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Neutron Diffraction Structure Analysis of a Triply-Bridged Binuclear Cobalt Hydride Complex, $[(\eta^5\text{-Cp*})\text{Co}]_2\text{H}_3$

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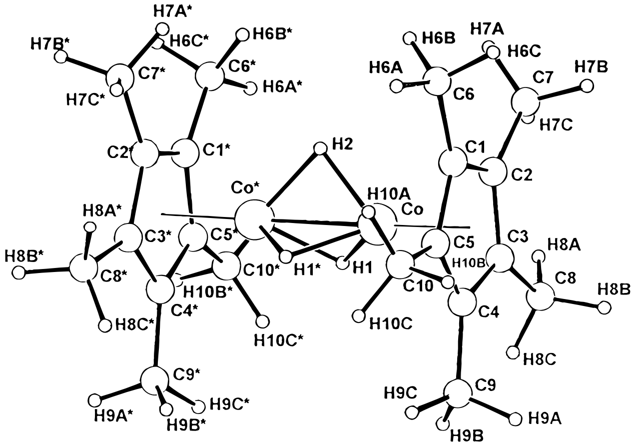

Figure 1. Molecular structure of **1**.

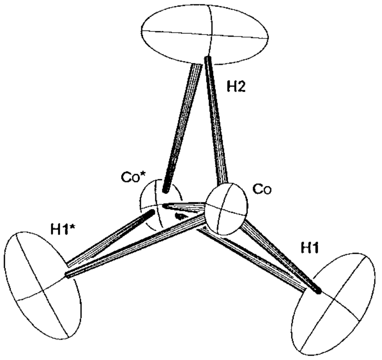

Figure 2. View along the Co−Co*-bonding vector. Displacement ellipsoides are drawn at the 50% probability level.

Table 1. Experimental Data

space group	$P2/c$ (No. 13)	volume (Å^3)	952.2
a (Å)	9.548(1)	d_{calc} (g/cm^{-3})	1.36
b (Å)	8.499(1)	T (K)	20.0 ± 0.1
c (Å)	12.214(2)	λ (Å)	1.15863(8)
β (deg)	106.11(2)	μ (cm^{-1})	3.151
Z	2		

abs cor	analytical (min 1.319/max 1.776)
(sin θ)/λ limit (Å^{-1})	0.705
cryst dimens (mm)	3.0 × 1.2 × 1.0
no. of measd reflcns ($+h$, $-k$, $\pm l$)	2919
no. of independent reflcns	2337
no. of variable parameters	338

$R(F^2)$	0.088	wR(F^2)	0.085
EOF	1.169	wR(F) [$F > 3\sigma(F)$]	0.043 (1407 reflcns)

Introduction

The reaction of cobalt atoms with pentamethylcyclopentadiene leads, beside other products, to the formation of $[(\eta^5\text{-Cp*})\text{Co}]_2\text{H}_3$ (**1**).[2] **1** is paramagnetic and contains a very short Co−Co bond of 2.253(1) Å. To explain this short bonding distance, a free Co−Co double bond was originally postulated. The three bridging hydrido ligands were missed in the original low temperature X-ray analysis. Although considerable residual electron density was observed on the crystallographic 2-fold axis perpendicular to the Co−Co bonding vector, the distances from this electron density to the Co atoms were not in a typical range expected for a metal hydride bond. In addition, as is well-known, the situation here is complicated by the fact that experimental errors may cause the accumulation of electron density on symmetry elements. The residual electron density was therefore not properly interpreted. The paramagnetism of **1**, as well as its inert behavior in the presence of CO, were not sufficiently investigated and this consequently led to an incomplete structural model.[3] In the meantime theoretical[4] and experimental[5] work by other groups led to the conclusion that **1** contains three μ_2-bridging hydrido ligands. This conclusion was supported by a new X-ray structural analysis of **1**, in which electron density was located that could be assigned to the hydrido ligands. In view of the remarkably short Co−Co bond, we were interested in obtaining more detailed information about the bridging hydride ligands. To this end, we have undertaken a neutron diffraction study, the results of which we report here.

