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Reactivity of tri- and tetra-nuclear ethylidyne cyclopentadienylcobalt clusters towards protonic acids

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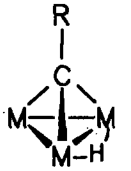
Abstract

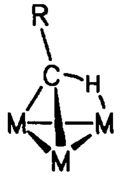
The bis(μ_3-ethylidyne) tricobalt cluster [$(CpCo)_3(\mu_3\text{-}CCH_3)_2$] (**1b**) is protonated by trifluoroacetic acid to give the dicobalt edge-protonated cation [$H(CpCo)_3(\mu_3\text{-}CCH_3)_2$]$^+$ [**1b** + H]$^+$. Protonation of the μ_3-ethylidyne tetracobalt cluster hydride [$H(CpCo)_4(\mu_3\text{-}CCH_3)$] (**3**) takes place in two consecutive steps. At low temperature [$H_2(CpCo)_4(\mu_3\text{-}CCH_3)$]$^+$ [**3** + H]$^+$ is formed first, and is then slowly converted into [$H_3(CpCo)_4(\mu_3\text{-}CCH_3)$]$^{2+}$ [**3** + 2H]$^{2+}$ by an excess of acid. As judged by the ^{1}H NMR data and the crystal structure of [**3** + X]$^+$[$(CF_3COO)_2X$]$^-$ (X = H or D) the *endo* hydrogens in [**3** + H]$^+$ and [**3** + 2H]$^{2+}$ occupy μ_3-(Co_3) face capping hydridic positions. The cations [**1b** + H]$^+$ and [**3** + H]$^+$ show hydride fluxionality in solution, which in the case of [**3** + H]$^+$ can be frozen out on the NMR timescale at low temperature ($\Delta G^{\neq}$ (203 K) = 40.8 kJ/mol). The structure of [**3** + X]$^+$ [$(CF_3COO)_2X$]$^-$ (X = H or D) was determined by X-ray crystallography. One of the hydrides/deuterides is located on the crystallographic mirror plane, capping a tricobalt face of the cluster cation. The other *endo* hydrogen atom is believed to be disordered between the other two μ_3-(Co_3) sites, which are related by space group symmetry. Deuteronation of **3** shows a strong normal kinetic deuterium isotope effect. From the temperature independence of the ^{1}H NMR spectrum of [**3** + 2D]$^{2+}$ a non-fluxional solution structure can be inferred. In all the systems studied, hydridic (μ_2- or μ_3-) sites are thermodynamically preferred to possible isomeric agostic CoHC or Co_2HC sites for the *endo* hydrogens. Agostic interactions cannot, however, be ruled out in transient intermediates during the course of the protonations.

1. Introduction

μ_3-Alkylidyne transition metal cluster hydrides with MHM bonds **A** can be in equilibrium with their tautomers involving agostic [1] CHM interactions **B**. The systems which have been studied in some detail include the trinuclear neutral "[$Fe_3(CO)_9(CH_4)$]", which exists in solution as a mixture of the three tautomers [$(\mu\text{-}H)_3Fe_3(CO)_9(\mu_3\text{-}CH)$], [$(\mu\text{-}H)_2Fe_3(CO)_9(\mu_3\text{-}HCH)$] and [$(\mu\text{-}H)Fe_3(CO)_9(\mu_3\text{-}H_2CH)$] [2], [$FeCo_2(CO)_9(\mu_3\text{-}CHR)$] (R = Me, Ph, 3-$PhC_6H_4$, 3-$^tBuC_6H_4$, β-naphthyl, 2,3-$Me_2C_6H_3$) [3,4], anionic [$(\mu\text{-}H)Fe_3(CO)_9(\mu_3\text{-}HCH)$]$^-$ [5] and cationic [$(\mu\text{-}H)_3M_3(CO)_9(\mu_3\text{-}CHR)$]$^+$ (M = Ru, R = Et; M = Os, R = Me) [6]. In other cases CHM bonded species are likely transition states or intermediates in hydrogen exchange reactions [7] or in reductive eliminations [8] from alkylidyne cluster hydrides. On transition metal surfaces μ_3-ethylidyne is one of the dissociative adsorption states of ethylene [9]. Ethylene is catalytically hydrogenated "on top" of such an overlayer. Transfer of hydrogen atoms from the metal surface to the α-carbons of the μ_3-ethylidyne is thought to be a key step in this reaction at temperatures below 350 K [10]. μ_3-Ethylidyne cluster hydrides could be molecular models for such heterogeneous catalysts.



A



B

The factors affecting the distribution of "*endo*" hydrogens [11*] on EM_3 clusters (E = B, C) have been

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* Reference number with an asterisk indicates a note in the list of references.

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TABLE 1. ^1H NMR data for complexes $[(CpCo)_3(\mu_3\text{-}CCH_3)_2]$ (**1b**) [14] and $[H(CpCo)_3(\mu_3\text{-}CCH_3)_2]^+$ $[\mathbf{1b}+H]^+$

		1b [a]	$[\mathbf{1b}+H]^+$		
			210 K [b]	297 K [b]	297 K [c]
Cp	(s,15H)	4.30	4.90	4.95	4.90
CH_3	(s,3H)	4.83	4.25	4.35	4.30
Hydride	(s,1H)		−26.97	−26.75	−26.35

[a] In benzene-d_6. [b] In dichloromethane-d_2. [c] In CF_3COOH.

analysed by Fehlner *et al.* [12,13]. The balance between *edge bridging* μ_2-MHM and CHM interactions present in these trinuclear systems was shown to depend on the identity of E, the overall cluster charge, and the total number of *endo* hydrogens. To our knowledge no equilibria between hydrogens in M_3 *face capping* hydridic and M_2C (μ_3-H) or MC (μ_2-H) bridging agostic sites have been reported.

In this paper we describe the reactions with Brönsted acids of three $[(C_5R_5Co)_n(\text{ethylidyne})_m]$ clusters, namely $[(CpCo)_3(\mu_3\text{-}CCH_3)_2]$ (**1b**) [14b], $[(Cp^*Co)_3(\mu_3\text{-}CCH_3)_2]$ (**2**) [15] and $[H(CpCo)_4(\mu_3\text{-}CCH_3)]$ (**3**) [14]. Complexes of the type $[(CpCo)_3(\mu_3\text{-}CR)_2]$ are known to form monoprotonated species on treatment with strong acids (HBF_4, CF_3COOH) as shown for **1a** (R = H) and **1c** (R = ^{n}Bu) by Vollhardt *et al.* [7b]. Although ^1H NMR spectroscopic data suggest protonation of a dicobalt edge of these clusters [7b], the observed rapid exchange of the methyne protons in **1a** with deuterated acids could well involve intermediates with agostic CHM interactions. In the tetranuclear cluster **3** the hydride ligand, which is already present in the neutral complex, probably occupies a Co_3 face capping position on the cluster [14]. The object of the present work is to establish the site of protonation and the structure of the protonated clusters. Previous protonation studies on the tetranuclear $[\{Fe(CO)_3\}_4(\mu_3\text{-}CCH_3)]^-$ [16], a species closely related to **3** [17*], were hindered by decomposition of the alkylidyne carbonyl cluster in acidic media [18]. The CpCo clusters are expected to be stable in acid for long periods, thus enabling investigations of very slow proton exchange reactions and of *endo* hydrogen fluxionality. In addition, the steric constraints imposed upon the metal cluster "surface" by the rigid C_5R_5-ligands are expected to be quite different from those in clusters with carbonyl ligands.

