tetrahydride tricobalt cluster **1** with acetylene have revealed distinctive mechanisms for the formation of mono(ethylidyne) trihydride cluster **3** and mono(ethylidyne) monohydride cluster **4**. The selective deuteration of trihydride cluster **3** is consistent with the presence of a μ-ethylidene intermediate. After loss of H_2, deuterium scrambled acetylene dihydride cluster **5** is formed which is subsequently converted to mono(ethylidyne) monohydride cluster **4**.

Experimental Section

General Methods. All manipulations were performed under a nitrogen atmosphere in an inert atmosphere glovebox or by standard high-vacuum techniques. Reactions were performed in 1.9 mL thick-walled resealable NMR tubes or in 35 mL thick-walled flasks equipped with Teflon valves. The molar amounts of H_2 and acetylene were measured on a high-vacuum line using pressure, volume, and temperature measurements. ^1H NMR spectra were obtained on a Bruker WP200, WP270, or AM500 spectrometer. $^{13}C\{^1H\}$ NMR spectra were obtained on a Bruker AM500 (126 MHz) spectrometer. Mass spectra of solid samples were determined on a Kratos MS-80 spectrometer. Mass spectra of gaseous samples were recorded on a VG Analytical ZAB-2F spectrometer operating at 70 eV of ionizing electrons at 25 °C. Elemental analyses were performed by Desert Analytics (Tucson, AZ). ^1H NMR simulations were performed employing the program RACCOON,[34] and kinetic data were simulated with the program GEAR.[81] The temperature dependence of the solubility of H_2 in benzene,[82] the density of benzene,[83] the vapor pressure of benzene,[83] and the temperature dependence of the solubility of acetylene in benzene[84] were obtained from the literature.

Diethyl ether, hexane, pentane, and benzene were distilled from purple solutions of sodium and benzophenone; toluene was distilled from sodium. Benzene-d_6 and toluene-d_8 were distilled from sodium and benzophenone or from sodium/potassium alloy. Acetylene (National Cylinder Gas) was passed through a trap cooled to −78 °C prior to use. $H^{13}C{\equiv}^{13}CH$, $DC{\equiv}CD$, $D^{13}C{\equiv}^{13}CD$, D_2, CD_3OD, $LiAlD_4$ (Cambridge Isotope Laboratories), and H_2 (Liquid Carbonic) were used as received.

$Cp^*_3Co_3(\mu_2\text{-}H)_3(\mu_3\text{-}H)$ (1). A solution of $LiAlH_4$ (0.31 g, 8.2 mmol) and $[Cp^*CoCl]_2$[85] (1.0 g, 2.2 mmol) in Et_2O (40 mL) was stirred at room temperature for 20 min. EtOH (10 mL) was added dropwise over 2 min and the resulting solution was stirred 30 min to form a purple solution. Solvent was evaporated and the residue was extracted with Et_2O and filtered through Celite. Evaporation of Et_2O yielded a black solid whose ^1H NMR showed a 1.2:1 ratio of Cp* resonances for **1**:$Cp^*Co(\mu\text{-}H)_3CoCp^*$.[11] Vacuum sublimation of the residue (120 °C, 24 h) gave $Cp^*Co(\mu\text{-}H)_3CoCp^*$ (200 mg, 23%) as a purple sublimate which was ~90% pure by ^1H NMR analysis. $Cp^*Co(\mu\text{-}H)_3CoCp^*$ was purified further by crystallization from pentane at −20

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°C. The sublimation residue was extracted with toluene, filtered through Celite, and evaporated to give **1** (444 mg, 53%) which was ~95% pure by ^{1}H NMR analysis and was used for subsequent preparative reactions without further purification. **1** used in NMR experiments was crystallized from pentane at −20 °C. ^{1}H NMR (C_6D_6, 200 MHz, 22 °C), δ 62.3. HRMS (EI, 45 eV, 200 °C), calcd (found) for $C_{30}H_{45}Co_3$: 586.1825 (586.1819, M^+). Anal. Calcd (found) for $C_{30}H_{45}Co_3$: C, 61.44 (61.42); H, 8.42 (8.39).