Experimental Section

1 was synthesized by the method described by Schneider et al.[2,3] Single crystals suitable for neutron diffraction were grown by slow cooling of a solution of **1** in diethyl ether to −20 °C. A crystal with a volume of 3.6 mm^3 was mounted on an aluminum pin oriented approximately along the crystallographic [010] direction and immediately placed in an indium-sealed aluminum can under argon, before being attached to the cold finger of an Air Products and Chemicals Inc. Model CS-202 Displex closed-cycle refrigerator. Measurements were made at the Brookhaven High Flux Beam Reactor, with an automated four-circle diffractometer operating under the Reactor Experimental Control Facility[6] and a wavelength of 1.15863(8) Å. The temperature was held at 20.0 (±0.1) K during measurements of the Bragg reflections.

The cell constants were determined by a least-squares fit of the $\sin^2 \theta$ values of 32 centered reflections ($35.3° < 2\theta < 76.5°$). The intensities of the 2919 Bragg reflections ($0 \leq h \leq 13$, $-11 \leq k \leq 0$, $-16 \leq l \leq +16$) were measured with a $\theta/2\theta$ step-scan technique. For $0 \leq d^* \leq 0.43$ Å^{-1} the scan range was varied according to $\Delta(2\theta) = 2.6°$, with a step size of 0.06°. For $0.43 \leq d^* \leq 0.70$ Å^{-1}, the scan range was varied according to $\Delta 2\theta = (0.149 + 5.919 \tan \theta)°$, and the

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Table 2. Structural Results on Triply Hydrogen-Bridged Metal−Metal Bonds [M(μ_2-H)$_3$M]

compound	distance (Å)			angle (deg)		ref
	M−M	M−H(br)	H···H	M−H−M	H−M−H	
$Co_2(\mu\text{-}H)_3(\eta^5\text{-}Cp^*)_2$ (neutron)	2.253(9)	1.641(6)	2.068(7)	86.8(3)	78.1(3)	this work
$[Ir_2(\mu\text{-}H)_3(\eta^5\text{-}Cp^*)_2]^+$ (neutron)	2.465(3)	1.78(1)	2.22(2)	87.8(4)	77.2(7)	11
$[Re_2(\mu\text{-}H)_3H_6(\text{triphos})]^-$ (neutron)	2.594(1)	1.86(4)	2.30(4)	89.6(10)	77.4(10)	13
$[Co_2(\mu\text{-}H)_3(as_3)_2]^+$ (X-ray)	2.377(8)	1.70	2.11	88.7	76.6	14

Table 3. Variation of Co−H Distance with Hydrogen Coordination Number

compound[a]	H coord no.	Co−Co dist Å	Co−H dist (Å)	Co−H−Co angle (deg)	ref
$CoH(CO)_4$	1		1.558(18)		15
$Co_2(\mu_2\text{-}H)_3(\eta^5\text{-}Cp^*)_2$	2	2.253(9)	1.641(6)	86.8(3)	this work
$Co_3Fe(\mu_3\text{-}H)(CO)_9[P(OMe)_3]_3$	3	2.489(7)	1.734(4)	91.8(2)	16
$[Co_6(\mu_6\text{-}H)(CO)_{15}]^-$	6	2.580(12)	1.823(13)	90.0(6)	17

[a] All entries in Table 3 are derived from neutron diffraction structure determinations, except those for $CoH(CO)_4$ which were derived from an electron diffraction study.

