C–H Bond Activation of Simple Alkenes with $(C_5H_5)Co$ Fragments: Preparation, Molecular Structure, and Dynamical Behaviour of Tri- and Tetranuclear Cyclopentadienylcobalt Cluster Complexes with μ-Cycloalkyne Ligands

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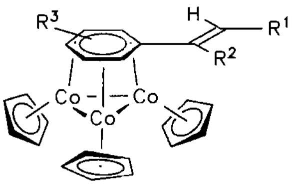
Vicinal C–H bonds of the cycloalkenes C_nH_{2n-2} ($n = 5-8$) were activated upon treatment under mild conditions with reactive sources of the $(C_5H_5)Co$ fragment. With $[(C_5H_5)Co(C_2H_4)_2]$ (**2a**), the trinuclear cluster complexes $[H_2\{(C_5H_5)Co\}_3\{\mu_3\text{-}C_2(CH_2)_{n-2}\}]$ (**5a**: $n = 5$; **5c**: $n = 7$; **5d**: $n = 8$) were formed. Using the more reactive $[(C_5H_5)_2Co]/K$, **5a**–**5d** were obtained, along with small amounts of the tetranuclear $[\{(C_5H_5)Co\}_4\{\mu_4\text{-}C_2(CH_2)_{n-2}\}]$ (**8a**–**c**: $n = 5-7$). X-ray structure analyses of **5c**, **d** and **8b**, **c** were performed. A μ_3-$\|$ (or μ_3-η^1:η^2:η^1) coordination of the cycloalkyne ligands was found in the trinuclear cluster complexes. The tetranuclear **8b**, **c** had the cycloalkynes quadruply bridging (μ_4-η^1:η^2:η^2:η^1) a butterfly arrangement of the metal atoms. The acetylenic carbon–carbon bonds are considerably lengthened upon coordination [1.392(4), 1.398(3) Å in **5c**, **d**; 1.464(8), 1.499(5) Å in **8b**, **c**]. Three dynamic processes – alkyne "walk" on top of the Co_3 triangle, μ_2-hydride migration, and μ_2/μ_3-hydride exchange – are operational in the trinuclear **5a**–**d**. Dynamic NMR data for **5a** are consistent with a "windshield-wiper" mechanism for the alkyne migration. Hydride exchange is associated with a higher energy barrier, and is probably an independent dynamic process.

From the very beginning of modern-day organometallic chemistry, the cyclopentadienyl d^9-metal fragment $(C_5H_5)M$ (M = Co, Rh, Ir) has played a central role in low-nuclearity cluster chemistry. Numerous transformations of small molecules have been reported to take place on a preformed $[(C_5H_5)M]_n$ frame, or during the assemblage of such a cluster core[1]. Oligonuclear complexes may be assembled by the stepwise addition of $(C_5H_5)M$ fragments, generated from suitable precursors, to an unsaturated organic substrate[2]. For example, a large number of cluster complexes **1** with face-capping arene ligands[3] can be synthesized in high yields from $[(C_5R_5)Co(C_2H_4)_2]$ (**2a**, **b**) and phenyl-substituted olefins[4]. However, with some ring-substituted styrene derivatives, formation of the μ-arylacetylene cluster complexes **3**, **4** was observed, along with the more expected **1**[5]. Obviously, for these substrates C–H activation, resulting in dehydrogenation of the vinyl group, had become competitive with the π-complexation of the arene nucleus.



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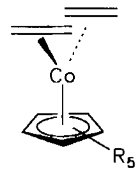
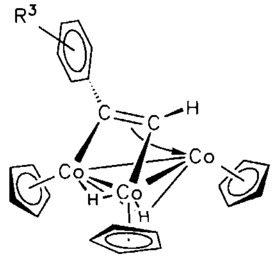


2a, R = H
2b, $R_5 = H_4Me$
2c, R = Me



3, R^3 = *p*-Me
4a-c, R^3 = *o*-, *m*-, *p*-F

Even at the time of the aforementioned studies, C–H activation by $(C_5H_5)Co$ fragments was known, and indeed, we ourselves used this very property for the synthesis of novel hydrocarbon-bridged oligonuclear complexes, starting from mononuclear substrates with enhanced ligand C–H reactivity[2,6,7]. It was tempting to try and achieve similar reactions with the less reactive, nonfunctionalized alkenes. Here, we fully describe reactions in which facile double C–H activation of simple cycloolefins takes place in the course of formation of tri- and tetranuclear cyclopentadienylcobalt

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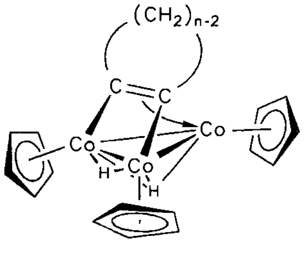
cluster complexes. Some of this work has already been communicated[8].

Results

1. Syntheses

i) Reaction of $[(C_5H_5)Co(C_2H_4)_2]$ (**2a**) *with Cycloalkenes C_nH_{2n-2} (n = 5–8):* Mixtures of **2a** and the cycloalkenes (either neat or in hexane solution) turned dark-brown when heated to 40–60 °C for several hours. After crystallization from *n*-hexane or column chromatography of the nonvolatile products on deactivated alumina, the trinuclear cluster complexes **5a**, **5c**, and **5d** were isolated in 20–40% yield. Surprisingly, in several experiments carried out under a variety of conditions, formation of the μ-cyclohexyne derivative **5b** was never observed. This complex could only be prepared from $[(C_5H_5)_2Co]$/K and cyclohexene (vide infra). A number of other products were also usually isolated. These included the tri- and tetranuclear μ_3-ethylidyne cluster complexes $[\{(C_5H_5)Co\}_3(\mu_3\text{-CMe})_2]$ (**6a**)[9] and $(\mu_3\text{-H})\{(C_5H_5)Co\}_4(\mu_3\text{-CMe})]$ (**7a**)[9,10], the mononuclear $[(C_5H_5)Co(\eta^4\text{-}C_5H_6)]$, and unreacted **2a**.



5a-d, n = 5-8

$[\{(C_5R_5)Co\}_3(\mu_3\text{-CMe})_2]$

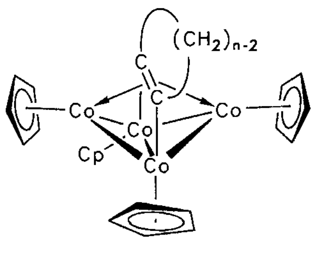
6a, R = H
6b, $R_5 = H_4Me$

$[(\mu_3\text{-H})\{(C_5R_5)Co\}_4(\mu_3\text{-CMe})]$

7a, R = H
7b, $R_5 = H_4Me$

The products **5a–d** are dark crystalline solids which are only moderately air-sensitive. They are moderately soluble in *n*-hexane and may be recrystallized from this solvent with some toluene (10–20%) added.

ii) Reactions of $[(C_5H_5)_2Co]$/K with Cycloalkenes C_nH_{2n-n} (n = 5–8): The reagent $[(C_5H_5)_2Co]$/K was prepared in diethyl ether at −50 °C from cobaltocene and a slight excess (1.1 to 1.2 equivalents) of potassium powder, and treated with the cycloalkene at −10 °C. After chromatographic work-up of the hexane-soluble components of the reaction mixtures, olive-green eluates containing principally the trinuclear **5a–d** were obtained. Some unreacted cobaltocene could also be recovered. In addition, after repeated chromatography on deactivated alumina, very small amounts (less than 1% yield) of the tetranuclear cluster complexes $[\{(C_5H_5)Co\}_4\{\mu_4\text{-}C_2(CH_2)_{n-2}\}]$ (**8b**: *n* = 6; **8c**: *n* = 7) could be isolated in pure crystalline form. The μ_4-cyclopentyne complex **8a** (*n* = 5) could be detected along with **5a** by mass and NMR spectroscopy. Enrichment of **8a** beyond 20% however proved to be impossible, even after repeated chromatography. No tetranuclear product was found in the product fractions of the reaction with cyclooctene. Pure **8b**, **c** are black crystalline solids with moderate solubility in *n*-hexane.



8a-c, n = 5-7

2. Crystal Structure Determinations

Single-crystal X-ray structure determinations were carried out for the trinuclear **5c**, **d** and tetranuclear **8b**, **c**. Crystal data are summarized in Tables 8 and 9; selected bond lengths and angles are collected in Tables 1 and 2. Views of the molecules are shown in Figures 1–4.