$Cp^*_3Co_3(\mu_3\text{-}CCH_3)_2$ (2). A black solution of **1** (70 mg, 0.12 mmol) and acetylene (6.16 mmol) in 5 mL of benzene was heated at 100 °C for 50 h. A precipitate was filtered from the resulting purple suspension, washed with hexane, and dried to give 48 mg of $Cp^*_3Co_3(\mu_3\text{-}CCH_3)_2$ (**2**) as a purple microcrystalline solid which was ~95% pure by ^{1}H NMR analysis. The combined filtrates were evaporated, washed with 5 mL of acetone, and dried to yield **2** (total 67 mg, 88%). ^{1}H NMR (200 MHz, C_6D_6) δ 4.48 (s, 6 H, μ_3-CCH_3), 1.57 (s, 45 H, C_5Me_5). HRMS (EI) calcd (found) for $C_{34}H_{51}Co_3$ (M^+): 636.1986 (636.2004).

$Cp^*_3Co_3(\mu_3\text{-}{}^{13}C^{13}CH_3)_2$ (2-$^{13}C_2$). An NMR tube containing **1** (4 mg, 0.007 mmol) and $H^{13}C{\equiv}^{13}CH$ (0.23 mmol) in 0.3 mL of C_6D_6 was heated at 80 °C for 50 h. Unreacted acetylene was removed via 5 freeze−pump−thaw cycles; ^{1}H NMR analysis indicated that **2-$^{13}C_2$** constituted ~95% of the material in solution. ^{1}H NMR (500 MHz, C_6D_6) δ 4.48 (dd, $^1J_{CH}$ = 124 Hz, $^2J_{CH}$ = 6 Hz, μ_3-CCH_3), 1.57 (s, C_5Me_5); $^{13}C\{^1H\}$ NMR (126 Hz, C_6D_6) δ 336 (d, J_{CC} = 27 Hz, μ_3-$\mathit{C}CH_3$), 91.6 (s, C_5Me_5), 44.3 (d, J_{CC} = 27 Hz, μ_3-$C\mathit{C}H_3$), 10.7 (s, $C_5\mathit{Me}_5$).

$Cp^*_3Co_3(\mu_2\text{-}H)_3(\mu_3\text{-}CCH_3)$ (3). A flask containing **1** (100 mg, 0.17 mmol) and acetylene (1.43 mmol) in 5 mL of benzene was sealed under 1 atm of H_2 at 77 K and heated at 80 °C for 3 h to produce a green solution (H_2 pressure at 80 °C is calculated to be ≤4.5 atm). After filtration through Celite, benzene was evaporated and the residue was washed with hexane to give $Cp^*_3Co_3(\mu_2\text{-}H)_3(\mu_3\text{-}CCH_3)$ (**3**) (51 mg, 53%) as a green microcrystalline solid which was >95% pure by ^{1}H NMR analysis. **3** was further purified by crystallization from toluene at −20 °C. ^{1}H NMR (200 MHz, C_6D_6) δ 5.12 (s, 3 H, μ_3-CCH_3), 1.67 (s, 45 H, C_5Me_5), −32.24 (s, 3 H, Co-μ-H). HRMS (EI) calcd (found) for $C_{32}H_{49}Co_3$ ($M^+ - 2H$): 610.1827 (610.1816). Anal. Calcd (found) for $C_{32}H_{51}Co_3$: C, 62.75 (63.03); H, 8.39 (8.09).

$Cp^*_3Co_3(\mu_2\text{-}H)_3(\mu_3\text{-}{}^{13}C^{13}CH_3)$ (3-$^{13}C_2$). An NMR tube containing **1** (4 mg, 0.007 mmol) and $H^{13}C{\equiv}^{13}CH$ (0.23 mmol) in 0.3 mL of C_6D_6 was heated at 80 °C for 30 min. Unreacted acetylene was removed via 5 freeze−pump−thaw cycles and the sample was analyzed without isolation. ^{1}H NMR analysis revealed Cp* resonances at δ 62 (**1**), 54 (**4-$^{13}C_2$**), and 1.67 (**3-$^{13}C_2$**) in a 1.0:3.2:2.5 ratio. ^{1}H NMR (500 MHz, C_6D_6) δ 5.12 (dd, $^1J_{CH}$ = 124 Hz, $^2J_{CH}$ = 7 Hz, μ_3-CCH_3), 1.67 (s, C_5Me_5), −32.24 (s, Co-μ-H); $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6) δ 316.1 (d, J_{CC} = 27 Hz, μ_3-$\mathit{C}CH_3$), 92.3 (s, C_5Me_5), 45.7 (d, J_{CC} = 27 Hz, μ_3-$C\mathit{C}H_3$), 11.6 (s, $C_5\mathit{Me}_5$).

