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THE SYNTHESIS AND X-RAY STRUCTURE OF $Co_3(C_5Me_5)_3(\mu_3\text{-}CCH_3)_2$; CONVERSION OF ETHYLENE DIRECTLY INTO A CARBYNE LIGAND

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Summary

Thermolysis of $Co(C_5Me_5)(C_2H_4)_2$ gave $Co_3(C_5Me_5)_3(\mu_3\text{-}CCH_3)_2$ in good yield. The cluster was characterised by X-ray crystallography. The crystals were hexagonal, space group $P6_3/m$, a 10.678(3), c 15.440(5) Å. The structure was solved by direct methods and refined by full matrix least squares to $R = 0.062$ and 534 unique reflections with $I > 3\sigma(I)$. The Co atoms lie in the mirror plane of the unit cell around a three-fold symmetry axis. Principle bond lengths are Co–Co 2.369(3); Co–C (C_5Me_5) 2.111(12), 2.108(7), 2.118(8); Co–C (μ-CCH_3) 1.936(8); C–CH_3 (μ-CCH_3) 1.529(35) Å.

The synthesis of polynuclear metal complexes containing bridging hydrocarbon species has been the subject of many recent publications. On the one hand, for example, bridging methylene complexes are thought to be formed from syn-gas in Fischer–Tropsch catalysis [1], while on the other hand there is evidence that olefins form similar species when adsorbed onto platinum surfaces [2]. However, there are relatively few examples of the direct formation of bridging methylene and carbyne ligands from either syn-gas or olefins in homogeneous systems [3,4].

Bridging vinyl and vinylidene ligands have been shown to be formed readily from olefins in Ru and Os clusters; $Os_3(CO)_{12}$ shows this type of reaction [5,6]. The product can then be converted into a μ_3-alkylidyne complex with hydrogen. $Ru_4(CO)_{12}H_4$ reacts with ethylene to give $Ru(CO)_9H(\mu_3\text{-}CCH_3)$ directly [7].

Bridging alkylidyne complexes are accessible by a number of other routes. For example, $Co_3(CO)_9(\mu_3\text{-}CR)$ (R = H, Me etc.) complexes are formed from $Co_2(CO)_8$ and halogenated hydrocarbons [8]. Addition of unsaturated metal centres to metal alkylidene complexes offers another route [9]. Also, acetylenes can be cleaved by metal centres to produce alkylidyne complexes. Thus $Co(C_5H_5)(CO)_2$ reacts with

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RC≡CR (R = Ph, n-Bu, $SiMe_3$, CO_2Me) in refluxing decalin to give $Co_3(C_5H_5)_3(\mu_3\text{-}CR)_2$ [10].

This paper describes the generation of a triple bridging carbyne ligand from ethylene alone in the absence of metal hydride or carbene species in the starting material.

Results

When $Co(C_5Me_5)(C_2H_4)_2$ (I) in n-octane or n-nonane was heated to 110°C for 24 h thermal decomposition took place. After cooling, black crystals of II were isolated. Under 1 bar of C_2H_4, temperatures over 120°C are required for the decomposition to proceed. Ethane (38%), butenes (13.5%), hexenes (8.2%), octenes (7.3%) and decenes (1.5%) were also detected by GLC (the percentages indicate approximate yields based on moles of Co present). The air sensitive complex II was stable in refluxing n-nonane and could be easily recrystallised.

The ^1H NMR spectrum of II in C_6D_6 showed broad unresolved signals, suggesting the formation of paramagnetic material. In cyclohexane-d_{12} the spectra were better resolved and singlets were observed at 1.4 and 5.1 ppm. No hydride resonances were seen.

The mass spectrum of II showed a very weak signal at ca. m/e 628, with a set of four, much stronger peaks at m/e 606–610. The data were insufficient to assign a structure to II, and so an X-ray structure determination was performed.

X-ray structure determination

Data collection

The thick hexagonal tablets were mounted in 0.3 mm diameter Lindemann tubes under nitrogen. A selected crystal was then mounted so that it could be rotated about the normal to its hexagonal face. Oscillation, zero and two upper layer equi-inclination Weissenberg photographs showed the crystals to be hexagonal and of low symmetry $6/m$. Space group absences were observed only for $00l$, l odd, indicating either $P6_3$ or $P6_3/m$. An approximate unit cell of a 10.6 and c 15.3 Å was obtained, which was estimated to contain 67 carbon atoms.

The same specimen was then mounted on a CAD 4 diffractometer and an accurate cell and orientation matrix obtained. Since the crystal is hexagonal the unique set of reflections lie in 1/12 of reciprocal space, and as the crystal has a relatively small cell volume, the opportunity was taken to measure 1/4 of reciprocal space corresponding to reflections with $h > 0$, k taking + or − values and $l > 0$. Symmetry equivalent reflections were taken then averaged to give statistically more accurate data. Data collection was made, recording reflection intensities up to $\theta = 73°$ using Cu-K_α radiation with three intensity control reflections measured every hour of counting time. Analysis of the control reflections showed negligible crystal decay. The raw data were then corrected for the usual Lp factors and averaged to give the unique reflection set for a hexagonal crystal. Table 1 lists crystal data and data collection parameters.