Table 1. Selected bond lengths [Å] and angles [°] for the complexes $[H_2\{(C_5H_5)Co\}_3\{\mu_3\text{-}C_2(CH_2)_{n-2}\}]$ (**5c**: *n* = 7; **5d**: *n* = 8) with estimated standard deviations in parentheses

	5c	**5d**
Co(1)–Co(2)	2.5003(13)	2.5004(12)
Co(1)–Co(3)	2.4483(14)	2.445(2)
Co(2)–Co(3)	2.438(2)	2.444(2)
Co(1)–C(1)	1.915(2)	1.914(3)
Co(2)–C(2)	1.912(2)	1.916(3)
Co(3)–C(1)	1.973(2)	1.967(3)
Co(3)–C(2)	1.985(2)	1.972(3)
C(1)–C(2)	1.398(3)	1.392(4)
C(1)–C(7)	1.515(3)	
C(1)–C(8)		1.502(4)
C(2)–C(3)	1.515(3)	1.516(4)
C(3)–C(4)	1.541(3)	1.529(5)
C(4)–C(5)	1.529(4)	1.523(8)
C(5)–C(6)	1.527(4)	1.549(14)
C(6)–C(7)	1.531(3)	1.506(7)
C(7)–C(8)		1.530(5)
Co(1)–C(Cp)	2.061(2)...2.128(3)	2.064(4)...2.122(4)
Co(2)–C(Cp)	2.044(3)...2.112(3)	2.031(5)...2.097(4)
Co(3)–C(Cp)	2.051(3)...2.098(3)	2.025(13)...2.168(14)
Co(1)–H(1)	1.66(3)	1.72(4)
Co(2)–H(1)	1.70(3)	1.68(4)
Co(3)–H(1)	1.65(3)	1.65(4)
Co(1)–H(2)	1.60(3)	1.56(3)
Co(2)–H(2)	1.56(3)	1.62(4)
C(2)–C(1)–C(7)	123.3(2)	
C(2)–C(1)–C(8)		124.5(3)
C(2)–C(1)–Co(1)	106.73(14)	106.7(2)
C(1)–C(2)–C(3)	123.8(2)	125.3(3)
C(1)–C(2)–Co(2)	106.75(14)	107.0(2)

Both types of complexes contain bridging cycloalkyne ligands. In the trinuclear **5c**, **d**, one face of an isosceles triangle of cobalt atoms is bridged by the cycloalkyne in the μ-‖[11] fashion. Two carbon atoms are connected to the tricobalt cluster via two shorter (Co1–C1, Co2–C2) and two longer (Co3–C1/2) bonds, making up a μ_3-η^1:η^1:η^2 coordination geometry. The hydrido ligands in **5c** and **5d** are found to bridge the Co1–Co2 edge and the Co_3 face, respectively.

The cluster core of the tetranuclear **8b**, **c** consists of a Co_4 butterfly, which is bridged in a μ_4-η^2:η^1:η^1:η^2 fashion

Figure 1. Molecular structure of $[H_2\{(C_5H_5)Co\}_3(\mu_3\text{-cycloheptyne})]$ (**5c**)

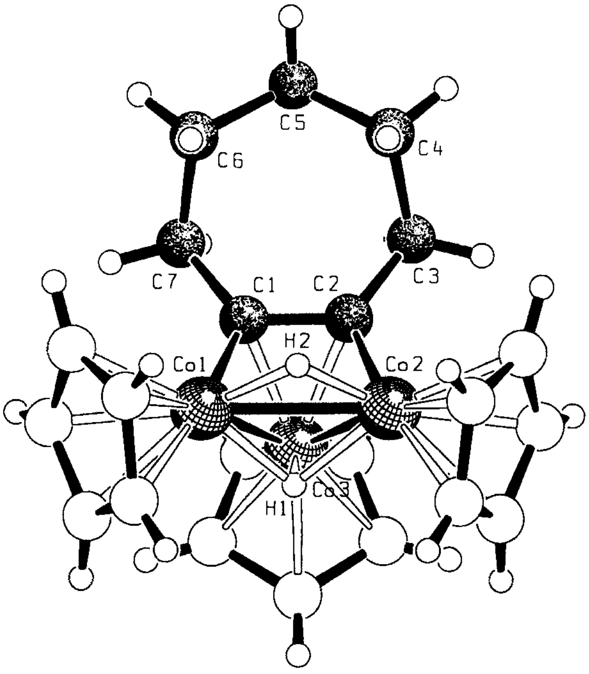
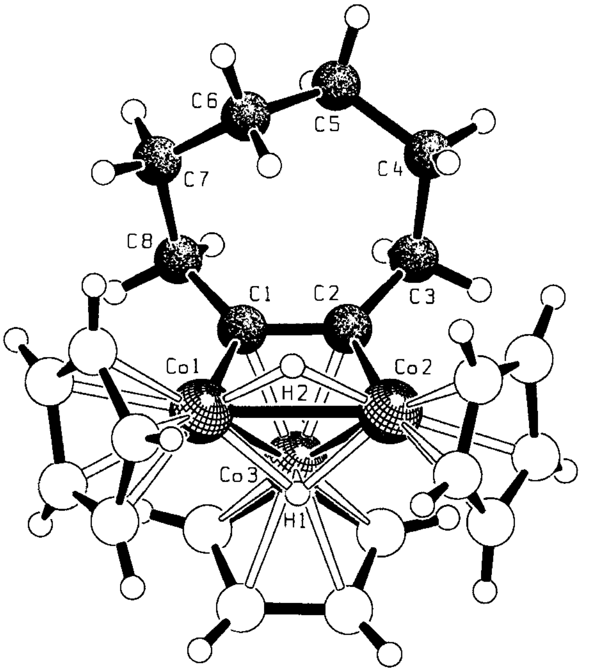


Figure 2. Molecular structure of $[H_2\{(C_5H_5)Co\}_3(\mu_3\text{-cyclooctyne})]$ (**5d**); only one of the sets of disordered atoms is shown

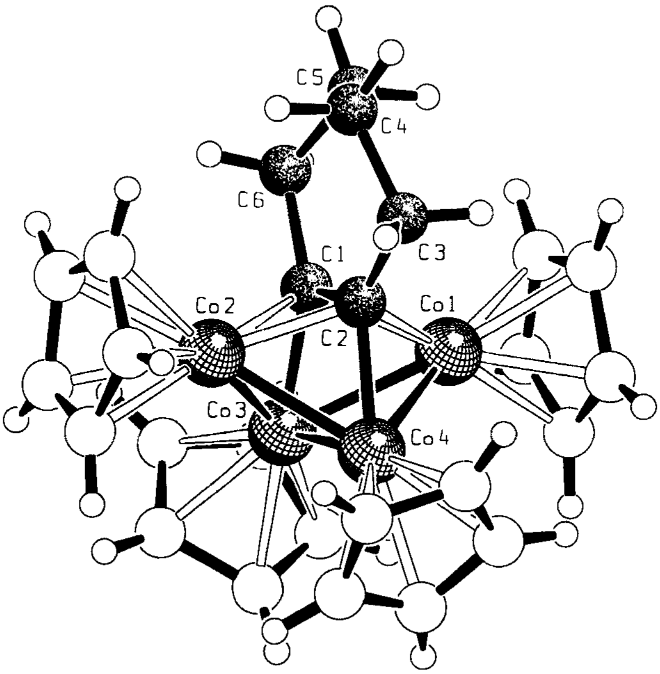


by the respective cycloalkyne ligand. Two shorter (to the "hinge" cobalt atoms) and four longer (to the "wing-tip" cobalt atoms) bonds are formed between the alkyne carbon atoms and the tetracobalt cluster. The Co_3C_2 and Co_4C_2 cluster cores of **5** and **8** are fairly symmetrical, with an approximate (or crystallographic in the case of **8c**) mirror plane bisecting the unsaturated carbon–carbon bond of the cycloalkyne.

Table 2. Selected bond lengths [Å] and angles [°] for the complexes $[\{(C_5H_5)Co\}_4\{\mu_4\text{-}C_2(CH_2)_{n-2}\}]$ (**8b**: n = 6; **8c**: n = 7) with estimated standard deviations in parentheses