$Cp^*_3Co_3(\mu_3\text{-}H)(\mu_3\text{-}CCH_3)$ (4). A green solution of **3** (130 mg, 0.21 mmol) in 15 mL of toluene was refluxed for 3 days in an open tube under N_2 to produce a brown solution. The solution was filtered through Celite and toluene was evaporated under vacuum to give $Cp^*_3Co_3(\mu_3\text{-}H)(\mu_3\text{-}CCH_3)$ (**4**) (97 mg, 75%) which was 95% pure by ^{1}H NMR analysis. Crystallization from toluene at −20 °C afforded pure **4** (41 mg, 32%) as brown crystals. ^{1}H NMR (200 MHz, C_6D_6) δ 53.6 (brs, C_5Me_5). HRMS (EI) calcd (found) for $C_{32}H_{49}Co_3$ (M^+): 610.1827 (610.1833). Anal. Calcd (found) for $C_{32}H_{49}Co_3$: C, 62.95 (63.01); H, 8.09 (8.22).

Generation of $Cp^*_3Co_3(\mu\text{-}H)_2(\mu_3\text{-}\eta^2\text{-}HCCH)$ (5). An NMR tube containing **1** (4 mg, 0.007 mmol) and acetylene (0.23 mmol) in 0.3 mL of C_6D_6 was shaken periodically at 23 °C for 11.5 h. Unreacted acetylene was removed via 5 freeze−pump−thaw cycles and the sample was analyzed without isolation due to thermal instability. ^{1}H NMR analysis (200 MHz, C_6D_6) revealed Cp* resonances for 40% **1** (δ 62), 7% **3** (δ 1.67), 24% **4** (δ 54). In addition, a Cp* resonance at δ 1.85 which accounted for 29% of the Cp* resonances along with resonances at δ 7.50 (s, 2 H, μ_3-η^2-HCCH) and −23.45 (s, 2 H, Co-μ-H) were assigned to the bridging acetylene cluster $Cp^*_3Co_3(\mu\text{-}H)_2(\mu_3\text{-}\eta^2\text{-}HCCH)$ (**5**).

Generation of $Cp^*_3Co_3(\mu\text{-}H)_2(\mu_3\text{-}\eta^2\text{-}H^{13}CCH)$ (5-$^{13}C_2$). Cluster (**5-$^{13}C_2$**) was prepared as a mixture of clusters including **1**, **3-$^{13}C_2$**, and **4-$^{13}C_2$** from the reaction of **1** (4 mg, 0.007 mmol) and $H^{13}C{\equiv}^{13}CH$ (0.23 mmol) in 0.3 mL of C_6D_6 using a procedure analogous to that used to prepare **5**. ^{1}H NMR (500 MHz, THF-d_8) δ 7.21 (AA′XX′: $^1J_{CH}$ + $^2J_{CH}$ = 152 Hz, $^1J_{CC}$ + $^3J_{HH}$ = 25 Hz, individual coupling constants of $^1J_{CH}$ = 150 Hz, $^1J_{CC}$ = 22 Hz, $^3J_{HH}$ = 3 Hz, $^2J_{CH}$ = 2 Hz were determined by comparison to a simulated spectrum), 1.80 (C_5Me_5), Co-μ-H signal not observed. $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6) δ 151.3 (s, μ_3-η^2-HCCH), 90.4 (C_5Me_5), 11.6 ($C_5\mathit{Me}_5$).

