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SYNTHESIS, CATALYTIC ACTIVITY AND THE MOLECULAR STRUCTURE OF (μ_3-CCH_3)$Co_3(CO)_7$-μ-($Ph_2PCH_2PPh_2$)

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Summary

Reaction of (μ_3-CCH_3)$Co_3(CO)_9$ (I) with dppm (dppm = bis-(diphenylphosphino)methane) affords the cluster (μ_3-CCH_3)$Co_3(CO)_7$-dppm (II). The crystal and molecular structure of II have been determined at −160°C. The dppm ligand bridges one of the three metal–metal edges in the equatorial plane to give a five-membered ring, which adopts an envelope conformation.

Cluster II functions as a catalyst for the hydroformylation of 1-pentene (80 bar of H_2/CO (1/1); 110°C). The results indicate that the dppm bridging ligand stabilizes and activates the cluster for catalysis, and open the way to the synthesis of chiral clusters.

Introduction

The reversible or complete fragmentation of metal clusters under catalytic conditions is a well recognized obstacle to the development of a complete kinetic picture and/or mechanistic understanding of how clusters function as catalysts [1,2]. In order to inhibit complete dissociation of clusters, ligating atoms and/or groups are often employed. Several research groups are currently exploring this strategy [3].

In the case of trinuclear ruthenium clusters, we have shown that the metal framework is stabilized by bridging bis(diphenylphosphino)methane (dppm) ligand [4]. Such a ligand has been shown to act in polymetallic complexes as a metal–metal edge bridging group not as a chelating species [5–8]. Our attention has recently focussed on the cobalt cluster (μ_3-CCH_3)$Co_3(CO)_9$ (I) which belongs to a family of

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clusters known for their catalytic activity in hydroformylation and hydrosilylation reactions [9,10]. In this paper we report the synthesis, the structural characterization, and the catalytic activity of (μ_3-CCH_3)Co_3(CO)-μ-dppm (II). The ultimate goal of the work is to replace two carbonyl groups by dissymmetric bridging diphosphinomethane ligands ($R_2PCH_2PR'_2$) in an effort to obtain structurally chiral clusters [1,11] for catalytic purposes.

Experimental section

Preparation of (μ_3-CCH_3)$Co_3(CO)_7$-μ-($Ph_2PCH_2PPh_2$)

The reaction was carried out under nitrogen. The (μ_3-CCH_3)$Co_3(CO)_9$ was prepared by a published procedure [12]. A benzene solution (20 ml) containing (μ_3-CCH_3)$Co_3(CO)_9$ (209 mg, 0.46 mmol) and bis(diphenylphosphino)methane (174 mg, 0.46 mmol) was heated at 45°C for 3 h. The solution was concentrated by evaporation under vacuum and chromatographed on a silica gel column. Elution with a (1/2) dichloromethane/pentane mixture gave a purple band followed by a brown band. The first fraction was evaporated to dryness and recrystallized from a (1/3) benzene/pentane mixture yielding purple crystals which were separated and washed with pentane (72%). Further recrystallization from pentane/ether involving the solvent diffusion technique gave crystals suitable for X-ray diffraction.

M.p. 232–233°C. Anal. Found: C, 51.99; H, 3.10; Co, 21.96; P, 7.98. $C_{34}H_{25}O_7Co_3P_2$ calcd.: C, 52.6; H, 3.21; Co, 22.54; P, 7.90%.

Spectroscopic data

IR. IR spectra were recorded on a Perkin–Elmer 237 spectrophotometer in KBr pellets. ν(CO) (cm^{-1}): 2040sh, 2010sh, 1980s, 1970s.

NMR. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a 250 MHz Cameca spectrometer. ^{13}C spectrum was recorded at −40°C. ^1H NMR: δ 7.5 (C_6H_5); 4.0–3.54 (CH_2), $J(^{31}P-^1H_A)$ 16 Hz; $J(^{31}P-^1H_B)$ 9 Hz). ^{13}C NMR: δ 283 (C apical), 133, 131, 130, 128 (C_6H_5); 46.3 (CH_2); 45.2 (CH_3).