2. Results and discussion

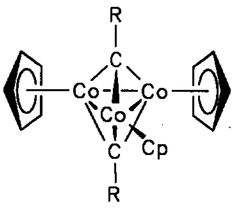
2.1. Trinuclear bis(μ_3-ethylidyne) clusters $[(CpCo)_3(\mu_3\text{-}CCH_3)_2]$ (1b) and $[(Cp^*Co)_3(\mu_3\text{-}CCH_3)_2]$ (2)

Dissolution of $[(CpCo)_3(\mu_3\text{-}CCH_3)_2]$ (**1b**) in CF_3COOH resulted in a colour change from red to green. The ^1H NMR spectra of the solution showed singlets at $\delta = 4.90$, 4.30 and −26.35 with relative intensities of 15 : 6 : 1. Evaporation of the acid *in vacuo* and redissolution of the green oily residue in CD_2Cl_2 gave the same ^1H NMR signals (Table 1), indicative of a monoprotonated species $[H(CpCo)_3(\mu_3\text{-}CCH_3)_2]^+$ $[\mathbf{1b} + H]^+$. The starting neutral cluster **1b** was regenerated immediately and quantitatively on treatment of $[\mathbf{1b} + H]^+$ with water. The spectrum of $[\mathbf{1b} + H]^+$ remained unchanged on cooling of the sample to temperatures down to 210 K. The high field ^1H resonance is only consistent with a proton ("hydride") associated with the metal framework of the cluster. For steric reasons, a dicobalt edge protonated structure is most likely. The high symmetry found in the ^1H and ^{13}C

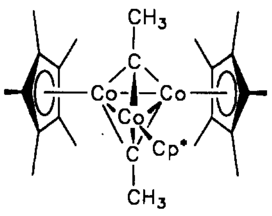
TABLE 2. $^{13}C\{^1H\}$ NMR data for complexes $[(CpCo)_3(\mu_3\text{-}CCH_3)_2]$ (**1b**) [14] and $[H(CpCo)_3(\mu_3\text{-}CCH_3)_2]^+$ $[\mathbf{1b}+H]^+$ (δ at ambient temperature)

	1b [a]	$[\mathbf{1b}+H]^+$ [b]
$\underline{C}CH_3$	407.36	[c]
Cp	83.83	89.4
CH_3	50.86	53.1

[a] In benzene-d_6. [b] In dichloromethane-d_2. [c] Resonance not observed.



1a, R= H
1b, R= CH_3
1c, R= n-C_4H_9



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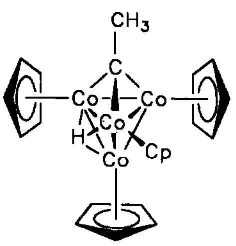

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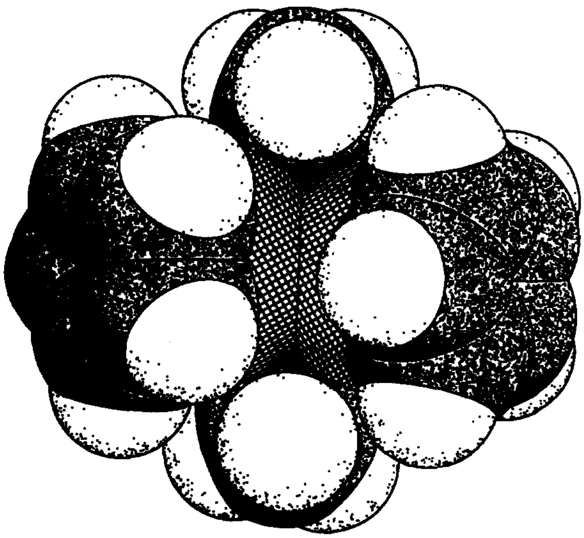

Fig. 1. Space filling representation of $[(CpCo)_3(\mu_3\text{-}CCH_3)_2]$ (**1b**). Cluster vertex carbon atoms C1 and C3 are drawn solid black.

TABLE 4. $^{13}C\{^1H\}$ NMR data [δ (multiplicity) at ambient temperature] for complexes $[H(CpCo)_4(\mu_3\text{-}CCH_3)]$ (**3**) [14], $[H_2(CpCo)_4(\mu_3\text{-}CCH_3)]^+$ ($[\mathbf{3}+H]^+$), $[H_3(CpCo)_4(\mu_3\text{-}CCH_3)]^{2+}$ $[\mathbf{3}+2H]^{2+}$ and $[HD_2(CpCo)_4(\mu_3\text{-}CCH_3)]^{2+}$ $[\mathbf{3}+2D]^{2+}$

	3 [a]	$[\mathbf{3}+H]^+$ [b]	$[\mathbf{3}+2H]^{2+}$ [c]	$[\mathbf{3}+2D]^{2+}$ [d]
Cp_e	82.17 (d)	85.85 (d)	88.19	91.55 (d)
Cp_a	74.89 (d)	80.10 (d)	83.65	86.98 (d)
CH_3	54.71 (q)	59.58 [e]	61.15	64.00

[a] In toluene-d_8. [b] In dichloromethane-d_2. [c] In D_2O/CF_3SO_3H. [d] In CF_3COOD. [e] Due to overlap with solvent resonances multiplicity could not be determined.

NMR spectra (Tables 1 and 2) can be due either to a dynamic process (which must still be fast at 210 K) equilibrating all three Cp ligands, or to an accidental degeneracy of the expected 2:1 pattern of the Cp protons and carbons. In an experiment in which an excess of CF_3COOH was added to a CD_2Cl_2 solution of **1b** at 200 K only the immediate formation of $[\mathbf{1b}+H]^+$ was observed by ^1H NMR spectroscopy. In particular, no resonances with $-25 < \delta < 4$ could be detected either after a short time (*ca.* 2 min) or several hours after the addition of the acid.

These results are consistent with the observations by Vollhardt *et al.* [7b], who generated the monocations of **1a** and **1c** by treatment of **1a** and **1c**, respectively, with $HBF_4 \cdot OEt_2$ or CF_3SO_3H. In contrast to $[\mathbf{1a}+H]^+$ [7b] and $[\mathbf{1b}+H]^+$ the ^1H Cp-resonance of $[\mathbf{1c}+H]^+$ was a 2:1 pattern at 203 K, as expected for a static dicobalt edge protonated structure.

The low temperature (220 K) reaction of $[(Cp^*Co)_3(CCH_3)_2]$ **2** with an excess of CF_3COOH in methylene chloride also gave a broad high field signal at $\delta = 23$ in the ^1H NMR spectrum. However, the presence of several strong broad resonances in the region $18 \le \delta \le 34$ indicated the formation of paramagnetic species, which remained in the spectra after warming the sample to 250 K. When the sample was brought to room temperature only strong broad resonances were visible in the region around δ 25 in addition to the protons of the acid (δ *ca.* 11) and a multitude of sharper signals in the region $0.5 \le \delta \le 2$. Obviously the reaction of **2** with acid is much less clean than that of **1**. Apparently hydridic species are formed among other products at low temperature, but are not stable at room temperature.

These differences can be attributed to the different shielding of the clusters by the Cp and Cp* ligands (Fig. 1). In **1b** the Co_2 edges of the Co_3C_2 trigonal bipyramid are the least hindered sites for protonation. In **2** steric congestion is much more pronounced. In both cases the CoC edges or Co_2C faces of the clusters are buried within the ligand shell (Fig. 1) and thus unavailable for protonation.