Kinetics of the Reaction of 1 with Acetylene. An NMR tube containing **1** (3 mg, 0.005 mmol), C_6Me_6 (1 mg, 0.006 mmol), and 0.087 mmol of acetylene (1.9 atm over solution at 80 °C) in 0.53 mL of C_6D_6 was heated at 80 °C with continual agitation for 15 min. Unreacted acetylene was removed via 3 freeze−pump−thaw cycles and the tube was analyzed by ^{1}H NMR spectroscopy. The concentration of **1** was determined by integrating the Cp* resonance for **1** (δ 62) relative to the hexamethylbenzene resonance (δ 2.12). The initial rate constant was determined according to the formula $k_{obs} = \ln[(\mathbf{1}_0 - \mathbf{1}_t)/\mathbf{1}_0]$/time. The second-order rate constant for the disappearance of **1** was obtained from a plot of initial rate constants versus initial acetylene pressure.

Kinetics of the Reaction of 4 with H_2. An NMR tube containing **4** (2.5 mg, 0.004 mmol) and C_6Me_6 (0.005 mmol) in 0.5 mL of C_6D_6 was sealed under H_2 (740 Torr) at room temperature and heated to 80 °C where the pressure of hydrogen was calculated to be 1.1 atm. The tube was shaken continuously and analyzed periodically by ^{1}H NMR spectroscopy; concentrations were determined by integrating the Cp* resonance of **3** (δ 1.67) relative to the hexamethylbenzene resonance (δ 2.12). The pseudo-first-order rate constant was obtained from a plot of $\ln\{[\mathbf{3}_{inf}] - [\mathbf{3}_t]/[\mathbf{3}_{inf}]\}$ versus time. In order to obtain the hydrogen pressure dependence of the rate of conversion of **4** to **3**, a slightly modified procedure was employed to achieve H_2 pressure >1 atm. An NMR tube containing **4** (2.5 mg, 0.004 mmol) and C_6Me_6 (0.005 mmol) in 0.5 mL of C_6D_6 was cooled to 77 K and opened to a small volume manometer (35.1 mL) containing ~0.5 atm of H_2. The pressure drop indicated that 0.14 mmol of H_2 (2.8 atm, 0.012 M at 80 °C) had been transferred into the tube. First-order rate constants were obtained for reactions carried out under 2.3 and 5.2 atm of H_2 by an analogous procedure.

Kinetics of the Conversion of 3 to 4. An NMR tube containing **3** (3 mg, 0.004 mmol) and C_6Me_6 (0.005 mmol) in 0.55 mL of C_6D_6 was heated to reflux under nitrogen (740 Torr, 80 °C). The reaction was analyzed periodically by ^{1}H NMR spectroscopy; concentrations were determined by integrating the Cp* resonance of **3** (δ 1.67) relative to the hexamethylbenzene resonance (δ 2.12). The first-order rate constant for the conversion of **3** to **4** was determined from a plot of ln[**3**] versus time.

Equilibrium between 3 and 4 + H_2. A 1.62 mL NMR tube containing **3** (4.3 mg, 0.0070 mmol, 0.016 M) and C_6Me_6 (0.003 mmol, 0.007 M) in 0.44 mL of C_6D_6 was flame sealed under nitrogen (500 Torr). The tube was heated at 80 °C and analyzed periodically by ^{1}H NMR spectroscopy. The concentration of **3** was determined by integrating the Cp* resonance for **3** (δ 1.67) relative to the hexamethylbenzene resonance (δ 2.12); the concentration of **4** was calculated from mass balance. The concentration of H_2 in solution was calculated from mass balance and from tables of the temperature dependence of the solubility of hydrogen in benzene. When no further decrease in the concentration of **3** was observed (4 days) the solution was heated at 80 °C under 4.5 atm of H_2 for 12 h to quantitatively regenerate **3** [103 ± 5% by ^{1}H NMR analysis] which indicated that no decomposition had occurred. The equilibrium constant for the interconversion of **3** with **4** and H_2 was determined according to the following equation: $K_{eq} = [\mathbf{4}][H_2]/[\mathbf{3}]$. Cluster **3** was also quantitatively regenerated by hydrogenation of mixtures of **3** and **4** equilibrated at 90 and 105 °C.