A statistical test on the distribution of the intensities favoured a centro-symmetric crystal so that space group $P6_3/m$ was adopted.

TABLE 1

SUMMARY OF CRYSTAL DATA AND INTENSITY DATA COLLECTION FOR $Co_3(C_5Me_5)_3(\mu_3\text{-}CCH_3)_2$

Compound	$Co_3(C_5Me_5)_3(\mu_3\text{-}CCH_3)_2$
Formula	$Co_3C_{34}H_{51}$
Colour	Black
Cell	Hexogonal a 10.678(3), c 15.440(4) Å V 1524.5 Å^3 $Z = 2$ $D_c = 1.391$ g cm^{-3}
Space group	$P\ 6_3/m$
Crystal dimensions	0.33 mm across hexagonal face 0.20 mm thick
X-radiation Cu-K_α	1.5418 Å
Monochromator graphite	
ϑ-range 2°–73°	
Scan $W/2\theta$	

Total	no. of reflections measured	3335
	no. with $I > 2\sigma(I)$	2093
	$I > 3\sigma(I)$	1748
	no. of unique reflections	1058
	no. with $I > 3\sigma(I)$	534

Structure determination

In the absence of a known chemical formula, $Co_6C_{72}H_{120}$ was arbitrarily assigned and fed into the direct methods solution program MULTAN. Taking the E map with the highest figure of merit, the strongest peak was taken as the cobalt atom lying in two sets of three-fold positions in the mirror plane at $Z = 1/4$ and $3/4$ around the $\bar{6}$ axes, with Co–Co distances of ~ 2.34 Å. The Patterson map was also calculated and could be interpreted to give the same solution for the coordinates of the Co atom. No attempt was made to find the C atom positions.

Using the independent Co atom coordinates as input, two cycles of refinement of the scale factor, followed by three cycles of structure factor refinement, using unit weights, served to reduce R to 0.26. A Fourier and difference map were than calculated which readily showed the positions of the C atoms.

Further least squares refinement including the newly found C atoms reduced R to 0.144, based on 657 unique reflections with intensity $I > 2\sigma(I)$. It was noted that the temperature factor of the apical carbon atoms on the three fold molecular axis, C(7), was very high, ca. 15 Å^{-2} and that C(7)–C(8) was very long, ca. 1.7 Å. At this point an absorption correction was applied by program [11] which required the use of all the symmetry related reflections. Applying this correction to 2077 reflections reduced R from 0.21 to 0.16. The data were then reaveraged as before.

The methyl H atoms attached to the cyclopentadienyl ligand were then estimated from the Fourier and difference maps and their positions regularised to conform to tetrahedral geometry. The hydrogen atoms associated with C(7) could not be located. These parameters were then included as a fixed contribution to the structure factors and further refinement steadily reduced R to 0.085 for 595 reflections using statistical weights, a fudge factor of 0.1 and a cut-off at $I > 3\sigma(I)$.

Anisotropic temperature factors were next applied to the non-hydrogen atoms and the temperature factors of the hydrogen atoms fixed at 6.0 Å^{-2}. Four more cycles of refinement reduced R to 0.064 with a C(7)–C(8) distance of 1.529 Å. An attempt to refine the H atoms coordinates proved abortive. However, it indicated that the temperature factors of the hydrogenation should be increased to 12 Å^{-2} and four cycles of refinement yielded R of 0.062, a significant reduction as judged by Hamilton's test [12]. The correction for anomalous dispersion was applied throughout the refinement.

Tables of structure factors can be obtained from the authors.

Discussion

The overall symmetry of II is trigonal bipyramidal $(\bar{6})$. The cobalt atoms lie in the mirror plane with the cyclopentadienyl rings perpendicular to the plane and symmetrically attached to the Co atoms. The two C_2 groups lie axially above and below the mirror plane. Figure 1 shows a drawing of the molecule and the atom numbering adopted. Table 2 gives the atomic coordinates and Table 3 lists the molecular geometry with the standard deviations in parentheses, referring to the last decimal places. The Co–Co distance of 2.369(3) Å is shorter than occurs in the metallic state, but longer than in $Co_2(C_5Me_5)_2(\mu_2\text{-}CH_2)(\mu\text{-}CO)$ where the distance is 2.320(1) Å [13]. In this latter molecule the Co–(CH_2) and Co–(CO) are 1.909(9) and 1.849(8) Å, respectively, compared to 1.936(18) Å for Co–(CMe) in II.