Mass spectrum. The mass spectrum was recorded on Ribermag R 10-10 spectrometer with field desorption chemical ionization technique.

Catalytic runs

Catalytic tests were runned in a 150 ml stainless steel autoclave fitted with a glass liner. In a typical procedure a solution of (μ_3-CCH_3)$Co_3(CO)_7$-μ-dppm (120 mg, 0.153 mmol) and 1-pentene (6 ml, 54.9 mmol) in toluene (24 ml) was introduced into the autoclave under argon. A pressure of 80 bar of a mixture CO/H_2 (1/1) was then applied at room temperature. The temperature was raised and maintained at 130 or 110°C during 24 h. At the end of the reaction the yields of 2-methyl-pentanal and -hexanal were measured by gas chromatography on a Carbowax 2.20 m column at 80°C using octanal as internal standard.

Solution and refinement of the structure

Precession photographs showed that the compound crystallizes in space group *Pbca* of the orthorhombic system. Crystal data and related details of data collection are given in Table 1. The procedure for the structure refinement is as described elsewhere [13].

TABLE 1

SUMMARY OF CRYSTAL AND INTENSITY DATA

Compound	$(\mu_3\text{-CCH}_3)\text{-}\mu\text{-(P-P)-(P(C}_6\text{H}_5)_2)\text{CH}_2)\text{CO}_3(\text{CO})_7$		
Mol. formula	$C_{34}H_{25}Co_3P_2O_7$		
Mol. wt.	784.3		
a (at −160°C) [a]	19.831 (3) Å	(at 22°C)	20.033 (7)
b	28.198 (3) Å		28.473 (9)
c	11.657 (2) Å		11.761 (3)
V	6518.5 Å^3		6708.5 Å^3
Z	8		
Density (calcd. at −160°C)	1.598 g cm^{-3}		
Density (meas. at room temperature in $ZnCl_2$ (aq.))	1.55(2) g cm^{-3}		
Space group	$Pbca\text{-}D_{2h}^{15}$		
Crystal dimensions	0.928×0.500×0.143 mm		
Boundary faces of the prism	{100}, {010}, {051}		
Temperature	−160±1°C		
Radiation	Mo-K_α (λ(Mo-K_{α_1}) 0.7093 Å) from monochromator		
Linear abs. coeff. (μ)	17.2 cm^{-1}		
Transmission coefficient	0.751–0.887		
Take-off angle	3.2°		
Scan speed	2°/min in 2θ		
2θ limits	3–52°		
Final no. of variables	248		
Reflections collected	7072		
Unique data used ($F_0^2 > 3\sigma(F_0^2)$)	4947		
Quantity minimized	$\Sigma w(\lvert F_0\rvert - \lvert F_c\rvert)^2$		
Weight	$w = 4\,F_0^2/\sigma^2(F_0^2)$		
$R = \Sigma\lVert F_0\rvert - \lvert F_c\rVert/\Sigma\lvert F_0\rvert$	0.055		
$R_w = (\Sigma w(\lvert F_0\rvert - \lvert F_c\rvert)^2/\Sigma_w F_0^2)^{1/2}$	0.065		
Error in observn of unit weight	3.47 electrons		

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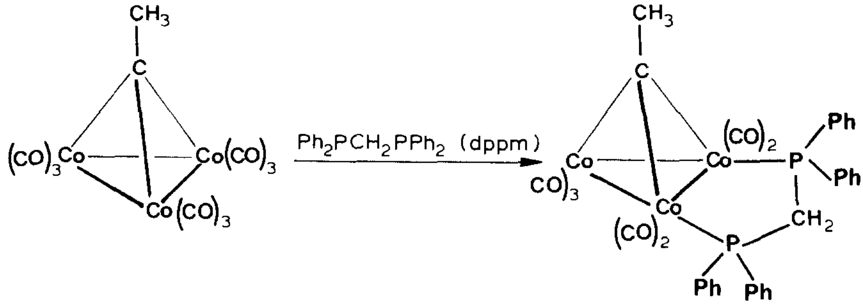
[a] The low-temperature system is an extensively modified version of a design by: J.C. Huffmann, Ph.D, Thesis, Indiana University, 1974. It is commercially available from Soterem, Zone Industrielle de VIC, 31320 Castanet (France).