2.2. *The tetranuclear μ_3-ethylidyne cluster $[H(CpCo)_4(\mu_3\text{-}CCH_3)]$ (3): preparative scale reactions*

Treatment of $[H(CpCo)_4(CCH_3)]$ (**3**) with one equivalent of CF_3SO_3H in diethyl ether gave a black solid, which was identified as the salt $[H_2(CpCo)_4(\mu_3\text{-}CCH_3)]^+[CF_3SO_3]^-$ $[\mathbf{3}+H]^+[CF_3SO_3]^-$, on the basis of ^1H and ^{13}C NMR spectroscopic data (Tables 3 and

TABLE 3. ^1H NMR data for complexes $[H(CpCo)_4(\mu_3\text{-}CCH_3)]$ (**3**) [14], $[H_2(CpCo)_4(\mu_3\text{-}CCH_3)]^+$ $[\mathbf{3}+H]^+$ and $[H_3(CpCo)_4(\mu_3\text{-}CCH_3)]^{2+}$ $[\mathbf{3}+2H]^{2+}$

	3 [a]		$[\mathbf{3}+H]^+$ [b]		$[\mathbf{3}+2H]^{2+}$ [c]
	293 K	190 K	293 K	166 K	293 K
CH_3	4.92 (s,3H)	4.87 (s,3H)	5.18 (s,3H)	5.13 (s,3H)	5.40 (s,3H) [d]
Cp_a	4.81 (s,5H)	4.82 (s,5H)	5.62 (s,5H)	5.54 (s,5H)	6.41 (s,5H)
Cp_e	4.56 (s,15H)	4.63 (s,10H)	5.01 (s,15H)	4.82 (s,10H)	5.52 (s,15H)
Cp_e		4.48 (s,5H)		5.04 (s,5H)	
Hydride	−19.6 (s,1H)	−19.7 (s,1H)	−22.1 (s,2H)	−22.2 (s,2H)	−25.2 (s,3H) [e]

[a] In toluene-d_8. [b] Trifluoromethylsulfonate in dichloromethane-d_2. [c] Trifluoroacetate in dichloromethane-d_2/CF_3COOH (10:1, v:v). [d] $w_{1/2} = 1.6$ Hz. [e] $w_{1/2} = 12$ Hz.

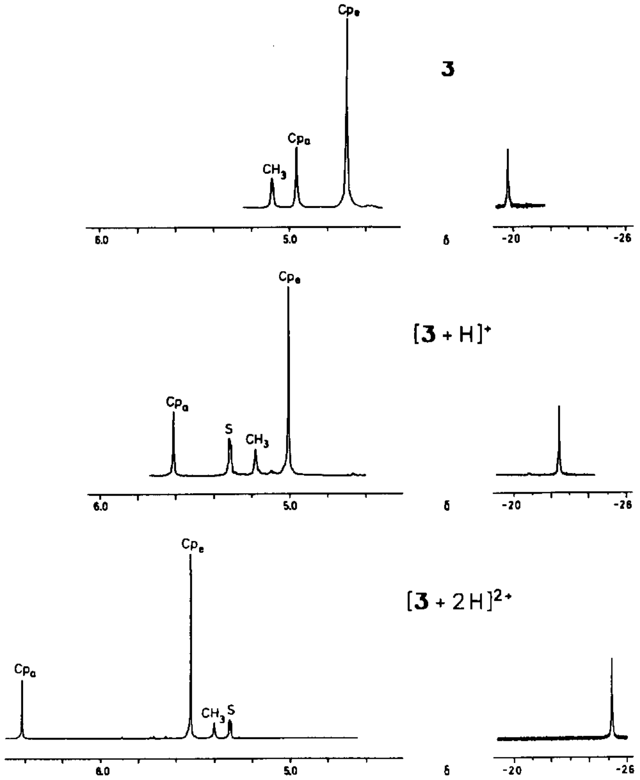

Fig. 2. 200 MHz ^1H NMR spectra of [H(CpCo)$_4$(μ_3-CCH$_3$)] **3** (top, in benzene-d_6), [H$_2$(CpCo)$_4$(μ_3-CCH$_3$)]$^+$ [**3** + H]$^+$ (centre, in dichloromethane-d_2) and [H$_3$(CpCo)$_4$(μ_3-CCH$_3$)]$^{2+}$ [**3** + 2H]$^{2+}$ (bottom, in dichloromethane-d_2). S = solvent resonances. Note change of horizontal and vertical scale for the high field resonances.

4) and C, H elemental analysis. Further treatment of [**3** + H]$^+$ with CF$_3$SO$_3$H or dissolution of **3** in CF$_3$COOH gave the dication [H$_3$(CpCo)$_4$(μ_3-CCH$_3$)]$^{2+}$ [**3** + 2H]$^{2+}$, which was isolated only as a black oil. Salts of [**3** + H]$^+$ and [**3** + 2H]$^{2+}$ are readily soluble in methylene chloride; trifluoroacetates and triflates of [**3** + 2H]$^{2+}$ are also soluble in water. The solubility in water of [**3** + H]$^+$ salts prepared from **3** and trifluoroacetic acid depends on the history of the particular sample. Since the acidic trifluoroacetate [**3** + X]$^+$[(CF$_3$COO)$_2$X]$^-$ (X = H, D) was found to be insoluble in water at room temperature (see below) we believe this effect to be due to the anions, which could be any combination of [CF$_3$COO]$^-$ and [(CF$_3$COO)$_2$H]$^-$. Cation [**3** + H]$^+$ was slowly deprotonated to **3** by Na$_2$CO$_3$ in water/ethanol. Further deprotonation to [(CpCo)$_4$(μ_3-CCH$_3$)]$^-$ ([**3** − H]$^-$) was not observed even on prolonged contact with strong bases such as NaH or Na(HBEt$_3$) [14b].

All three μ_3-ethylidyne tetracobalt clusters **3**, [**3** + H]$^+$ and [**3** + 2H]$^{2+}$ show the same pattern of resonances in the ^1H NMR spectra (Fig. 2, Table 3). The methyl group of the μ_3-ethylidyne ligand gives a singlet at relatively low field. The protons of the four cyclopentadienyl rings give rise to two signals with an intensity ratio of 15:5. In addition there are broad resonances at very high field, proving the presence of one, two, or three hydride ligands bound to the metal clusters. The observation of only two cyclopentadienyl resonances in the ^1H and ^{13}C NMR spectra for the four CpCo groups of **3** could be attributed to a fluxional process in which the hydride ligand moves around the metal cluster in a merry-go-round fashion [14b]. Since the maximum symmetry of static [**3** + H]$^+$ is only C_s (as of **3** also), a similar fluxionality must operate in [**3** + H]$^+$ (see below). Putting three hydride ligands on to the three tricobalt faces not capped by the ethylidyne ligand (as in [**3** + 2H]$^{2+}$) results in a maximum (static) symmetry of C_{3v}; therefore no information about the fluxionality can be obtained from the spectra in this case (but see below for the dideuterated cluster).

The increased positive charge on the molecules in the series **3**, [**3** + H]$^+$, [**3** + 2H]$^{2+}$ results in remarkable paramagnetic (low field) shifts of the ^1H resonances of the Cp and CH$_3$ groups. The observed shifts are roughly additive, with the methyl group experiencing the smallest influence ($\Delta\delta \approx 0.24$ per proton added to the metal cluster). The $\Delta\delta$ values for the two sets of Cp protons are significantly different ($\Delta\delta \approx 0.5$ for the "equatorial" and $\Delta\delta \approx 0.80$ for the "axial" CpCo groups [19*]). The hydride resonances are strongly shifted to high field ($\Delta\delta \approx -2.8$). This behaviour indicates that the positive charge is mainly localised on the metal cluster.

Lowering the temperature causes the ^1H resonance at $\delta = 5.01$ of [**3** + H]$^+$ to collapse and split into two singlets (relative intensity 2:1) at 166 K (Table 3). The chemical shift and to a lesser degree the line width of the hydride resonance [20*] are nearly temperature independent. This behaviour is consistent with slowing down of the above-mentioned hydride fluxionality. At low temperature, the two hydride ligands are localised in capping positions on two of the three Co$_3$ faces of the tetracobalt cluster, giving rise to C_s molecular symmetry on the NMR time scale.