The presence of an alkylidyne group is established by the C(7)–C(8) distance of 1.529(35) Å, which corresponds to a C–C single bond. The methyl group of the bridging ligand appears from its high thermal ellipsoid to be undergoing some kind of fluxionality although this is not apparent from the ^{1}H NMR. The high freezing point of cyclohexane prevented a low temperature study.

It is of interest to note that similarities have been pointed out between the

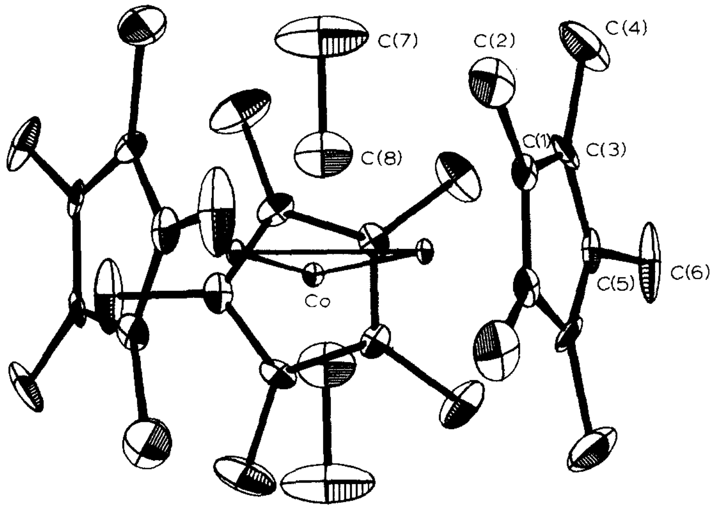

Fig. 1. Molecular drawing of molecule II.

TABLE 2

ATOM COORDINATES FOR $Co_3(C_5Me_5)_3(\mu_3\text{-}CCH_3)_2$

Atom	x/a	y/b	z/c
Co	0.6936(2)	0.2209(1)	0.2500(0)
C(1)	0.3891(7)	0.3800(8)	0.2953(6)
C(2)	0.4269(10)	0.5058(10)	0.3531(8)
C(3)	0.3370(8)	0.2375(10)	0.3242(6)
C(4)	0.3089(13)	0.1859(14)	0.4156(9)
C(5)	0.3046(11)	0.1513(13)	0.2500(0)
C(6)	0.2229(15)	0.0124(16)	0.2500(0)
C(7)	0.6667(10)	0.3333(0)	0.4377(20)
C(8)	0.6667(0)	0.3333(0)	0.3387(17)

TABLE 3

BOND DISTANCES AND ANGLES (standard deviations in brackets)

Atoms	Distance (Å)	Atoms	Angle (°)
Co–Co	2.369(3)	C(1)–C(1)–C(2)	126.8(0.7)
Co–C(1)	2.108(7)	C(1)–C(1)–C(3)	108.5(0.5)
Co–C(3)	2.118(8)	C(2)–C(1)–C(3)	124.6(0.9)
Co–C(5)	2.111(12)	C(1)–C(3)–C(4)	126.7(1.0)
C(1)–C(1)	1.400(18)	C(1)–C(3)–C(5)	106.7(0.9)
C(1)–C(2)	1.491(13)	C(4)–C(3)–C(5)	126.4(1.1)
C(1)–C(3)	1.406(12)	C(3)–C(5)–C(3)	109.8(1.3)
C(3)–C(4)	1.490(14)	C(3)–C(5)–C(6)	124.7(0.6)
C(3)–C(5)	1.400(12)		
C(5)–C(6)	1.514(17)		
C(7)–C(8)	1.529(35)		

infra-red spectrum of $Co_3(CO)_9(\mu\text{-}CCH_3)$ and the electron energy loss spectrum of ethylene absorbed on platinum (111) surface [2]. The authors interpret these similarities as a rearrangement of C_2H_4 to bridging ethylidyne and hydride on adsorption to Pt(111). The synthesis of II provides support for this rearrangement.

The dependence of decomposition temperature of I on the ethylene pressure is evidence for the reversible dissociation of ethylene from I. It is impossible to be precise about the mechanism of formation of II, but a 16e species $Co(C_5Me_5)(C_2H_4)$ probably inserts into ethylene C–H to form a vinyl hydride complex, which then reacts further, losing hydrogen by hydrogenating ethylene to ethane and forming II by agglomeration.

Experimental

Manipulations were carried out using Schlenk tube techniques under nitrogen atmosphere. I was made by a published procedure [14]. ^1H NMR spectra were recorded on a Bruker 200 MHz instrument.

Preparation of bis(μ$_3$-ethylidyne)tris(pentamethylcyclopentadienyl)tricobalt

A solution of 1.03 g (4.12 mmol) I in 15 cm^3 n-octane was heated at 110°C for 24

h. Black crystals of the product formed during this time and further material crystallised out on cooling. Yield 0.53 g, 60%. The sample was recrystallised from hot octene. Co 27.3% (calculated 27.8%). Crystals suitable for X-ray crystallography were obtained by slow cooling of hot octane solutions.

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