Synthesis of 2 from 4 and Acetylene. A flask containing a brown solution of **4** (30 mg, 0.05 mmol) and acetylene (0.44 mmol) in 10 mL of benzene was heated to 100 °C for 8 h to form a purple solution. After evaporation of benzene under vacuum, the residue was washed with acetone and dried to give **2** (28 mg, 90%) which was >95% pure by ^{1}H NMR.

Kinetics of the Reaction of 4 with Acetylene. An NMR tube containing **4** (3 mg, 0.005 mmol), C_6Me_6 (1 mg, 0.006 mmol), and 0.23 mmol of acetylene (3.5 atm over solution at 80 °C) in 0.54 mL of C_6D_6 was heated at 80 °C with continual agitation for 48 min.

Unreacted acetylene was removed via 3 freeze−pump−thaw cycles. The concentration of **4** was determined by integrating the Cp* resonance for **4** (δ 54) relative to the hexamethylbenzene resonance (δ 2.12) in the ^{1}H NMR spectrum. Initial rate constants were calculated from the following formula: $k_{\text{obs}} = \ln[(\mathbf{4}_0 - \mathbf{4}_t)/\mathbf{4}_0]$/time.

Kinetics of the Conversion of 5 to 4. An NMR tube containing **1** (3 mg, 0.005 mmol), C_6Me_6 (0.9 mg, 0.005 mmol), and acetylene (0.23 mmol) in 0.31 mL of C_6D_6 was shaken periodically at 23 °C for 16.5 h. Unreacted acetylene was removed via 5 freeze−pump−thaw cycles and the sample was analyzed periodically by ^{1}H NMR spectroscopy at 23 °C. Concentrations were determined by integrating the Cp* resonances for **1** (δ 62), **3** (δ 1.67), **4** (δ 54 H), and **5** (δ 1.85) relative to the hexamethylbenzene resonance (δ 2.12). The first-order rate constant for the disapperance of **5** was obtained from a plot of ln[**5**] versus time.

$Cp^*_3Co_3(\mu_2\text{-}H)_2(\mu_2\text{-}D)(\mu_3\text{-}CCH_2D)$ (3-CH_2D). The reaction of **1** (4 mg, 0.007 mmol) and DC≡CD (0.23 mmol) using a procedure analogous to that used to prepare **3-$^{13}C_2$** generated **3-CH_2D** as the only diamagnetic product (40% of total clusters). **3-CH_2D** was analyzed without isolation. ^{1}H NMR (500 MHz, C_6D_6) δ 5.10 (brs, 2 H, μ_3-CCH_2D), 1.67 (s, 45 H, C_5Me_5), −32.27 (s, 2 H, Co-μ-H). Solid **3** (~1 mg) was then added to the solution and the resulting ^{1}H NMR spectrum provided the isotope shifts for the ethylidyne methyl resonance and the hydride resonance (Figure 4).

$Cp^*_3Co_3(\mu_2\text{-}H)_2(\mu_2\text{-}D)(\mu_3\text{-}^{13}C^{13}CH_2D)$ (3-$^{13}C^{13}CH_2D$). The reaction of **1** (4 mg, 0.007 mmol) and $D^{13}C{\equiv}^{13}CD$ (0.23 mmol) using a procedure analogous to that used to prepare **3-$^{13}C_2$** generated **3-^{13}C-$^{13}CH_2D$** as the only diamagnetic product (40% of total clusters). **3-$^{13}C^{13}CH_2D$** was analyzed without isolation (Figure 4). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6) δ 92.3 (s, C_5Me_5), 45.4 (dt, J_{CC} = 27 Hz, J_{CD} = 20 Hz, μ_3-CCH_2D), 11.6 (s, C_5Me_5).