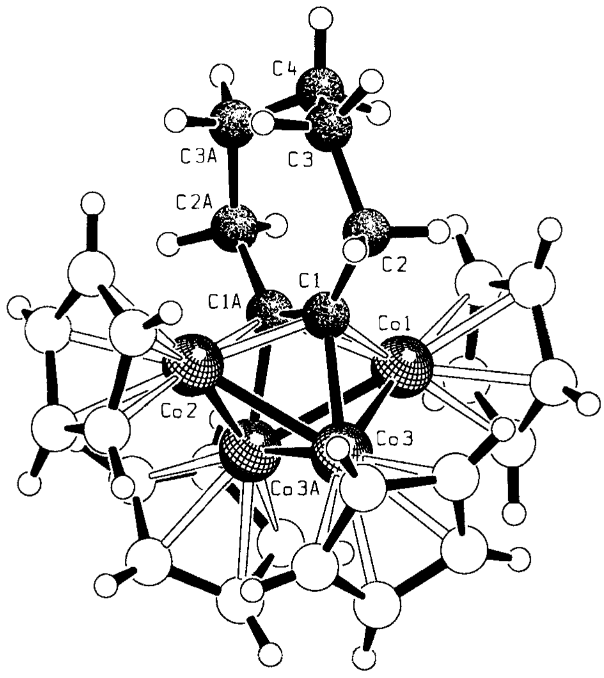
	8b	**8c**
Co(1)–Co(3)	2.356(2)	2.3661(12)
Co(1)–Co(4)	2.361(2)	
Co(2)–Co(3)	2.356(3)	2.3775(12)
Co(2)–Co(4)	2.367(3)	
Co(3)–Co(4)/Co(3a)	2.443(2)	2.417(2)
Co(1)–C(1)	1.960(9)	1.965(2)
Co(1)–C(2)	1.972(9)	
Co(2)–C(1)	1.959(9)	1.961(2)
Co(2)–C(2)	1.979(10)	
Co(3)–C(1)	1.936(5)	1.923(3)
Co(4)–C(2)	1.894(5)	
C(1)–C(2)/C(1a)	1.464(8)	1.499(5)
C(1)–C(6)/C(2)	1.566(7)	1.528(4)
C(2)–C(3)	1.501(7)	1.518(4)
C(3)–C(4)	1.543(11)	1.493(4)
C(4)–C(5)	1.50(2)	
C(5)–C(6)	1.547(11)	
Co(1)–C(Cp)	2.050(4)...2.101(7)	2.038(4)...2.105(3)
Co(2)–C(Cp)	1.985(9)...2.154(8)	2.01(2)...2.135(11)
Co(3)–C(Cp)	2.054(9)...2.139(9)	2.01(3)...2.142(13)
Co(4)–C(Cp)	2.030(12)...2.111(11)	
C(2)–C(1)–C(6)/C(1a)	115.7(5)	131.2(2)
C(2)/C(1a)–C(1)–Co(3)	104.4(5)	103.80(7)
C(1)–C(2)–C(3)	128.2(5)	
C(1)–C(2)–Co(4)	105.3(5)	

Figure 3. Molecular structure of $[\{(C_5H_5)Co\}_4(\mu_4\text{-cyclohexyne})]$ (**8b**)



The bond length between the two cluster-coordinated carbon atoms of the cycloalkyne ligands is much shorter in the trinuclear than in the tetranuclear systems [1.392(4) Å (**5c**), 1.398(3) Å (**5d**) vs. 1.464(8) Å (**8b**), 1.499(5) Å (**8c**)]. All cycloalkyne rings are puckered. The conformation of the cyclohexyne ligand in **8b** is close to a twist form. The

Figure 4. Molecular structure of $[\{(C_5H_5)Co\}_4(\mu_4\text{-cycloheptyne})]$ (**8c**); only one of the sets of disordered atoms is shown



cycloheptyne ligands adopt a chair conformation both in **5c** and in **8c**. The puckered cyclooctyne ligand in **5d** is disordered with C5 and C6 in two positions of occupancy with SOF's of 0.8 and 0.2, respectively.

3. Spectroscopic Investigations

For all members of the series of complexes **5** and **8**, molecular ions are observed in the electron impact mass spectra. While complexes **8** are quite resistant to fragmentation in the mass spectrometer, mass peaks due to loss of two hydrogen atoms from the molecules are found for **5**, along with those of other fragment ions, notably strong peaks at $m/z = 370$ $[\{(C_5H_5)Co\}_3 - 2\,H]^+$.

At room temperature, the proton NMR spectra (Table 3) of the trinuclear complexes **5** are broadened. Only one resonance ($\delta \approx 4.69$) is found for the three cyclopentadienyl ligands. However, two separate signals are observed in the high field region for the two hydrido ligands ($\delta \approx -12$, -29). The resonances of the $(n - 2)$ methylene groups appear as two groups of multiplets, $2.3 \leq \delta \leq 2.6$ with relative intensity 4, and $1.5 \leq \delta \leq 2.0$ with relative intensity $2 \times (n - 4)$. Likewise, in the carbon spectra (Table 4) one methylene resonance is found at $43 \leq \delta \leq 47$, along with one (**5a**, **b**) or two (**5c**, **d**) such signals at somewhat higher field ($26 \leq \delta \leq 33$). Broad resonances due to quaternary carbons appear at $160 \leq \delta \leq 166$. The Cp ligands give only one ^{13}C resonance around $\delta = 81$, except in the case of **5d**, where a broadened unequal doublet is observed.

On cooling, the ^1H-NMR resonances of the Cp groups broaden further and finally split into two components with an intensity ratio of 2:1 below 270 K. The resonances of the methylene groups also change. A representative series of spectra is shown in Figure 5. The carbon spectra also show a temperature dependence, although only the Cp resonances split into two signals on cooling; the resonances of the cycloalkyne ligands remain unchanged (save for minor changes in chemical shift). The signals in the high field region of the proton spectra of **5** sharpen on cooling. Each of the two resonances is resolved into a doublet below about 230 K [J(HH) about 8 Hz]. When the samples are heated above room temperature, progressive broadening of the hydride signals occurs, followed by coalescence to a broad resonance at $\delta = [\delta(\mu_2\text{-H}) + \delta(\mu_3\text{-H})]/2$ (Figure 6). In contrast, the cyclopentadienyl and methylene proton resonances sharpen above room temperature. Only one sharp ^{13}C resonance is observed for the three cyclopentadienyl rings in any of **5a–d** above 310 K. Unlike those of the trinuclear cluster complexes **5**, the NMR spectra of the tetranuclear derivatives **8** are not temperature-dependent. Two resonances of equal intensity are invariably found for the Cp ligands, both in the ^1H- and ^{13}C-NMR spectra (Table 5). Two groups of proton and carbon resonances are observed for the methylene groups. Compared to **5**, these signals are shifted downfield, especially in the proton spectra.

Table 3. ^1H-NMR data (δ, 200 MHz, in C_6D_6 at ambient temperature) for the complexes $[H_2\{(C_5H_5)Co\}_3\{\mu_3\text{-}C_2(CH_2)_{n-2}\}]$ (**5a–d**)

	5a ($n = 5$)	**5b** ($n = 6$)	**5c** ($n = 7$)	**5d** ($n = 8$)	mult.	int.
C_5H_5	4.68	4.68	4.68	4.69	s, br	15 H
$CH_2(CH_2)_{n-2}CH_2$	2.3–2.5	2.56	2.50	2.3–2.5	br	4 H
$CH_2(CH_2)_{n-2}CH_2$	1.96	1.58	1.57/1.75	1.5–1.8	br	2×(n–4) H
μ_2-H	–11.4	–11.8	–11.8	–11.8	s, br	1 H
μ_3-H	–28.8	–28.7	–28.3	–28.7	s, br	1 H

Table 4. $^{13}C\{^1H\}$-NMR data (δ, in C_6D_6 at ambient temperature) for the complexes $[H_2\{(C_5H_5)Co\}_3\{\mu_3\text{-}C_2(CH_2)_{n-2}\}]$ (**5a–d**)

	5a ($n = 5$)	**5b** ($n = 6$)	**5c** ($n = 7$)	**5d** ($n = 8$)	mult.[a]
alkyne-C	165.7	160.2	165.5	166.2	o, br
C_5H_5	80.6	81.1	81.6	81.1, 81.4	e
$CH_2(CH_2)_{n-2}CH_2$	42.9	44.7	47.0	43.3	o
$CH_2(CH_2)_{n-2}CH_2$	30.0	26.0	29.0, 33.2	26.9, 31.8	o

[a] e (even): CH or CH_3; o (odd): C or CH_2.

4. Electrochemistry

The redox chemistry of the μ_3-cyclooctyne cluster complex **5d** was investigated by means of cyclic voltammetry in 1,2-dimethoxyethane solution. For comparison, cyclic voltammograms were also recorded for the complex **4c** with the acyclic *para*-fluorophenylacetylene ligand. The data are compiled in Table 6. Both complexes show a similar potential/current response. At room temperature, irreversible oxidation takes place at around 0 V. This wave becomes essentially reversible at low temperature (−55 °C) for both complexes. A second, invariably irreversible oxidation is ob-

Figure 5. Temperature-dependent ^1H-NMR spectra (low-field region only) of $[H_2\{(C_5H_5)Co\}_3(\mu_3\text{-cyclopentyne})]$ (**5a**); S denotes residual solvent resonance ($[D_8]$toluene)