A quantitative analysis of the temperature dependent NMR spectra is made difficult by the strong correlation of the exchange rate constant k and the effective transversal relaxation time T_2^*, both contributing to the line widths of the exchanging resonances. Exchanging singlets are, indeed, the worst cases encountered in the kinetic analysis of dynamic NMR spectra [21]. An attempt was made to simulate the dynamic ^1H NMR spectra of **3** and [**3** + H]$^+$ in the temperature range of 170–270 K. T_2^* values were extracted from the half widths $w_{1/2}$ of the resonances of the methyl and axial Cp groups at each temperature using the relation $T_2^* = (\pi \cdot w_{1/2})^{-1}$ [22] and assumed also to be valid for the equatorial Cp groups. For each temperature theoretical spectra were calculated [23] for various k values and visually compared with the experimental spectra of **3** and $[\mathbf{3} + H]^+[CF_3SO_3]^-$ in CD_2Cl_2 solution. Analysis of the data in terms of the Eyring activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ was, however, not considered to be realistic because of the problems mentioned above and the limited temperature range over which reasonable k values could be obtained. We therefore only give values for $\Delta G^{\neq}$ at the coalescence temperatures, namely $\Delta G^{\neq}$ (225 K) = 45.9 kJ/mol for **3** and $\Delta G^{\neq}$ (203 K) = 40.8 kJ/mol for $[\mathbf{3} + H]^+$. Such values are known to be quite insensitive to errors in temperature and exchange rate [24].

Assuming $\Delta S^{\neq}$ to be similarly small and probably positive in both cases (as is, in fact, suggested by the data) the energy barrier for the hydride exchange appears to be somewhat lower for $[\mathbf{3} + H]^+$ than for **3**.

2.3. *Crystal and molecular structure of* $[H_{2-x}D_x(CpCo)_4(\mu_3\text{-}CCH_3)]^+[(CF_3COO)_2X]^-$ $[\mathbf{3} + X]^+[(CF_3COO)_2X]^-$ $(x = 0\text{–}2, X = H, D)$

The salt $[\mathbf{3} + X]^+[(CF_3COO)_2X]^-$ (X = H, D) crystallised slowly from a saturated solution of the trifluoroacetate of $[HD_2(CpCo)_4(\mu_3\text{-}CCH_3)]^{2+}$ in D_2O. Crystal data are summarised in Table 5. Fractional atomic coordinates are given in Table 6. The presence of the cation $[H_{2-x}D_x(CpCo)_4(\mu_3\text{-}CCH_3)]^+$ in the crystals was confirmed by the ^1H NMR spectra of a CD_2Cl_2 solution.

TABLE 5. Details of the crystal structure determination of $[H_{2-x}D_x(CpCo)_4(\mu_3\text{-}CCH_3)]^+[(CF_3COO)_2X]^-$ $[\mathbf{3} + X]^+[(CF_3COO)_2X]^-$ $(x = 0\text{–}2, X = H, D)$

Crystal habit, colour	plate, black
Crystal size (mm)	0.42×0.077×0.21
Crystal system	orthorhombic
Space group	*Pbcm*
a (Å)	8.695(5)
b (Å)	16.292(10)
c (Å)	19.211(10)
V (Å^3)	2721
Z	4
μ(Mo Kα) (cm^{-1})	24.65
X-Radiation (Å)	Mo Kα (graphite monochromated), 0.71069
Data collection temperature	ambient
hkl-range	$0 \le h \le 10, 0 \le k \le 19, -22 \le l \le 22$
Reflections measured	6089
unique	2553
observed $[I \ge \sigma(I)]$	2170
Absorption correction	numerical
T_{max}, T_{min}	0.85, 0.60
Parameters refined	300
R-values R	0.055
R_w $(w = (\sigma^2(F) + 0.0003\, F^2)^{-1})$	0.047

TABLE 6. Fractional atomic coordinates with e.s.d.s in parentheses and equivalent isotropic thermal parameters (Å^2) for $H_{2-x}D_x$-$(CpCo)_4(\mu_3\text{-}CCH_3)]^+[(CF_3COO)_2X]^-$ $[\mathbf{3}+X]^+[(CF_3COO)_2X]^-$ $(x = 0\text{–}2, X = H, D)$

Atom	x	y	z	$\bar{U}$
Co1	0.15173(9)	0.38468(5)	0.250	0.034
Co2	0.17914(7)	0.25668(4)	0.31414(3)	0.035
Co3	0.39542(9)	0.31245(5)	0.250	0.034
C1	0.3105(7)	0.2085(4)	0.250	0.037
C2	0.3865(9)	0.1256(4)	0.250	0.056
C11	−0.0452(13)	0.4492(8)	0.250	0.072
C12	0.0358(9)	0.4706(5)	0.1895(5)	0.064
C13	0.1822(9)	0.5033(4)	0.2115(4)	0.043
C11a	0.188(2)	0.5094(11)	0.250	0.068
C12a	0.0962(15)	0.4840(8)	0.3065(7)	0.059
C13a	−0.0421(16)	0.4507(8)	0.2845(7)	0.070
C21	0.1608(9)	0.2855(4)	0.4174(3)	0.070
C22	0.0111(9)	0.2706(4)	0.3923(3)	0.070
C23	0.0059(9)	0.1893(4)	0.3671(3)	0.072
C24	0.1525(9)	0.1541(4)	0.3766(3)	0.067
C25	0.2483(9)	0.2135(4)	0.4077(3)	0.068
C21a	0.2444(17)	0.2664(8)	0.4196(5)	0.087
C22a	0.0949(17)	0.2981(8)	0.4103(5)	0.092
C23a	0.0020(17)	0.2350(8)	0.3828(5)	0.076
C24a	0.0941(17)	0.1643(8)	0.3751(5)	0.068
C25a	0.2439(17)	0.1837(8)	0.3978(5)	0.070
C31	0.6295(11)	0.2771(8)	0.250	0.068
C32	0.5955(9)	0.3269(5)	0.3072(4)	0.057
C33	0.5439(9)	0.4051(5)	0.2852(4)	0.061
C31a	0.541(2)	0.4145(11)	0.250	0.065
C32a	0.5628(13)	0.3639(8)	0.1902(6)	0.046
C33a	0.6099(15)	0.2844(8)	0.2137(8)	0.067
C3	0.6633(6)	0.1266(4)	0.4716(3)	0.056
O1	0.6555(6)	0.1800(2)	0.51854(19)	0.083
O2	0.6362(5)	0.1321(3)	0.4106(2)	0.080
C4	0.7221(8)	0.0438(4)	−0.0001(3)	0.077
F1	0.8688(8)	0.0486(5)	−0.0147(5)	0.169
F2	0.6489(9)	0.0201(4)	−0.0556(3)	0.122
F3	0.7072(9)	−0.0185(3)	0.0425(3)	0.117
F1a	0.8630(11)	0.0336(9)	0.0214(7)	0.132
F2a	0.7241(15)	0.0370(6)	−0.0664(4)	0.102
F3a	0.6424(15)	−0.0143(7)	0.0314(8)	0.138
H1	0.070(8)	0.305(4)	0.250	0.071

The X-ray crystal structure determination revealed isolated $[H_{2-x}D_x(CpCo)_4(\mu_3\text{-}CCH_3)]^+$ clusters (Fig. 3) packed together with $[(CF_3COO)_2X]^-$ anions. A projection of the unit cell is shown in Fig. 4. Important bond lengths and angles are presented in Table 7. The cluster cations have crystallographic mirror symmetry, the plane of symmetry passing through Co3, C1, C2 and C31. Co–Co bond lengths are 2.43 Å from the "axial" Co1 to the "equatorial" Co2 and Co3. In the equatorial Co_3 plane the Co2–Co2′ bond is somewhat longer (2.464 Å) than the other two metal–metal bonds