Analysis of Isotopomers of 4 from Reaction of 1 with DC≡CD. An NMR tube containing **1** (4 mg, 0.007 mmol), C_6Me_6 (1 mg, 0.006 mmol), and DC≡CD (0.23 mmol) in 0.3 mL of C_6D_6 was heated at 80 °C for 30 min. Unreacted acetylene was removed via 5 freeze−pump−thaw cycles and the sample was analyzed by ^{1}H NMR spectroscopy. The concentration of **3-CH_2D** formed directly from **1** was determined by integration of the Cp* resonance for **3-CH_2D** (δ 1.67) relative to the hexamethylbenzene resonance (δ 2.12). The sample was then sealed under 1 atm of H_2 at 77 K and heated at 80 °C for 12 h to convert the initially formed paramagnetic mono(ethylidyne) isotopomers (δ 54) into diamagnetic clusters and the sample was reanalyzed by ^{1}H NMR spectroscopy. The amount of **3** formed by hydrogenation of **4** was then determined from the increase in intensity of the δ 1.67 resonance relative to the hexamethylbenzene resonance. The ratio of **3-CH_2D** to **3-CHD_2** was determined by cutting and weighing the resonances at δ 5.10 (μ_3-CCH_2D) and at δ 5.08 (μ_3-$CCHD_2$). The ratio was confirmed and error limits were established by comparison of the actual spectrum and simulated spectra of various mixtures of μ_3-CCH_2D:μ_3-$CCHD_2$ clusters.

MS Analysis of H_2 from Reaction of 1 with DC≡CD. ^{1}H NMR analysis of the reaction of **1** with DC≡CD in C_6D_6 at 80 °C for 30 min showed a 6:46:48 ratio of **1** (δ 62), **3** (δ 1.67), and **4** (δ 54). The tube was cooled to 77 K and mass spectral analysis of the noncondensable gases revealed the presence of H_2, HD, and D_2 in a 95.0:5.0:<0.5 ratio.

Similarly, reaction at 23 °C for 24 h gave a 19:36:10:37 ratio of **1** (δ 62), **3** (δ 1.67), **4** (δ 54), and **5** (δ 1.84) and mass spectral analysis of the noncondensable gases revealed a 97.5:2.5:<0.5 ratio of H_2, HD, and D_2.

$Cp^*_3Co_3(\mu_3\text{-}CCH_3)(\mu_3\text{-}CCHD_2)$ (2-CHD_2). An NMR tube containing **4** (3 mg, 0.005 mmol) and DC≡CD (0.23 mmol) in 0.3 mL of C_6D_6 was heated at 80 °C for 24 h to form **2-CHD_2** (~95% pure by ^{1}H NMR) which was analyzed without isolation. ^{1}H NMR (500 MHz, C_6D_6) δ 4.48 (s, 3 H, μ_3-CCH_3), 4.44 (brs, 1 H, μ_3-$CCHD_2$), 1.57 (s, 45 H, C_5Me_5). Benzene was evaporated and the purple solids were analyzed. HRMS (EI) calcd (found) for $C_{34}H_{49}D_2Co_3$ (M^+): 638.2112 (638.2135).

$Cp^*_3Co_3(\mu_2\text{-}D)_3(\mu_3\text{-}D)$ (1-d_4). $LiAlD_4$ (0.67 g, 30.5 mmol) was added over 10 min to a solution of $[Cp^*CoCl]_2$ (2.08 g, 4.53 mmol) in 125 mL of Et_2O and the solution was stirred for 30 min. CD_3OD (6.0 mL, 148 mmol) was then added dropwise over 20 min and the resulting red-brown solution was stirred for 30 min. Evaporation of solvent produced a black residue which was extracted with Et_2O and filtered through Celite. Evaporation of Et_2O and vacuum sublimation (120 °C, 17 h) of the residue gave **1-d_4** as the sublimation residue (590 mg, 33%) which was >95% pure by ^{1}H NMR analysis. Deuteration of the bridging positions of **1-d_4** was determined by degradation with CO and mass spectral analysis of the gases over solution. An NMR tube containing a black benzene solution of **1-d_4** was sealed under 1 atm of CO and heated at 80 °C for 30 min to form a clear orange solution of $Cp^*Co(CO)_2$.[11] Analysis of the gases above solution by mass spectrometry indicated the presence of D_2, HD, and H_2 in a 6:3:1 ratio which corresponds to 75% D.