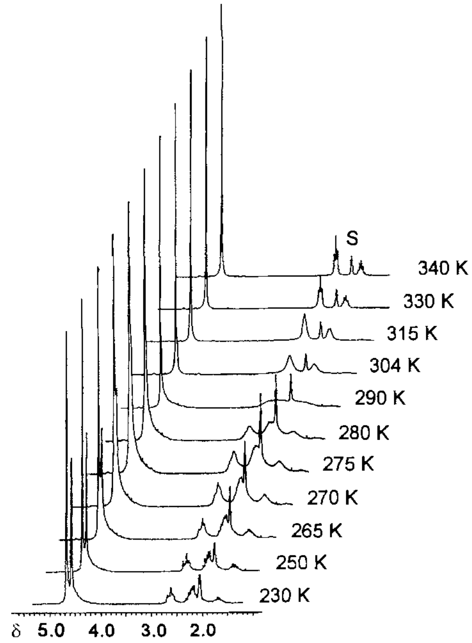
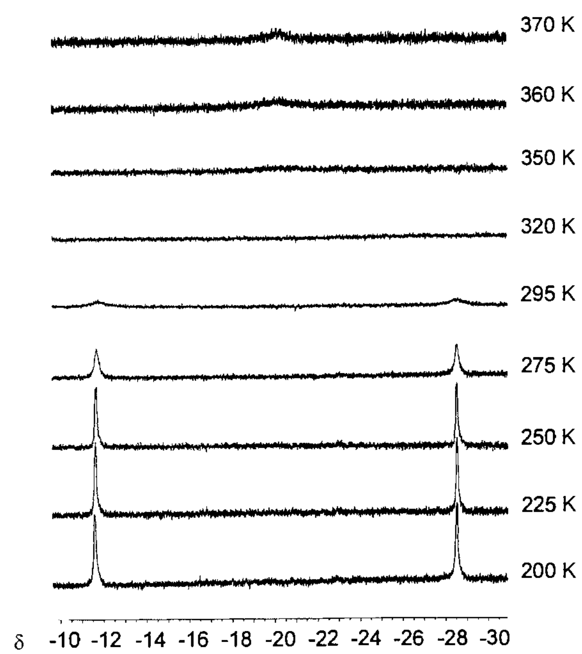


Figure 6. Temperature-dependent ^1H-NMR spectra (hydride-region only) of $[H_2\{(C_5H_5)Co\}_3(\mu_3\text{-cyclohexyne})]$ (**5b**)



served at 0.76 V. Irreversible reduction waves are found at rather negative potentials, −1.73 V (**5d**) and −1.54 V (**4c**), respectively. Again, a more reversible behaviour is observed on cooling.

Discussion

Table 5. ^1H- (200 MHz) and $^{13}C\{^1H\}$-NMR data (δ, in C_6D_6 at ambient temperature) for the complexes $[\{(C_5H_5)Co\}_4\{\mu_4\text{-}C_2(CH_2)_{n-2}\}]$ (**8a−c**)

	8a ($n = 5$)	**8b** ($n = 6$)	**8c** ($n = 7$)	mult.[a]	int.
$C_5\mathit{H}_5$	4.36, 4.45	4.39, 4.44	4.36, 4.50	s, s	2×10 H
C_5H_5	81.0, 81.8	81.1, 82.3	81.2, 82.8	e	
$C\mathit{H}_2(CH_2)_{n-2}C\mathit{H}_2$	3.72	3.32	3.31	br	4 H
$\mathit{C}H_2(CH_2)_{n-2}\mathit{C}H_2$	52.4	54.8	59.5	o	
$CH_2(C\mathit{H}_2)_{n-2}CH_2$	2.84	2.09	1.93	br	2×(n−2) H
$CH_2(\mathit{C}H_2)_{n-2}CH_2$	[b]	27.2	30.2, 34.0	o	
alkyne-C	[b]	[b]	164.5	o, br	

[a] e (even): CH or CH_3; o (odd): C or CH_2. − [b] not detected.

Table 6. Cyclic voltammetry data (in 1,2-dimethoxyethane, E^0 [V] (ΔE_p [mV]) vs. SCE for the complexes $[H_2\{(C_5H_5)Co\}_3\{\mu_3\text{-}C_2(CH_2)_6\}]$ (**5d**) and $[H_2\{(C_5H_5)Co\}_3\{\mu_3\text{-}(4\text{-}F{-}C_6H_5)C_2H_4\}]$ (**4c**); scan rate: 100 mV/s, supporting electrolyte $[nBu_4N][PF_6]$

	2+/+	+/0	0/−
5d	0.76[a]	0.00(35)[b]	−1.73(35)[b]
4c	0.76[a]	0.09(80)[b]	−1.54(80)[b]

[a] Irreversible. − [b] At −55 °C.

Among the many types of metal complexes which are able to activate C−H bonds, those with electrophilic early transition metals and/or 4d or 5d metals are predominant[12]. However, C−H activation at late first-row transition metal centres can also be a facile and favourable process. In such reactions, one or more of the following conditions are usually met: (1) highly reactive metal ligand fragments, (2) enhanced reactivity of the C−H bond(s), and (3) the formation of a very stable product. For example, many metal carbonyl fragments activate the C−H bonds of the reactive methylene group of cyclopentadiene to form a very stable cyclopentadienyl metal carbonyl complex. In the cobalt group, the short-lived fragments $[(C_5Me_5)(L)M]$ (M = Rh, L = PMe_3; M = Ir, L = CO, PMe_3) readily activate sp^3 and sp^2 C−H bonds in a variety of hydrocarbons R−H to give alkyl, alkenyl, and aryl derivatives $[(C_5Me_5)(L)M(R)(H)]$[12]. Activation of olefinic C−H bonds has also been observed with $[(C_5R_5)Co(C_2H_4)_2]$ (**2**). Cluster complexes such as $[\{(C_5R_5)Co\}_3(\mu_3\text{-CMe})_2]$ (**6a**: R = H[9]; **6b**: R_5 = H_4Me[9]), $[\{(C_5Me_5)Co\}_3(\mu_3\text{-CMe})(\mu_3\text{-H})]$[13], $[\{(C_5H_4Me)Co\}_3(\mu_3\text{-CMe})(\mu_2\text{-H})_3]$[14], and $[(\mu_3\text{-H})\{(C_5R_5)Co\}_4(\mu_3\text{-CMe})]$ (**7a**: R = H[9,10]; **7b**: R_5 = H_4Me[9]) are formed, along with other C−H activation products, when the complexes **2** are heated[10,13,14] or treated with dihydrogen[9]. It is obvious that such complex reactions must be driven by the high stability of the cyclopentadienyl cobalt cluster complexes, and by the high reactivity of the mononuclear starting materials.

For the present work, the cycloalkenes C_nH_{2n-2} (n = 5−8) were chosen as substrates because any double-bond shift reactions, which may be catalysed by the $(C_5H_5)Co$ reagent[15], are degenerate and do not lead to isomerization. In the reactions with the Jonas reagent **2a**, formation of the trinuclear cycloalkyne complexes **5** can be made competitive with the "decomposition" of **2a** by using a large excess of the cycloalkene and by judicious choice of the reaction conditions. However, at least some of the aforementioned "decomposition products" of **2a** are invariably present in the reaction mixtures. The difficult-to-separate μ_3-ethylidyne cluster complexes cannot form when the very reactive ethylene-free $[(C_5H_5)_2Co]/K$[16] is used as the source of $(C_5H_5)Co$ fragments instead of the more conventional **2a**. Hence, although the reactions with this reagent do not proceed cleanly, separation of the products **5** and **8** from the mainly insoluble by-products in such instances is usually less laborious.

Formally, the reactions leading to **5** and **8** represent activation of two vicinal C–H bonds of the cycloalkene, the two cleaved hydrogen atoms still being retained in the products **5** as hydrido ligands. Such reactions are known to take place with many olefins on trinuclear carbonyl metal cluster complexes[17]. Mechanistic information is available for some such cases[18]. The reactions described here are however much more complicated, since the metal cluster is only being formed from mononuclear fragments during the course of the reaction. In particular, we do not have any experimental information about at which stage of the reaction the C–H bonds are actually cleaved. The reactions with cobaltocene/K are particularly messy, and even potassium could be directly involved in the reaction with the olefin. Furthermore, we have no indication as to whether **5** are intermediates during the formation of **8**. At least with **2a**, cluster expansion to generate **8** from **5** is not possible.

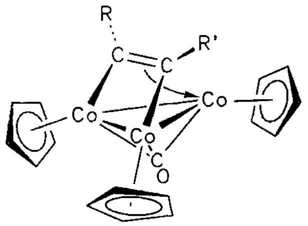
Mononuclear complexes of the type $[(C_5H_5)Co(C_2H_4)_{2-n}(\text{cycloalkene})_n]$ (n = 1, 2) could not be detected by ^{1}H-NMR spectroscopy during the reaction of **2a** with the cycloalkenes. Since π-coordination does not necessarily have to precede C–H activation of an olefin[19], such complexes are not required as intermediates. The generation of free cycloalkynes by some metal-promoted dehydrogenation reaction is unlikely. This would rather lead to mono- or dinuclear complexes, which are the known products of the reactions of **2a** with alkynes[16c].

Apart from **8**, only two other complexes based on a $[(C_5R_5)M]_4$ frame, namely $[\{(C_5H_5)Co\}_4(\mu_4\text{-1-oxa-3-cyclopentyne})]$ (**9**)[20] and $[\{(C_5H_5)Co\}_4(\mu_3\text{-H})_2(\mu_4\text{-HBBH})]$[21], have been reported. The former complex forms when the trinuclear precursor $[\{(C_5H_5)Co\}_3(\mu_3\text{-CO})(\mu_3\text{-1-oxa-3-cyclopentyne})]$ (**10b**) is heated to 190 °C for 24 hours. However, it appears that this reaction is peculiar to the cyclic alkyne. Derivatives with non-cyclic alkyne ligands and second-row transition metals undergo alkyne scission at high temperature, thereby forming carbonyl-free trinuclear bis(μ_3-alkylidyne) cluster complexes[22]. In contrast to such reactions, the complexes **8** are formed under mild thermal but fairly harsh chemical conditions. In view of the extremely low yield, we do not wish to speculate on possible mechanisms of formation for these complexes.