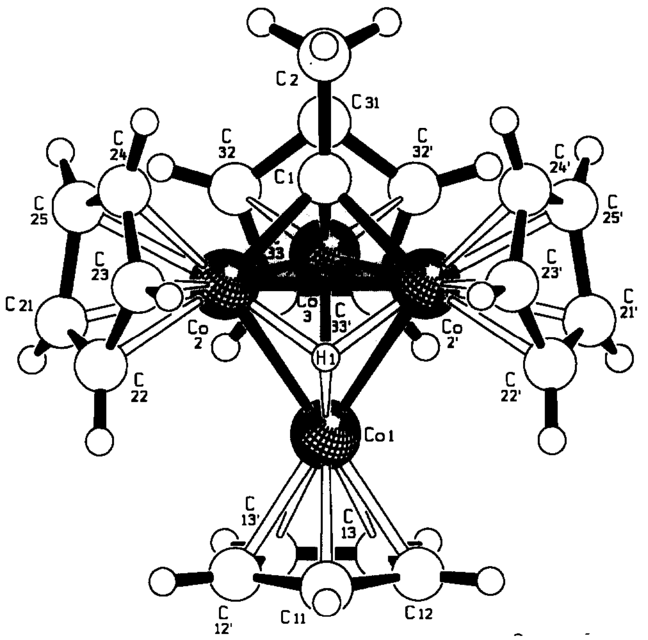

Fig. 3. Molecular structure of the cation $[H_{2-x}D_x(CpCo)_4(\mu_3\text{-}CCH_3)]^+$ $[3+X]^+$ in the crystal. Only one of the two disordered sets of Cp ligands is shown.

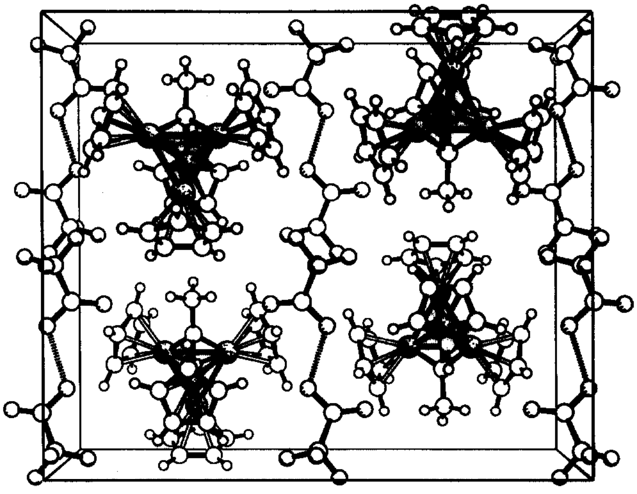

Fig. 4. View of the contents of the unit cell of $[H_{2-x}D_x(CpCo)_4(\mu\text{-}CCH_3)]^+[(CF_3COO)_2X]^-$ $[3+X]^+[(CF_3COO)_2X]^-$ showing the arrangement of cations and anions in the crystal (projection along a^*). Only one of the disordered sets of Cp ligands and CF_3 groups is shown.

(2.425 Å), indicating the presence of a bridging hydride ligand. The corresponding values in **3** range from 2.38–2.43 Å for Co_{eq}–Co_{eq} bonds and 2.36–2.44 Å for Co_{eq}–Co_{eq} bonds [14]. Difference Fourier syntheses for $[3+X]^+$ showed indeed a maximum of electron density bridging the Co1Co2Co2′ face, which was refined as a hydride (H1) with an isotropic temperature factor. Balance of charge however requires a further *endo* hydrogen on the cluster. Since no suitable peaks could be located in the difference Fourier maps, possible sites were inspected by the semiquantitative potential energy method of Orpen [25]. The results are summarised in Table 6. A very deep "hole" was indeed found bridging the Co1Co2Co2′ face, close to the position of the crystallographically located hydride H1. Other possible hydridic or agostic sites have much higher potential energies (Table 8).

The arrangement of the Cp ligands around the Co_4C core of the cluster is shown in Fig. 3, and in the space filling representations in Fig. 5. The position of H1 is clearly evident in Fig. 5. A second μ_3-hydridic site capping the face Co1Co2Co3 of the cluster is by space group symmetry mirrored to the face Co1-Co2′Co3. Occupation of this site by a proton in addition to H1 would result in a composition $[3+2X]^{2+}$, in obvious contradiction to the required electroneutrality. There is however the possibility of a statistical disorder of the second hydride across the apparent crystallographic mirror plane. Owing to the disorder found for the Cp ligands such a pseudosymmetry would not necessarily be obvious in the structure.

The vector C1–C2 is perpendicular to the plane Co2Co2′Co3 and the thermal ellipsoid of C1 is almost spherical. The bond lengths Co–C1 (1.855(5), 1.848(6) Å) are equal with the error limits and within the range of the values found in **3** (1.78–1.88 Å [14]). This makes

TABLE 7. Bond lengths (Å) and angles (°) for $[H_{2-x}D_x(CpCo)_4(\mu_3\text{-}CCH_3)]^+[(CF_3COO)_2X]^-$ $[3+X]^+[(CF_3COO)_2X]^-$ ($x = 0$–2, X = H, D)

Co1–Co2	2.434(3)	Co2–H1	1.746(72)	C3–O1	1.255(7)
Co1–Co3	2.424(3)	Co2–C1	1.855(5)	C3–O2	1.199(7)
Co1–H1	1.476(69)	Co3–C1	1.848(6)	C3–C4	1.543(8)
Co2–Co3	2.425(3)	Co2–Co2′	2.464(3)	C1–C2	1.503(9)
Co2–Co1–Co2′	60.8(1)	Co2′–Co3–Co2	61.1(1)	C2–C1–Co3	130.3(4)
Co3–Co1–Co2	59.9(1)	Co3–C1–Co2	81.8(2)	O2–C3–O1	129.7(5)
Co2′–Co2–Co1	59.6(1)	Co2′–C1–Co2	83.3(2)	C4–C3–O1	111.7(4)
Co3–Co2–Co1	59.8(1)	Co1–H1–Co2	97.8(17)	C4–C3–O2	118.5(5)
Co3–Co2–Co2′	59.5(1)	Co2′–H1–Co2	89.8(16)		
Co2–Co3–Co1	60.3(1)	C2–C1–Co2	130.6(2)		

TABLE 8. Potential energy of possible sites for the *endo*-hydrogens in $[3 + H]^+$

Type	x	y	z	d(M–H) (Å)	d(M–C) (Å)	Potential energy [a]
M_3H	0.055	0.292	0.250	1.73, 1.74		0.05
M_3H	0.275	0.350	0.314	1.73, 1.72		1.44
M_2CH	0.165	0.191	0.250	1.64	1.30	5.65
M_2CH	0.366	0.241	0.305	1.60, 1.65	1.28	8.84
M_2H	0.043	0.241	0.250	1.73		4.58
M_2H	0.027	0.311	0.279	1.73, 1.70		6.72
M_2H	0.330	0.323	0.333	1.69, 1.74		8.69
M_3H [b]	0.070	0.305	0.250	1.75, 1.48		

Only one of the two disordered sets of Cp ligands was used in these calculations. [a] Arbitrary units. [b] Refined position from X-ray crystallographic study.

the possible Co_2C face bridging or CoC edge bridging positions for the *endo* hydrogens in $[3 + X]^+$ quite unlikely.