Analysis of the Isotopomers of 3 from the Reaction of 1-d_4 with Acetylene. An NMR tube containing **1-d_4** (4 mg, 0.007 mmol), C_6Me_6 (1 mg, 0.006 mmol), and acetylene (0.23 mmol) in 0.3 mL of C_6D_6 was heated at 80 °C for 20 min. Unreacted acetylene was removed via 5 freeze−pump−thaw cycles. ^{1}H NMR analysis (500 MHz) revealed that 70% of **1-d_4** had reacted to form a 32:68 mixture of **3** (δ 1.67) and **4** (δ 54). Ethylidyne resonances were observed at δ 5.08 (**3-CHD_2**), δ 5.10 (**3-CH_2D**), and δ 5.12 (**3**). Cutting and weighing of these resonances indicated a 73:21:6 ratio of μ_3-$CCHD_2$:μ_3-CCH_2D:μ_3-CCH_3 ligands which was confirmed by comparison to simulated spectra. Hydride resonances for $(\mu_2\text{-}H)_3$ (δ −32.24), $(\mu_2\text{-}H)_2(\mu_2\text{-}D)$ (δ −32.27), and $(\mu_2\text{-}H)(\mu_2\text{-}D)_2$ (δ −32.30) were also observed. Due to broadening ($w_{1/2}$ = 9 Hz), the ratio of the hydride resonances could not be quantitatively determined. However, the major hydride isotopomer was $(\mu_2\text{-}H)(\mu_2\text{-}D)_2$. Solid **3** (~1 mg) was then added to the solution and the ^{1}H NMR spectrum of the mixture was obtained. The hydride resonance for $(\mu_2\text{-}H)(\mu_2\text{-}D)_2$ was shifted upfield from the resonance for **3** by 32 Hz which corresponds to an isotope shift of 64 ppb.

Analysis of the Isotopomers of 4 from the Reaction of 1-d_4 with Acetylene. An NMR tube containing **1-d_4** (4 mg, 0.007 mmol), C_6Me_6 (1 mg, 0.006 mmol), and acetylene (0.23 mmol) in 0.3 mL of C_6D_6 was heated at 80 °C for 20 min. Unreacted acetylene was removed via 5 freeze−pump−thaw cycles. ^{1}H NMR analysis (500 MHz) revealed that 70% of **1-d_4** had reacted to form a 32:68 mixture of **3** (δ 1.67) and **4** (δ 54) and that a 73:21:6 ratio of **3-CHD_2:3-CH_2D:3** was present. The sample was then sealed under 1 atm of H_2 at 77 K and heated at 80 °C for 12 h to convert **4** into **3** and the mixture was reanalyzed by ^{1}H NMR spectroscopy. The concentration of diamagnetic mono(ethylidyne) isotopomers increased by 210% and a 67:28:5 ratio of **3-CHD_2:3-CH_2D:3** was determined by cutting and weighing the ethylidyne methyl resonances and by comparison to simulated spectra. Comparison of the spectrum of the final reaction mixture to simulated spectra of a mixture containing 32% of a 73:21:6 ratio of **3-CHD_2:3-CH_2D:3** (initially formed **3**) and 68% of a 65:35:<5 ratio of **3-CHD_2:3-CH_2D:3** gave a good fit.

MS Analysis of Hydrogen from Reaction of 1-d_4 with Acetylene. An NMR tube containing **1-d_4** (4 mg, 0.007 mmol) and acetylene (0.23 mmol) in 0.3 mL of C_6D_6 was shaken periodically at 23 °C for 24 h. Mass spectral analysis revealed that the noncondensable gases consisted of 66% D_2, 25% HD, and 9% H_2.

Acknowledgment. Financial support from the National Science Foundation and the Department of Energy, Office of Basic Energy Sciences, is gratefully acknowledged. R.A.W. and S.L.H. thank the Department of Education for fellowships. We thank Dr. Cornelis E. C. A. Hop for performing the mass spectral analysis of gas samples and the Amoco Corporation is acknowledged for their donation of the VG Analytical ZAB-2F spectrometer.

Supplementary Material Available: Table for the temperature dependence of the ^{1}H NMR chemical shift of **4**, tables and figures for the rate of reaction of **1** and **4** with acetylene and for the interconversion of **3** and **4**, and spectra of deuterated isotopomers of **2** and **3** (11 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA943016W