The μ_3-‖ coordination mode of the alkyne ligands, as found in **5** and the arylacetylene derivatives **3** and **4**[5], is quite common for trinuclear alkyne cluster complexes[23]. Many examples for complexes of the type $[\{(C_5R_5)(d^9\text{-}M)\}_3(\mu\text{-CO})(\mu\text{-alkyne})]$ (M = Co, Rh, Ir) have been reported in the literature[1]. These cluster complexes are isoelectronic with **5** and **3**, the μ_2- or μ_3-bridging carbonyl ligand formally replacing the two hydrides in **5** and **3**.

$[\{(C_5H_5)Co\}_4\{\mu_4\text{-}cyclo\text{-}(\text{-}OCH_2CCCH_2\text{-})\}]$

9



10a, R = R' = Et

10b, R⌒R' = CH_2OCH_2

The coordination geometry of the alkyne to the tricobalt cluster in **5c**, **d** corresponds to the pattern generally found for all the cluster complexes with μ_3-‖ alkyne coordination: two shorter (σ-)bonds from the two alkyne carbons to the two cobalt atoms forming the edge of the Co_3-cluster that is bridged by the alkyne in a parallel fashion, and two longer (π-)bonds to the third cobalt atom. The actual distances found in **5c** and **5d** (1.91 Å and 1.97...1.99 Å, respectively) compare well with those found in other symmetrical μ_3-‖ alkynes, for example in $[\{(C_5H_5)Co\}_3(\mu_3\text{-CO})(\mu_3\text{-alkyne})]$ (**10a**: alkyne = 3-hexyne[24]; **10b**: alkyne = 1-oxa-3-cyclopentyne[20]). The length of the unsaturated carbon–carbon bond C1–C2 of the μ_2-alkynes [1.398(3) Å in **5c**, 1.392(4) Å in **5d**] is longer than a typical double bond; it is comparable to that in **3** but appears to be somewhat longer than in the carbonyl derivatives **10a**, **b**.

The bond Co1–Co2, which is bridged both by the alkyne and the μ_2-hydrido ligand, is slightly longer than the other two cobalt–cobalt bonds in **5c** and **5d**. In contrast, all the cobalt–cobalt bonds in **3** are of equal length, while in the carbonyl derivatives **10a**, **b** they are more irregular. Although the positions of the hydrido ligands are not expected to be very precise, the refined cobalt–hydrogen distances lie in the range found in other μ_2-(Co_2) and μ_3-(Co_3) bridging hydrides[10,25,26,27].

Tetranuclear butterfly clusters with μ_4-alkyne ligands are relatively common[23], but have almost exclusively been restricted to metal carbonyl derivatives. Unfortunately, the problems of disorder and pseudosymmetry in the crystals of **8b**, **c** result in a poorly-defined geometry of the cycloalkyne rings. The structures of the Co_4C_2 cores are quite similar to the one other example based on a $[(C_5R_5)M]_4$ frame, namely **9**. Although the actual bond lengths and angles differ somewhat between the individual molecules, the general pattern with shorter "wing" cobalt–cobalt bonds, a longer "hinge" cobalt–cobalt bond, and a fairly long alkyne carbon–carbon bond is preserved. The angle between the two wings of the Co_4 butterfly (112.2° in **8b**, 110.2° in **8c**, 112.5° in **9**) is also comparable in all three structures. The unsaturated carbon–carbon bond lengths in the cycloalkyne ligands are among the longest observed in any alkyne cluster complex[28,29].

Judging by the bond angles through the alkyne units (C1–C2–C3, C1a–C1–C2, and C2–C1–C7/8), there is very little strain within the seven- and eight-membered cycloalkyne rings. These angles are only slightly smaller in **5c**, **d** than in the non-cyclic derivatives **3** and **10a** (124, 125° vs. 127°). In the tetranuclear **8b**, **c** the corresponding angles average 127°, but are less reliable due to the constraints which had to be introduced to refine the structures. In contrast, much smaller values (109° and 107°, respectively) have been reported for the five-membered cycloalkyne rings in **9** and **10b**[*].

The NMR spectra of the tetranuclear clusters **8** are straightforward. The small number of resonances reflects the high symmetry of the complexes. The temperature dependence of the NMR spectra of the trinuclear clusters **5** indicates molecular fluxionality on the NMR time scale (vide infra). Within both series of complexes, trinuclear **5**, and tetranuclear **8**, the NMR properties of all the ligands (cycloalkyne, C_5H_5, and hydride) are remarkably insensitive of the ring size of the cycloalkyne.

The availability of the series **5a** through **5d**, and of **8a** through **8c**, allows us to make some more general statements concerning the influence of the different coordination modes of the cycloalkynes on the NMR shifts. The carbon and proton resonances of the methylene groups in positions alpha to the unsaturated carbon–carbon bond are shifted downfield on going from the μ_3-η^1:η^1:η^2- to the μ_4-η^1:η^1:η^2:η^2-cycloalkyne ligand [$\Delta\delta(^1H) \approx 1$, $\Delta\delta(^{13}C) = 8...13$]. However, the quaternary carbon resonance for **8c** was found in the same region as those for **5** (around $\delta = 165$). This is in contrast to the μ-1-oxa-3-cyclopentyne ligand, where the corresponding resonance in the tetranuclear **9** was found 34 ppm downfield of that in the trinuclear **10b**. However, since only one experimental value is available for the series **8a** through **8c**, and the resonances are broad and difficult to detect, we do not wish to put too much emphasis on this observation.

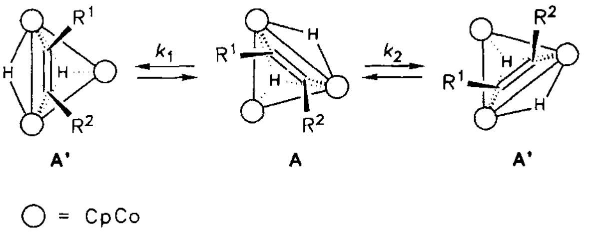
The two high-field resonances observed for each of **5a–d** are indicative of bridging hydrido ligands. The chemical shifts in solution are consistent with μ_2 (edge-bridging) ($\delta = 11...12$) and μ_3 (face-bridging) ($\delta = 28...29$) hydrides, in accord with the solid-state structures of **5c** and **5d**.

The changes in the NMR spectra of **5** which occur on cooling, indicate a hindered migration of the cycloalkynes on top of the metal clusters. Migration of the μ_2-hydrido ligand around all the edges of the Co_3-triangle must also take place. These two processes could in principle be independent or, more likely, be coupled to one another. From the dynamic NMR spectra alone, no conclusion can be reached about a possible retardation of hydride fluxionality on cooling. In order to explain the spectra, it suffices that the alkyne be *static* on the NMR time scale at low temperature[30].

We have previously commented on the fluxionality of the μ_3-arylacetylene cluster complexes **3** and **4**[5]. In contrast to these systems, some mechanistic information can be gained from an analysis of the temperature-dependent NMR spectra of the μ_3-cycloalkyne derivatives **5**.

Migration of μ_3-η^1:η^1:η^2-coordinated alkynes on top of trinuclear clusters has been studied experimentally in some detail, especially by Deeming[31a] and more recently by D'Agostino and McGlinchey[31b]. A "windscreen wiper" mechanism (Scheme 1) has been suggested[31,32].

Scheme 1



For **3** (R^1 = *p*-tolyl, R^2 = H) and **4** (R^1 = *p*-F–C_6H_4, R^2 = H), the three CpCo groups in any of the two chemical configurations **A** and **A'** (Scheme 1) are inequivalent. Since **A** and **A'** are mirror images, three anisochronous Cp resonances are observed in the slow exchange limit. However, **A** may be reached from **A'** by either of two inequivalent routes, with a priori different rate constants k_1 and k_2.

For a cycloalkyne ligand, $R^1 = R^2$, and hence **A** and **A'** become identical (Scheme 1). Therefore, only one energy barrier exists between **A** and **A'** (= **A**), and $k_1 = k_2$. Because of the effective mirror symmetry of the molecules, two cyclopentadienyl resonances are observed with an intensity ratio of 2:1 in the slow exchange regime. For the same reason, the ^{13}C resonances of the cycloalkyne are essentially independent of the temperature, and no line-splitting is observed. However, in the proton spectra of **5a** a quintuplet and a triplet are found for the methylene protons at high temperature, each of which splits into two components [relative intensities 2:2:1:1 with some overlap, effectively giving the observed 2:3:1 pattern (Figure 5)] at low temperature. Such an exchange of the two diastereotopic protons of each methylene group is consistent with the "windscreen-wiper" movement of the cycloalkyne (Scheme 1), where the two enantiofaces of the cycloalkyne ligand are interchanged (Scheme 2), but not with a simple rotation of the alkyne. In the other derivatives of **5** there are similar changes in the region of the CH_2 proton resonances with temperature. However, due to considerable overlap of the multiplets, the spectra cannot be assigned completely.