The anions in the crystal are the centrosymmetric dimers $[(CF_3COO)_2X]^-$. There are no unusually close contacts between cations and anions. Although the hydrogen bridging the two trifluoroacetates could not be located, the short O1 ··· O1′ distance of 2.389(6) Å is indicative of an OHO bridge between these two oxygen atoms. Similar O ··· O distances have been found, for example, in $K[(CF_3COO)_2H]$ (2.437(4) Å) [26], $[H_5O_2]^+[H(CF_3COO)_2]^- \cdot 6H_2O$ (2.445 Å) [27] and $[(CpMo)_2(C_8H_8)(H)]^+[(CF_3COO)_2H]^-$ (2.429(8) Å) [28].

2.4. *In situ protonations and deuteronations*

When samples of **3** were dissolved in CF_3SO_3H or CF_3COOH at room temperature, quantitative conversion to $[3 + 2H]^{2+}$ was observed within a few minutes by ^1H NMR spectroscopy. When a sample of $[3 + 2H]^{2+}$, prepared in neat CF_3COOH, was pumped dry *in vacuo* and then redissolved in D_2O the ^1H NMR spectrum showed the sole presence of $[3 + 2H]^{2+}$ in solution. No H/D exchange was apparent after a few hours. When the solution was kept overnight a black precipitate separated leaving a pale yellow solution. The ^1H NMR spectrum of this solid in CD_2Cl_2 solution showed resonances at $\delta = 5.8$ (4.9H, Cp_{ax}), 5.14 (2.9H, CH_3), 4.97 (15H, Cp_{eq}) and -22.15 ($w_{1/2} = 30$ Hz, 2.2H, hydrides), characteristic of $[3 + H]^+$. After standing for a further 14 days at 280 K, the same solution gave a different spectrum with resonances at $\delta = 5.05$ (4.8H), 4.46 (2.9H), 4.40 (15H) and -22.7 ($w_{1/2} = 32$ Hz, 1.8H). Addition of one drop of D_2O to the sample immediately changed the spectrum back to its initial appearance, with the integration ratio of approximately 5 : 3 : 15 : 2 still unchanged after several hours.

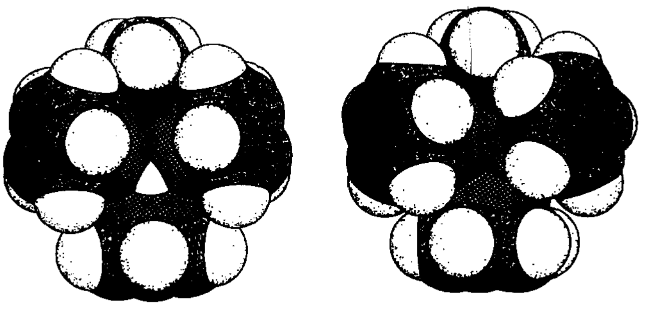

Fig. 5. Space filling representations of $[H_{2-x}D_x(CpCo)_4(\mu_3\text{-}CCH_3)]^+$ $[3+X]^+$. Left: projection perpendicular to Co2–Co2′, right: projection perpendicular to Co2–Co3. The cluster vertex carbon atom C1 is drawn solid black. Only one of the two disordered sets of Cp ligands is shown.

Protonation of **2** with CF_3COOH was also carried out in CD_2Cl_2 solution at low temperature. Owing to the low solubility of the acid in this solvent at low temperatures the lowest temperature that could be used was 230 K. After an excess of acid had been added at 230 K only the hydride resonance of $[3 + H]^+$ ($\delta \approx -22$) was observed in the high field region of the ^1H NMR spectrum after a few minutes. On warming to 250 K the peaks due to $[3 + 2H]^{2+}$ grew up slowly; the relative concentrations of $[3 + H]^+$ and $[3 + 2H]^{2+}$ were about 20 : 1 after 8 h. Warming to room temperature during 1.5 h resulted in a 1 : 5 mixture of $[3 + H]^+$ and $[3 + 2H]^{2+}$. However, owing to partial crystallisation of the acid spectral resolution at low temperature was poor. Therefore, and because of the line broadening due to the dynamic behaviour of the complexes in solution, spectra which were well resolved in the region of the Cp and CH_3 resonances could only be obtained above 270 K. In the spectra taken in the range 270 K $\leq T \leq$ 295 K about 9–12 h after addition of the acid the resonance of the methyl protons of $[3 + H]^+$ was very broad. The sample was completely converted into $[3 + 2H]^{2+}$ after a further 10 h at 280 K. At all temperatures, there was no sign of ^1H resonances with $0 \geq \delta$

≥ -20, which would indicate possible CoC edge or Co_2C face bridging agostic hydrogens.

After 7 days the sample was pumped dry and treated with D_2O. The ^1H NMR spectrum of the cloudy solution, taken a few minutes after adding the D_2O, showed only the resonances of $[\mathbf{3}+H]^+$. The solution was almost clear after standing for a further 4 days at room temperature. Careful integration of the spectra indicated that no H/D exchange had taken place (resonances at $\delta = 5.49$ (5.1H, Cp_{ax}), 4.98 (3.0H, CH_3), 4.87 (15H, Cp_{eq}) and -22.2 (2.0H, hydride)).

A strong kinetic isotope effect was observed when **3** was dissolved in deuterated trifluoroacetic acid. Immediately after preparation of the sample the ^1H NMR spectrum showed the presence of an approximately 10:1 mixture of $[\mathbf{3}+D]^+$ and $[\mathbf{3}+2D]^{2+}$, which was only slowly (≈ 12 h) completely converted into $[\mathbf{3}+2D]^{2+}$. During the first few hours of the reaction a transient broad ^1H resonance at $\delta = -5.6$ was observed in addition to the resonances of $[\mathbf{3}+D]^+$ and $[\mathbf{3}+2D]^{2+}$. The resonance of the methyl protons of $[\mathbf{3}+D]^+$ was initially quite broad, but became sharper with time without significant change in its chemical shift. Relative intensities of the high field signals at $\delta = -5.56$ ($w_{1/2} \approx 56$ Hz), $\delta = -22.4$ ($w_{1/2} \approx 65$ Hz, $[\mathbf{3}+D]^+$) and $\delta = -25.4$ ($w_{1/2} \approx 15$ Hz, $[\mathbf{3}+2D]^{2+}$) were 0.84:1.0:2.5 *ca.* 1 h after dissolution of **3** in the acid. When the resonances of $[\mathbf{3}+2D]^{2+}$ had grown in intensity it became obvious that the signal attributed to the three equatorial Cp ligands of $[\mathbf{3}+2D]^{2+}$ consisted in fact of two components of unequal intensities separated by about 1.5 Hz. This feature remained in the spectrum when the sample was heated to 330 K. In the $^{13}C\{^1H\}$ NMR spectrum (Table 4) a shoulder was barely visible on the resonance at $\delta = 91.55$.

When the deuteronation of **3** was carried out with an excess of CF_3COOD in CD_2Cl_2 solution $[\mathbf{3}+D]^+$ was also initially formed. After about 30 min, less than 5% $[\mathbf{3}+2D]^{2+}$ was present in the solution. Minor amounts of $[\mathbf{3}+D]^+$ could still be detected after 6 days at 280 K, the major product then being $[\mathbf{3}+2D]^{2+}$. In this reaction, no ^1H resonances were observed in the range $0 \geq \delta \geq -20$. However, a transient broadening of the resonance of the methyl protons of $[\mathbf{3}+D]^+$ was observed, similar to that in the reaction with neat CF_3COOD. No H/D exchange between the acid and $[\mathbf{3}+D]^+$ and $[\mathbf{3}+2D]^{2+}$ was observed either in neat CF_3COOD or in CD_2Cl_2/CF_3COOD during several days.