step size was varied to give approximately 60 points in each scan. The scan profiles were integrated, and the background corrections were determined by summing the counts for four steps on either end of each scan. The experimental stability was monitored by three intensity standards scanned every 100 reflections. Symmetry equivalent reflections were averaged to yield 2337 reflections [$wR_{int}(F^2) = 0.018$]. A Lorentz correction and analytical absorption correction were applied.[7] Neutron scattering lengths used are $b_{Co} = 2.780$, $b_C = 6.6484$ and $b_H = -3.709$ fm.[8] Initial atomic positions of Co and C as well as of the H atoms on the Cp* ring were taken from the X-ray results.[2] The three hydride ligands were located in a difference-Fourier synthesis. Least-squares refinements were carried out using the program UPALS,[9] minimizing the quantity $\Sigma w|F_o^2 - F_c^2|$. Weights were chosen as $w = [\sigma_c^2(F_o^2) + (0.02F_o^2)^2]^{-1}$. The total of 338 parameters included positional and anisotropic thermal parameters for the 28 independent atoms, a scale factor, and an extinction parameter. The effects of extinction were negligible. In the last refinement cycle, 33 weak reflections were omitted because they were influenced by aluminum powder diffraction from the cryostat. The refinement converged [$\Delta p_i/\sigma(p_i) < 0.001$] to $R(F^2) = 0.088$, $wR(F^2) = 0.085$, and EOF = 1.169[9] [$wR(F) = 0.043$ for 1407 reflections having $F > 3\sigma(F)$]. The final difference-Fourier synthesis was essentially featureless.

Results and Discussion

Compound **1** crystallizes in the monoclinic space group *P*2/*c* (No. 13), as reported earlier.[2,5] The molecular structure is given in Figure 1. The center of gravity of the molecule lies on the crystallographic 2-fold axis perpendicular to the Co−Co bonding vector. The methyl groups lie almost ideally in the plane of the Cp* ring. The bond distances and angles are within the expected values. Three hydrido ligands were localized bridging the metal−metal bond. The hydrido ligands form an equilateral triangle [Figure 2; average H···H distance: 2.068(7) Å], and thus the existence of ideal μ_2-hydrido ligands[5] has been confirmed. H(2) lies on the 2-fold axis, while H(1) is in a general position. The Co−H−Co and H−Co−H angles amount in average to 86.8(3) and 78.1(3)°, respectively, and the Co−H distances to 1.641(6) Å. As expected, these values differ significantly from those obtained by the X-ray diffraction experiment [Co−H−Co angle = 97(3)°; Co−H distance = 1.47(5) Å].[5]

These results allow us to compare the central bonding region in a number of triply hydrogen-bridged metal−metal bonds, M(μ_2-H)$_3$M (Table 2). Neutron diffraction analyses have been carried out on two other complexes, $[Ir_2H_3(\eta^5\text{-}Cp^*)_2]^+[ClO_4]^-\cdot 2C_6H_6$[11,12] and $[Re_2(\mu_2\text{-}H)_3H_6(\text{triphos})]^-[N(C_2H_5)_4]^+$,[13] and an X-ray analysis has been obtained for a compound with a similar Co_2H_3 core, $[Co_2(\mu_2\text{-}H)_3(as_3)_2]^+$ $[B(C_6H_5)_4]^-$ [$as_3 = CH_3C(CH_2AsPh_2)_3$].[14] Despite differences in the metals and their oxidation states, these results show a remarkably constant geometry for the M(μ_2-H)$_3$M cores of these molecules (Table 2), with H···H nonbonding contacts remaining fairly constant in the range 2.0−2.3 Å, and M−H−M and H−M−H angles confined within the narrow limits 88 ± 2 and 77 ± 1°, respectively.

Also instructive is a comparison of Co−H distances as a function of the coordination number of hydrogen (Table 3). The present neutron analysis of **1** fills one of the missing entries in the sequence Co−H (terminal), $Co_2(\mu_2\text{-}H)$, $Co_3(\mu_3\text{-}H)$, $Co_6(\mu_6\text{-}H)$, and allows one to see a gradual increase in Co−H distance (1.56, 1.64, 1.73, 1.82 Å) along the above series.[15−17] This may reflect a decrease in Co−H bond order as the coordination number of hydrogen increases.

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Supporting Information Available: For compound **1**, Table S1 (crystal data and details of data collection), Table S-2 (fractional atomic coordinates), Table S-3 (anisotropic displacement parameters), and Table S-4 (bonding distances and angles) (5 pages). Ordering information is given on any current masthead page.

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