As a third dynamic process, mutual exchange of the μ_2- and μ_3-bridging hydrido ligands occurs in **5a–d**, as is obvious from the coalescence of the two high-field proton resonances. The averaged signals are observed at a chemical shift close to the arithmetic mean of the μ_2- and μ_3-H resonances. Therefore, a possible transient intermediate with two μ_2-hydrides cannot be present in significant concentration. This would bias the averaged signal in the direction

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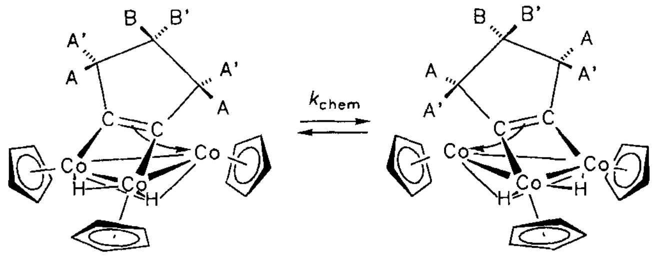
[*] Note added in proof (February 21, 1997): Recently, we prepared and crystallized the methylcyclopentadienyl derivatives of **5**, $[H_2\{(C_5H_4Me)Co\}_3\{\mu_3\text{-}C_2(CH_2)_{n-2}\}]$. Within the cyclopentyne ligand, the endocyclic angles through the alkyne unit [*d*(CC) = 1.394(3) Å] are 110.4(2) and 111.4(2)°.

Scheme 2



of the μ_2-H resonance, i.e. to a field lower than that actually observed.

Kinetic data ($\Delta G^{\ddagger}$ at the coalescence temperature) for both NMR-observable dynamic processes are summarized in Table 7. For the alkyne "walk", translation of the observed rate constant k_{obs} into that of the elementary chemical process $k_{chem} = c \times k_{obs}$[33] is by no means trivial. k_{obs} can be obtained at the coalescence temperature T_c with the standard formula for exchange of unequal doublets [i.e. the $(C_5H_5)Co$ resonances][34]. However, exchange of all $(C_5H_5)Co$ groups is only complete when the alkyne has undergone at least two of the elementary chemical steps. On the other hand, starting from configuration **A**, **A'** may be reached in two ways with equal probabilities ("clockwise" and "anti-clockwise" migration of the alkyne). The correction factors derived from these considerations cancel, hence $c = 2 \times 0.5 = 1$, $k_{chem} = k_{obs}$. The transmission factor k in the Eyring equation was set to 0.5, to account for the 50% probability for product formation from the transition state.

Our experimental values pertinent to alkyne migration in **5** are well within the range of those reported for similar complexes (Table 7). If we assume $\Delta H^{\ddagger}$ to be approximately constant for all derivatives of **5**, negative entropies of activation $\Delta S^{\ddagger}$ follow from the dependence of the observed $\Delta G^{\ddagger}$ (T_c) on T_c. The same conclusion appears to hold for the hydride exchange reactions as well, although the uncertainties are much larger here, due to the difficulty in determining T_c for the weak and broad hydride resonances.

Table 7. Activation parameters for alkyne migration and hydride exchange in the complexes $[H_2\{(C_5H_5)Co\}_3\{\mu_3\text{-}C_2(CH_2)_{n-2}\}]$ (**5a**–**d**) and related complexes

	alkyne[a]		hydride		ref.
	T_c[b]	$\Delta G^{\ddagger}(T_c)$[c]	T_c[b]	$\Delta G^{\ddagger}(T_c)$[c]	
5a ($n = 5$)	273±2	57.3(4)	335±20	58(4)	[d]
5b ($n = 6$)	210±1	44.9(2)	325±25	56(5)	[d]
5c ($n = 7$)	265±1	55.3(2)	335±25	58(5)	[d]
5d ($n = 8$)	284±1	64.4(2)	370±25	64(5)	[d]
$[H_2(CO)_9Ru_3(\mu_3\text{-}C_6H_{10})]$	263	52.5	263	49.0	[e]
$[H_2(CO)_9Ru_3(\mu_3\text{-}C_8H_{12})]$	319	65.3	264	49.3	[e, f]
$[H_2(CO)_9Os_3(\mu_3\text{-}C_9H_6)]$	295	58–62	268	49–51	[g]
$[H_2(CO)_9Os_3(\mu_3\text{-}C_8H_{12})]$	325	66.9	370	70.7	[f]
$[(\mu_2\text{-}CO)(CpCo)_3(\mu_3\text{-}HC_2tBu)]$	378	73.2			[h]

[a] From the coalescence of the C_5H_5 proton resonances. – [b] In K. – [c] In kJ/mol. – [d] This work. – [e] J. Evans, G. S. McNulty, *J. Chem. Soc., Dalton Trans.* **1981**, 2017. – [f] Ref.[18a]. – [g] Ref.[31a]. – [h] Ref.[24].

The alkyne "walk" on top of the Co_3 triangle and the mutual exchange of μ_2- and μ_3-hydrides could be coupled processes (i.e. be describable by a single mechanism) or else be independent. A likely sequence of steps for the first case would involve the partial opening of the μ_3-H bridge to give a species with two edge-bridging hydrides. Migration of the alkyne could then occur, followed by reformation of the μ_3-H bridge. As explained above, any intermediate with two edge-bridging hydrides can only be present in a low equilibrium concentration. Therefore, opening of the μ_3-hydrido bridge would be the rate-determining step. In such a scenario, a single set of chemical activation parameters should suffice to describe both NMR-observable dynamic processes. However, in **5**, coalescence of the resonances relevant to the two processes occurs in distinctly different temperature ranges (Table 7). If the two processes were in fact coupled, $\Delta G^{\ddagger}$ should be much larger than is actually observed for the high temperature process (assuming a negative entropy of activation, as explained above).

It has been pointed out[35] that the trinuclear μ_3-$\|$-alkyne complexes may be considered as polyhedral M_3C_2 clusters with a *nido* structure. Likewise, the tetranuclear alkyne-bridged butterfly complexes may be viewed as *closo*-M_4C_2 polyhedra. In accordance with theory, 14 cluster bonding electrons (cbe) are attained in both cases[36]. In the case of **3**, **4**, and **5**, two of the cbe are donated to the cluster by the two "*endo*" hydrogen atoms (the hydrides). A similar role is played by the bridging carbonyl ligand in **10**. The similar electronic structure of the dihydrides **3**–**5** and the carbonyl derivatives **10** is reflected in the electrochemical data. Reversible oxidations and reductions around 0.2 and −1.5 V vs. SCE, respectively, have been reported for two derivatives of **10**[20]. The respective anodic and cathodic shifts of the reduction and first oxidation potential of **10** may be explained by the electron-acceptor properties of the CO ligand.

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Experimental Section

Genral Procedures: All operations were carried out under an atmosphere of purified nitrogen or argon (BASF R3-11 catalyst) using Schlenk techniques. Solvents were dried by conventional methods. Alumina used as a stationary phase for column chromatography was first heated to 180–200°C under vacuum for several days, then treated with 5% of deoxygenated water and stored under nitrogen. The cycloalkenes C_nH_{2n-2} (n = 5–8) were obtained from commercial sources and distilled before use. The Jonas reagent $[(C_5H_5)Co(C_2H_4)_2]$ **2a** was prepared by published methods[37]. – NMR spectra were obtained on a Bruker AC 200 (200.1 MHz for ^1H, 50.3 MHz for ^{13}C) instrument. ^1H and ^{13}C chemical shifts are reported vs. $SiMe_4$ and were determined by reference to internal $SiMe_4$ or residual solvent peaks. To assign the carbon resonances their multiplicities were determined using the DEPT technique. The built-in thermocouple of the NMR probe was carefully calibrated before and after each series of variable temperature measurements with an acidified methanol standard. – Mass spectra were measured in the electron impact ionisation mode (EI) at 70 eV on Finnigan MAT 8230 and MAT CH7 spectrometers. – Electrochemical experiments were carried out using an EG&G PARC Model 173 potentiostat and a Model 175 Universal Programmer; a glassy carbon disk working electrode was employed. Redox potentials are referenced to the standard calomel electrode (SCE). – Elemental analyses were performed locally by the microanalytical laboratory of the organisch-chemisches Institut der Universität Heidelberg and by Mikroanalytisches Labor Beller, Göttingen.

Note: Potassium powder is extremely pyrophoric. Extreme care has to be exercised when residues from reactions with the cobaltocene/potassium reagent are disposed of. On several occasions, spontaneous ignition took place on exposure to air.