A very puzzling observation was also made with this particular sample. The ^1H resonance of the axial Cp groups of $[\mathbf{3}+D]^{2+}$ was a doublet with a splitting of *ca.* 0.5 Hz, while the methyl resonance of this species appeared to be somewhat like a broad triplet. When enough $[\mathbf{3}+2D]^{2+}$ had been formed it became apparent that the resonances of this compound were a

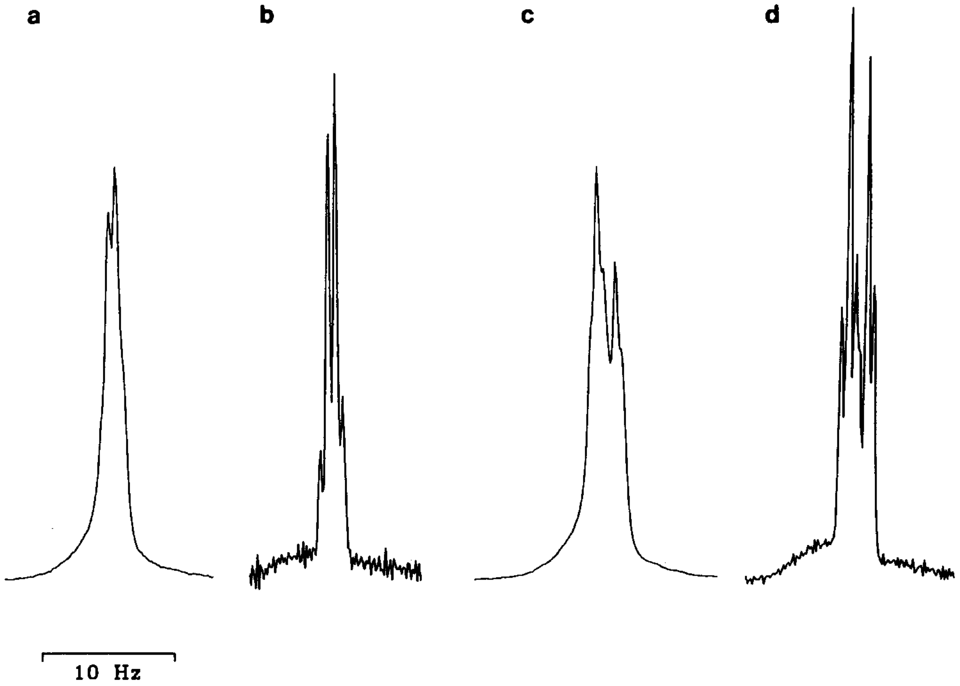

Fig. 6. Partial 200 MHz ^1H NMR spectra of $[HD_2(CpCo)_4(\mu_3\text{-}CCH_3)]^{2+}$ $[\mathbf{3}+2D]^{2+}$ in CD_2Cl_2/CF_3COOD. Multiplets at $\delta = 6.36$ (a, raw data; b, resolution enhanced) and $\delta = 5.48$ (c, raw data; d, resolution enhanced). Digital resolution is 0.1 Hz.

$$\underset{\mathbf{3}}{[H(CpCo)_4(CCH_3)]} \xrightleftharpoons[CO_3^{2-}]{X^+} \underset{[\mathbf{3}+X]^+}{[HX(CpCo)_4(CCH_3)]^+} \xrightleftharpoons[H_2O]{X^+} \underset{[\mathbf{3}+2X]^{2+}}{[HX_2(CpCo)_4(CCH_3)]^{2+}}$$

X = H, D

Scheme 1.

quartet ($\delta = 6.36$, *ca.* 0.5 Hz splitting, Cp_{ax}), two triplets ($\delta = 5.484$, 5.477, *ca.* 0.5 Hz, Cp_{eq}), a broad multiplet ($\delta = 5.38$, CH_3) and a broad singlet ($\delta = -25.2$, hydride) (Fig. 6). The splitting did not change when the hydride resonance was irradiated.

The results are discussed in terms of the protonation/deprotonation equilibrium shown in Scheme 1.

In neat acids, quantitative deprotonation of **3** occurs within a few minutes. With lower concentrations of acid in methylene chloride the second protonation step ($[\mathbf{3} + H]^+ + H^+ \rightarrow [\mathbf{3} + 2H]^{2+}$) is much slower, so that both $[\mathbf{3} + H]^+$ and $[\mathbf{3} + 2H]^+$ can be observed simultaneously for several hours at ambient temperature. As expected [31], deuteronation of **3** with CF_3COOD shows a strong normal kinetic isotope effect but is still thermodynamically favoured. The absence of H/D exchange in solutions of $[\mathbf{3} + D]^+$ and $[\mathbf{3} + 2D]^+$ in CF_3COOD or CD_2Cl_2/CF_3COOD is not surprising. Trifluoroacetate is only a very weak base, making the protonation/deuteronation reactions essentially irreversible. Deprotonations of $[\mathbf{3} + 2H]^{2+}$ and $[\mathbf{3} + 2D]^{2+}$ by D_2O are quite slow. Since no further deuterons are incorporated into the clusters the reverse reactions, *e.g.* $[H_{3-x}D_xO]^+ + [\mathbf{3} + H]^+ \rightarrow H_{3-x}D_{x-1}O + [\mathbf{3} + H + D]^{2+}$ ($x = 1$–3), do not seem to play an appreciable rôle. Alternatively the observed lack of D incorporation could be attributed to a very large equilibrium isotope effect [30], which would render the concentration of $[\mathbf{2} + D]^+$ too small to be observed as a reduction of the integral of the hydride resonance of the isotopomeric mixture.

The transient broadening of the ^1H NMR resonance of the methyl group of $[\mathbf{3} + H]^+$ and $[\mathbf{3} + D]^+$, apparent during the initial stages of protonation and deuteronation, cannot be explained uniquely on the basis of our data. It could be taken as a sign for a reversible initial addition of a proton/deuteron to a CoC edge or Co_2C face of the cluster **3**. The ^1H NMR resonance at δ -5.56 which was observed during the reaction of **3** with CF_3COOD would be consistent with an agostic CHCo or $CHCo_2$ interaction. However, observation of an agostic *hydrogen* during *deuteronation* necessarily means that the Co_3 face capping hydride in **3** is temporarily shifted to an agostic position after addition of a deuteron to the cluster. This could be the case when the deuteron is first added to the agostic position and subsequently exchanges with the hydride. It is, however, difficult to imagine how and why such a dynamic species should be converted into $[\mathbf{3} + D]^+$ with both *endo* H and *endo* D in "hydridic" positions on a slower timescale. In addition, the "agostic" ^1H NMR resonance (δ -5.56) is not observed during the protonation of **3** although the broadening of the methyl resonance still occurs. It is, however, likely that the μ_3-alkylidyne is not an "innocent" ligand in a possible primary kinetically controlled protonation/deuteronation product, although we do not know its structure.

The observed splitting of the ^1H NMR resonance of the equatorial Cp groups in two components shows that hydride/deuteride mobility in $[\mathbf{3} + 2D]^{2+}$ is much more hindered than in $[\mathbf{3} + H]^+$, $[\mathbf{3} + D]^+$ or **3**. In a structure which is static on the NMR timescale, two of the three equatorial CpCo groups are part of Co_3H and Co_3D bridges whilst the third is part of two Co_3D bridges. The small deuterium isotope effect then causes the two different types of equatorial CpCo groups to become unequivalent in the ^1H and ^{13}C NMR spectra.