Reactions of Cycloalkenes with **2a** *(Method A):* Cyclopentene (dissolved in *n*-hexane) is added to a solution of **2a** in *n*-hexane. The solution is heated for 3.5 h at 40–45°C, followed by 2.5 h at 60°C. After cooling to room temperature the reaction mixture is filtered. The filtrate is concentrated to a small volume and chromatographed on alumina. The trinuclear cluster complexes **5** are eluted with *n*-hexane/toluene or toluene as an olive-green fraction. The products can be recrystallized from *n*-hexane with some toluene added. A second brown fraction obtained from the chromatography column with toluene consists of **7a**.

Reactions of Cycloalkenes with $[(C_5H_5)_2Co]/K$ *(Method B):* Cobaltocene is added to a suspension of potassium powder in ca. 100 ml of diethyl ether at –50°C. The mixture is slowly warmed to room temperature. The cycloalkene (neat or in diethyl ether) is slowly (approximately 0.5 h) added at around –10 to 0°C. The brown slurry is stirred for a further 1 h at room temperature. All volatiles are then removed under reduced pressure. An *n*-hexane extract (ca. 100 ml) of the residue is chromatographed on alumina. Unreacted cobaltocene is washed from the column with *n*-hexane. With *n*-hexane/toluene or toluene an olive-green fraction is eluted. When this fraction is again chromatographed on alumina, separation into two bands usually occurs. The first fraction affords the trinuclear cluster complexes **5** after removal of solvent. The second fraction (if any) consists of a mixture of **5** and the tetranuclear cluster complexes **8**, or pure **8**.

$[H_2\{(C_5H_5)Co\}_3(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-cyclopentyne})]$ (**5a**): – *Method A:* A 100 mg yield (31%) of **5a** was obtained from 5 ml of cyclopentene and 400 mg (2.22 mmol) of **2a** (chromatography with *n*-hexane/toluene, 10:1). As a by-product, 70 mg (24% based on Co) of **7a** was isolated.

Method B: The complex **5a** (480 mg, 7%) was obtained from 9.0 g (47.6 mmol) of cobaltocene, 2.1 g (52.5 mmol) of potassium, and 20 ml of cyclopentene. The second fraction of the final chromatographic separation (eluent: *n*-hexane/toluene, 3:1) consisted of a mixture of **5a** and 10–20% of the tetranuclear cluster complex **8a**. 150 mg (1.7%) of cobaltocene was recovered.

5a: M.p. (dec.) above 125°C. – ^1H NMR ($[D_8]$toluene, 370 K): $\delta = -20.2$ (br., 2H, hydrides), 1.86 [quint, *J*(HH) = 6.8 Hz, 2H, $\mathrm{CH_2C}H_2\mathrm{CH_2}$], 2.34 [t, *J*(HH) = 6.8 Hz, 4H, $\mathrm{C}H_2\mathrm{CH_2C}H_2$], 4.58 (s, 15H, Cp); ($[D_8]$toluene, 200 K): δ –28.8 [d, *J*(HH) = 8 Hz, 1H, μ_3-hydride], –11.3 [d, *J*(HH) = 8 Hz, 1H, μ_2-hydride], 1.65 (m, 1H, cyclopentyne), 2.17 (m, 3H, cyclopentyne), 2.58 (m, 2H, cyclopentyne), 4.55 (s, 5H, 1 Cp), 4.65 (s, 10H, 2 Cp). – $^{13}C\{^1H\}$ NMR ($[D_8]$toluene, 220 K): δ = 29.9 (CH_2), 42.8 (CH_2), 80.3 (Cp), 80.6 (Cp), 165.4 (br., alkyne-C). – MS (EI); *m/z* (%): 440 (24) $[M]^+$, 438 (10) $[M - 2]^+$, 372 (20) $[(CpCo)_3]^+$, 371 (20) $[(CpCo)_3 - H]^+$, 370 (100) $[(CpCo)_3 - 2H]^+$, 338 (10), 312 (10), 310 (10), 247 (20) $[(CpCo)_2 - H]^+$, 189 (46) $[Cp_2Co]^+$, 124 (7) $[CpCo]^+$. – $C_{20}H_{23}Co_3$ (440.21): calcd. C 52.65, H 5.27; found C 54.58, H 5.27.

$[H_2\{(C_5H_5)Co\}_3(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-cyclohexyne})]$ (**5b**) *and* $[\{C_5H_5)Co\}_4(\mu_4\text{-}\eta^1{:}\eta^2{:}\eta^2{:}\eta^1\text{-cyclohexyne})]$ (**8b**). – *Typical Attempt According to Method A:* A 660 mg (3.11 mmol) sample of **2a** and 10 ml of cyclohexene were used. A 90 mg (22%) yield of **7a** crystallized from the reaction mixture at –20°C. After chromatographic separation, 220 mg (33%) of **2a** and 110 mg (19%) of $[(C_5H_5)Co(C_5H_6)]$ were obtained (eluent: *n*-hexane), along with 80 mg (20%) of **7a** (eluent: toluene).

Method B: From 10.0 g (52.9 mmol) of cobaltocene, 2.5 g (62.5 mmol) of potassium powder, and 20 ml of cyclohexene, 850 mg (12%) of **5b** was obtained. Pure **8b** (10 mg) was obtained from the second fraction of the final chromatographic separation (eluent: *n*-hexane/toluene, 3:1). 860 mg (9%) of cobaltocene was recovered.

5b: M.p. (dec.) above 130°C. – ^1H NMR ($[D_8]$toluene, 370 K): $\delta = -20.3$ (br., 2H, hydrides), 1.57 [m, 4H, $\mathrm{CH_2(C}H_2)_2\mathrm{CH_2}$], 2.54 [m, 4H, $\mathrm{C}H_2\mathrm{(CH_2)_2C}H_2$], 4.64 (s, 15H, Cp); ($[D_8]$toluene, 200 K): δ –28.7 [d, *J*(HH) = 8 Hz, 1H, μ_3-hydride], –11.7 [d, *J*(HH) = 8 Hz, 1H, μ_2-hydride], 1.55 [br., 4H, $\mathrm{CH_2(C}H_2)_2\mathrm{CH_2}$], 2.46 [br., 4H, $\mathrm{C}H_2\mathrm{(CH_2)_2C}H_2$], 4.58 (s, 5H, 1 Cp), 4.62 (s, 10H, 2 Cp). – MS (EI); *m/z* (%): 454 (38) $[M]^+$, 452 (37) $[M - 2]^+$, 370 (100) $[(CpCo)_3 - 2H]^+$, 306 (20), 247 (34) $[(CpCo)_2 - H]^+$, 189 (76) $[Cp_2Co]^+$, 149 (50). – $C_{21}H_{25}Co_3$ (454.24): calcd. C 53.54, H 5.46; found C 55.54, H 5.55.

8b: MS (EI); *m/z* (%): 576 (96) $[M]^+$, 387 (11), 305 (20), 246 (10) $[(CpCo)_2 - 2H]^+$, 189 (100) $[Cp_2Co]^+$.

$[H_2\{(C_5H_5)Co\}_3(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-cycloheptyne})]$ (**5c**) *and* $[\{(C_5H_5)Co\}_4(\mu_4\text{-}\eta^1{:}\eta^2{:}\eta^2{:}\eta^1\text{-cycloheptyne})]$ (**8c**). – *Method A:* A total of 230 mg (19%) of **5c** was obtained from 10 ml of cycloheptene and 1.44 g (8.00 mmol) of **2a**. A first fraction of the product **5c** (110 mg, 9%) crystallized as black microcrystals from the reaction mixture at –20°C. A second crop (120 mg, 10%) was obtained as described above after chromatographic separation (eluent: *n*-hexane/toluene, 3:1). As a by-product, 20 mg (10%) of **7a** was isolated.

Method B: From 10.3 g (54.5 mmol) of cobaltocene, 2.4 g (60.0 mmol) of potassium powder, and 40 ml of cycloheptene, 830 mg (11%) of **5c** was obtained. Pure **8c** (10 mg) was isolated from the second fraction of the final chromatographic separation (eluent: *n*-hexane/toluene, 3:1). 850 mg (8%) of cobaltocene was recovered.

5c: M.p. (dec.) above 132°C. – ^1H NMR ($[D_8]$toluene, 370 K): $\delta = -20.2$ (br., 2H, hydrides), 1.6 (br., 4H, $\mathrm{CH_2C}H_2\mathrm{CH_2C}H_2\mathrm{CH_2}$), 1.8 [br., 2H, $\mathrm{(CH_2)_2C}H_2\mathrm{(CH_2)_2}$], 2.5 [br., 4H, $\mathrm{C}H_2\mathrm{(CH_2)_3C}H_2$], 4.66 (s, 15H, Cp); ($[D_8]$toluene, 220 K): δ –28.5 [d, *J*(HH) = 8 Hz, 1H, μ_3-hydride], –11.8 [d, *J*(HH) = 8 Hz, 1H, μ_2-hydride], 1.55 (br., 4H, $\mathrm{CH_2C}H_2\mathrm{CH_2C}H_2\mathrm{CH_2}$), 1.93 [br., 2H, $\mathrm{(CH_2)_2C}H_2\mathrm{(CH_2)_2}$], 2.58 and 2.22 [br., 4H, $\mathrm{C}H_2\mathrm{(CH_2)_3C}H_2$], 4.60 (s, 10H, 2 Cp), 4.63 (s, 5H, 1 Cp). – $^{13}C\{^1H\}$ NMR ($[D_8]$toluene, 220 K): δ 28.8 (CH_2), 33.7 (CH_2), 46.8 (CH_2), 81.6 (Cp), 81.8 (Cp), alkyne-C not detected. – MS (EI); *m/z* (%): 468 (13) $[M]^+$, 466 (12) $[M - 2]^+$, 371 (10) $[(CpCo)_3 - H]^+$, 370 (43) $[(CpCo)_3 - 2H]^+$, 247 (18) $[(CpCo)_2 - H]^+$, 189 (100) $[Cp_2Co]^+$, 124 (31) $[CpCo]^+$, 59 (18) $[Co]^+$. – $C_{22}H_{27}Co_3$ (468.23): calcd. C 57.30, H 6.02; found C 56.43, H 5.81.

8c: MS (EI); *m/z* (%): 590 (62) $[M]^+$, 397 (24), 189 (100) $[Cp_2Co]^+$, 124 (18) $[CpCo]^+$.

$[H_2\{(C_5H_5)Co\}_3(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-cyclooctyne})]$ (**5d**). – *Method A:* A 440 mg yield (38%) of **5d** was obtained from 80 ml of cycloheptene and 1.28 g (7.11 mmol) of **2a**. The product **5d** precipitated as a brown powder from the reaction mixture at –20°C.

Method B: From 10.0 g (52.8 mmol) of cobaltocene, 2.45 g (62.7 mmol) of potassium powder, and 80 ml of cycloheptene, 2.37 g (30%) of pure **5d** was obtained. Unreacted cobaltocene (770 mg, 8%) was removed from the reaction mixture by crystallization at –20°C. Crude **5d** (3.10 g, 39%) crystallized from the mother liquor at –78°C and was purified by the usual chromatographic procedure (eluent: toluene).

5d: M.p. (dec.) above 120°C. – ^{1}H NMR ([D$_8$]toluene, 370 K): δ = 1.7–1.4 [m, 8H, CH$_2$(C*H*$_2$)$_4$CH$_2$], 2.4–2.3 [m, 4H, C*H*$_2$(CH$_2$)$_4$C*H*$_2$], 4.65 (s, 15H, Cp); ([D$_8$]toluene, 220 K): δ = −28.7 [d, *J*(HH) = 8 Hz, 1H, μ_3-hydride], −11.8 [d, *J*(HH) = 8 Hz, 1H, μ_2-hydride], 1.8–1.5 [br., 8H, CH$_2$(C*H*$_2$)$_4$CH$_2$], 2.4–2.1 [br., 4H, C*H*$_2$(CH$_2$)$_4$C*H*$_2$], 4.57 (s, 5H, 1 Cp), 4.63 (s, 10H, 2 Cp). – ^{13}C{^{1}H} NMR ([D$_8$]toluene, 220 K): δ = 26.6 (CH$_2$), 31.6 (CH$_2$), 42.8 (CH$_2$), 81.0 (Cp), 81.2 (Cp), 166.2 (br., alkyne-C). – MS (EI); *m*/*z* (%): 482 (38) [M]$^+$, 480 (28) [M − 2]$^+$, 408 (10), 372 (10) [(CpCo)$_3$]$^+$, 371 (18) [(CpCo)$_3$ − H]$^+$, 370 (100) [(CpCo)$_3$ − 2 H]$^+$, 306 (10), 247 (28) [(CpCo)$_2$ − H]$^+$, 189 (65) [Cp$_2$Co]$^+$, 124 (16) [CpCo]$^+$. – $C_{23}H_{29}Co_3$ (482.25): calcd. C 57.23, H 5.80; found C 57.28, H 6.06.

Crystal-Structure Determinations: Single crystals were grown by slow evaporation of solvent (C$_6$D$_6$) from NMR samples at ambient temperature. Intensity data were collected on a Siemens STOE STADI-4 four circle diffractometer and corrected for Lorentz, polarisation, and absorption effects (Tables 8, 9). The structures were solved by the heavy atom method or direct methods, and refined by full-matrix least-squares based on F^2 using all measured unique reflections. All nonhydrogen atoms were given anisotropic displacement parameters. Cyclopentadienyl groups (except those in **5c** and **8c**) were treated as rigid pentagons. All hydrogen atoms (except the hydrido ligands in **5c**, **d**, which were located in difference Fourier syntheses, and refined) were inserted in calculated positions.

Table 8. Details of the crystal structure determinations of the complexes [H$_2${(C$_5$H$_5$)Co}$_3${μ_3-C$_2$(CH$_2$)$_{n-2}$}] (**5c**: n = 7; **5d**: n = 8)

	5c	**5d**
Formula	$C_{22}H_{27}Co_3$	$C_{23}H_{29}Co_3$
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	P–1
a [Å]	14.204(9)	9.015(5)
b [Å]	9.082(6)	9.114(5)
c [Å]	15.164(11)	13.899(7)
α [°]		86.74(4)
β [°]	102.28(5)	79.23(4)
γ [°]		64.65(4)
V [Å^3]	1911(2)	1013.5(9)
Z	4	2
M_r	468.23	482.25
d_c [g·cm^{-3}]	1.627	1.580
F_{000}	960	496
μ(Mo-$K\alpha$) [mm^{-1}]	2.57	2.43
X-Radiation, λ [Å]	Mo-$K\alpha$, graphite monochromated, 0.71069	
Data collect. temp. [K]	218	ambient
$2\Theta_{max}$ [°]	60	54
hkl-Range	−19/19, 0/12, 0/21	−11/11, −11/11, 0/17
Reflections measured	5564	4429
unique	5560	4429
observed [$I \geq 2\sigma(I)$]	4870	3466
Absorption correction	empirical	
Parameters refined	237	295
GooF	1.063	1.031
R (obs. reflections only)	0.032	0.035
$wR2$ (all reflections)	0.087	0.083
$w = 1/[\sigma^2(F)+(A\cdot P)^2+B\cdot P]$		
A, B	0.0423, 1.08	0.033, 0.61
P	$[\max(F_o^2, 0)+2 F_c^2]/3$	

Table 9. Details of the crystal structure determinations of the complexes [{(C$_5$H$_5$)Co}$_4${μ_4-C$_2$(CH$_2$)$_{n-2}$}] (**8b**: n = 6; **8c**: n = 7)

	8b	**8c**
Formula	$C_{26}H_{28}Co_4$	$C_{27}H_{30}Co_4$
Crystal system	orthorhombic	orthorhombic
Space group	$Pc2_1n$	$Pcmn$
a [Å]	9.105(5)	9.423(7)
b [Å]	14.280(7)	14.255(10)
c [Å]	17.076(8)	17.046(10)
V [Å^3]	2220(2)	2290(3)
Z	4	4
M_r	576.21	590.23
d_c [g·cm^{-3}]	1.724	1.712
F_{000}	1168	1200
μ(Mo-$K\alpha$) [mm^{-1}]	2.95	2.86
X-Radiation, λ [Å]	Mo-$K\alpha$, graphite monochromated, 0.71069	
Data collect. temp. [K]	218	218
$2\Theta_{max}$ [°]	55	60
hkl-Range	−9/11, −15/18, −18/22	0/13, 0/20, 0/23
Reflections measured	3864	3876
unique	3863	3454
observed [$I \geq 2\sigma(I)$]	3046	2842
Absorption correction	empirical	
Parameters refined	245	208
GooF	1.045	1.059
R (obs. reflections only)	0.039	0.033
$wR2$ (all reflections)	0.098	0.090
$w = 1/[\sigma^2(F)+(A\cdot P)^2+B\cdot P]$		
A, B	0.038, 5.28	0.0397, 1.52
P	$[\max(F_o^2, 0)+2 F_c^2]/3$	

5d: The C$_5$H$_5$ ligand on Co3 showed a twofold rotational disorder [refined site occupation factors (SOF) were 0.45 and 0.55]. C5 and C6 were also found disordered in two positions with final SOFs 0.8 and 0.2. – **8b**: Solution of the structure in the centrosymmetrical space group *Pcmn* did not give a well-defined cyclohexyne ring. Refinement in *Pc*2$_1$*n* caused large correlations, which resulted in several chemically non-sensible carbon–carbon distances. Therefore, chemically equivalent carbon–carbon and carbon–cobalt distances within the C$_6$ ring and Co$_4$C$_2$ core were restricted to be equal during refinement. – **8c**: The bonds C2–C3 and C3–C4 were restricted to be of equal length during refinement. The C$_5$H$_5$ ligands on Co2 and Co3 showed a twofold rotational disorder (refined SOFs were 0.48/0.52 and 0.65/0.35)[38].

The calculations were performed using the programs SHELXS-86 and SHELXL-93[39]. Graphical representations were drawn with SCHAKAL-88[40].

☆ Dedicated to Professor *Rolf Gleiter* on the occasion of his 60th birthday.

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