There is no clear cut explanation for the observed shifts of the ^1H NMR resonances of $[\mathbf{2} + H]^+$ in CD_2Cl_2 solution on prolonged standing. The observed behaviour on addition of water points to an effect of ion pairing [31]. The observed multiplet structure of the ^1H NMR resonances of $[\mathbf{3} + D]^+$ and $[\mathbf{3} + 2D]^{2+}$ in CD_2Cl_2/CF_3COOD may also be due to a close association of cations and anions. The only feasible reason for the small but significant splitting is a weak coupling with the ^{19}F nuclei of the trifluoroacetate anions or excess trifluoroacetic acid. This would require a particular orientation of the trifluoromethyl groups relative to the ethylidyne cluster cations in solution, which must be static on the NMR time scale. Compatible with the spectra is an arrangement for $[\mathbf{3} + 2D]^{2+}$, in which the axial Cp ligand is in contact with three and each of the equatorial Cp ligands with two fluorine atoms. Confirmation of this interesting phenomenon, which was only observed with one sample, must await a variable temperature ^{19}F NMR spectroscopic investigation.

3. Conclusions

In contrast to many μ_3-alkylidyne metal carbonyl clusters, structures with *endo* hydrogens in agostic positions are not thermodynamically stable for the μ_3-alkylidyne cyclopentadienylcobalt clusters $[H(C_5R_5$-

$Co)_3(CR)_2]^+$ and $[H_n(CpCo)_4(CCH_3)]^{(n-1)+}$ (n = 1–3) and their deuteronated analogues. They cannot, however, be ruled out as transient kinetically controlled primary products or intermediates during the protonation/deuteronation of the clusters **1** and **3**. We are currently investigating the stability of such structures by MO theoretical methods.

4. Experimental section

4.1. *General procedures*

All operations were carried out under purified nitrogen (BASF R3-11 catalyst) by use of Schlenk techniques. Solvents were dried by conventional methods. CF_3COOH (Merck), CF_3COOD (Aldrich) and CF_3SO_3H (Merck) were degassed by several freeze-pump-thaw cycles and stored under nitrogen. Complexes **1–3** were prepared as previously described [14b,15]. NMR spectra were obtained with a Bruker WH 300 instrument (300 MHz for ^1H, 75.46 MHz for ^{13}C) and a Bruker AC 200 (200.1 MHz for ^1H, 50.3 MHz for ^{13}C) instrument. ^1H NMR spectra in proton-containing solvents were recorded with elimination of solvent signals by use of the standard presaturation pulse sequence. In critical cases special care was taken to obtain precise integrals. Typical parameters on the 200 MHz instrument were: 26° pulses (2.4 μs), 10 s relaxation delay, 64 K FIDs using quadrature phase detection, acquisition time 4.4 s corresponding to 7.5 KHz spectral width, apodisation by exponential multiplication with a line broadening factor of 0.2 to 0.4 Hz. In some cases 128 K FIDs corresponding to 65536 complex data points were collected to achieve good ($\approx$ 0.1 Hz) digital resolution. Saturation transfer was not observed in the presaturation experiments. Chemical shifts are given as δ values determined relative to internal solvent resonances ($\delta(CHDCl_2)$ 5.32, $\delta(CF_3COOH)$ 11.19. $\delta(HDO)$ 4.63, $\delta(CD_2Cl_2)$ 53.8, $\delta(CF_3COOD)$ 116.6). Since the ^1H resonance of water is pH- and temperature-sensitive small differences in the chemical shifts occurred between samples. Mass spectra were obtained on a Finnigan MAT 8230 instrument (electron impact ionization (EI) mode (70 eV) or field desorption (FD)). Elemental analyses were performed at the microanalytical laboratory of the Chemische Institute, Universität Heidelberg.

4.2. *Preparation of* $[H_2(CpCo)_4(\mu_3\text{-}CCH_3)]^+[SO_3CF_3]^-$ ($[3+H]^+[SO_3CF_3]^-$)

The acid CF_3SO_3H (31 μl, 53 mg, 0.35 mmol) was added to a solution of 180 mg (0.34 mmol) of $[H(CpCo)_4(\mu_3\text{-}CCH_3)]$ (**3**) in 50 ml of ether. A dark precipitate was formed immediately, and was filtered off after 30 min, washed with 20 ml of ether, and dried *in vacuo*. Black powder, yield 206 mg (90%). $C_{23}H_{25}Co_4F_3O_3S$ (674.237), calc. C 40.97, H, 3.74, found C 40.97, H. 3.80%.

4.3. *Preparation of* $[H_{2-x}D_x(CpCo)_4(\mu_3\text{-}CCH_3)]^+[(CF_3COO)_2X]^-$ ($[3+X]^+[(CF_3COO)_2X]^-$) (x = 0–2, $X = H, D$)

A 10 mg sample of **3** was dissolved in 0.5 ml of CF_3COOD. After 12 h at room temperature the solvent was removed *in vacuo*. The resulting dark brown oil was treated with 0.2 ml of D_2O to give a brown suspension. After several weeks the solution had turned pale yellow and large dark crystals formed on the wall of the sample tube. The mother liquor was removed with a syringe and the product briefly dried *in vacuo*.

4.4. *X-ray crystal structure determination of* $[H_{2-x}D_x(CpCo)_4(\mu_3\text{-}CCH_3)]^+[(CF_3COO)_2X]^-$ ($[3+X]^+[(CF_3COO)_2X]^-$) (x = 0–2, $X = H, D$)

A plate-shaped crystal was mounted in a Lindemann tube and transferred to a STOE STADI-2 Weissenberg two circle diffractometer. Intensity data were collected at ambient temperature and corrected for Lorentz, polarisation and absorption effects (Table 5). From systematic absences the possible space groups were *Pbcm* or *Pbc*2_1. The structure was solved by the heavy atom method and refined by full matrix least squares [32*]. All non-hydrogen atoms were given anisotropic thermal parameters. Hydrogen atoms (except H1, whose isotropic thermal and positional parameters were refined) were placed in calculated positions. During refinement of the structure the cyclopentadienyl rings and CF_3 groups were treated as rigid groups (either symmetrical pentagons or constrained C–C, C–F and F–F distances). In *Pbcm* the Cp rings showed disorder, which was resolved satisfactorily in terms of a model with two rigid C_5H_5 pentagons staggered relative to each other with site occupation factors of 1/3 and 2/3, respectively. Two disordered positions were also assumed for the CF_3 group. Refinement in *Pbc*2_1 gave high correlations and did not converge. The calculations were performed with the SHELX-76 program [33] on an IBM 3090 mainframe computer. Scattering factors were those given by Cromer and Mann [34]. Anomalous dispersion factors were taken from ref. 35. Graphical representations were drawn with the SCHAKAL-88 [36] program on an Atari 520 ST$^+$ microcomputer fitted with a Motorola 68020/68881 processor board.

4.5. *Preparation of* $[H_3(CpCo)_4(\mu_3\text{-}CCH_3)]^{2+}2[CF_3COO]^- \cdot xCF_3COOH$ ($[3+2H]^+2[CF_3COO]^- \cdot xCF_3COOH$)

Complex **3** (180 mg, 1.2 mol) was dissolved in 15 ml CF_3COOH. After 2 h the solvent was removed under reduced pressure. The residual black oil was washed with diethyl ether and dried *in vacuo*. Apart from variable amounts of CF_3COOH the product was pure as indicated by ^1H NMR spectroscopy. No reproducible C/H analyses could be obtained owing to slight contamination with acid.

4.6. Low temperature protonation of 1b and 3

A solution of the relevant metal cluster in 0.5 ml of CD_2Cl_2 was placed in a 5 mm NMR tube under nitrogen. The NMR tube was capped with a septum stopper, the solution frozen with liquid nitrogen, and CF_3COOH added from a microlitre syringe. The frozen solution was then allowed to warm to just above the melting point, and briefly agitated to allow mixing with the acid, and the tube quickly transferred to the precooled probe of the NMR spectrometer. Spectra were taken at suitable intervals.

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