The direct method approach (MULTAN) yielded the correct atomic coordinates for all non-hydrogen atoms. In order to reduce the number of variable parameters, phenyl rings were treated as rigid groups (D_{6h} symmetry; C–C 1.395, C–H 0.95 Å). Further refinements of a model including 22 independent atoms with anisotropic thermal parameters and 4 rigid groups converged to $R = 0.055$ and $R_w = 0.065$.

Final values for all the independent atoms are listed in Table 2 and those of rigid groups are in Table 3. Lists of observed and calculated structure factor amplitudes and thermal parameters are available from the authors.

Results and discussion

The reaction of $(\mu_3\text{-CH}_3\text{C})\text{Co}_3(\text{CO})_9$ with one equivalent of bis(diphenylphosphino)methane (dppm) in benzene at 45°C readily gives the expected compound $(\mu_3\text{-CCH}_3)\text{Co}_3(\text{CO})_7\text{-}\mu\text{-dppm}$. This product results from replacement of two carbonyls by the dppm ligand.



(I) (II)

The crystal structure of (μ_3-CCH$_3$)Co$_3$(CO)$_7$-μ-dppm involves a unit cell containing of eight well separated discrete molecules. Interatomic bond distances and angles are given in Tables 4 and 5, respectively. Figure 1 shows a perspective view of the cluster including the labeling scheme. Figure 2 is a stereoscopic diagram of the whole molecule.

To a first approximation, we can regard the structure of (μ_3-CCH$_3$)Co$_3$(CO)$_7$-μ-dppm as differing from that of (μ_3-CCH$_3$)Co$_3$(CO)$_9$ [14] by a simple replacement of

TABLE 2

ATOMIC POSITIONAL PARAMETERS FOR (μ_3-CCH$_3$)Co$_3$(CO)$_7$-μ-(C$_6$H$_5$)$_2$PCH$_2$P(C$_6$H$_5$)$_2$)[a]

Atom	x	y	z
Co(1)	0.07087(4)	0.33477(3)	0.52082(7)
Co(2)	−0.05019(4)	0.31481(3)	0.52903(6)
Co(3)	−0.00878(3)	0.39099(3)	0.60997(6)
P(1)	−0.15117(7)	0.32250(5)	0.6037(1)
P(2)	−0.09529(7)	0.40725(5)	0.7208(1)
O(1)	0.0753(2)	0.3725(2)	0.2844(4)
O(2)	0.1199(2)	0.2382(2)	0.4914(5)
O(3)	0.1895(2)	0.3698(2)	0.6412(4)
O(4)	−0.0805(2)	0.3278(2)	0.2827(4)
O(5)	−0.0306(2)	0.2135(2)	0.5560(4)
O(6)	−0.0316(2)	0.4460(2)	0.3988(4)
O(7)	0.0859(2)	0.4466(2)	0.7454(4)
C(1)	0.0739(3)	0.3585(3)	0.3749(5)
C(2)	0.1001(3)	0.2757(2)	0.5025(6)
C(3)	0.1429(3)	0.3571(2)	0.5927(5)
C(4)	−0.0703(3)	0.3234(2)	0.3769(5)
C(5)	−0.0402(3)	0.2530(2)	0.5435(5)
C(6)	−0.0240(3)	0.4256(2)	0.4822(5)
C(7)	0.0488(3)	0.4249(2)	0.6923(5)
C(8)	0.0093(3)	0.3285(2)	0.6509(4)
C(9)	0.0261(3)	0.3016(2)	0.7588(5)
C(10)	−0.1476(3)	0.3541(2)	0.7414(4)
H$_A$C(9)	0.014	0.320	0.824
H$_B$C(9)	0.002	0.272	0.761
H$_C$C(9)	0.073	0.295	0.762

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables.

TABLE 3

ATOMIC POSITIONAL PARAMETERS FOR $(\mu_3\text{-CCH}_3)\text{Co}_3(\text{CO})_7\text{-}\mu\text{-}(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{P}(\text{C}_6\text{H}_5)_2)$

Atom	x	y	z	B (Å^2)	Atom	x	y	z	B (Å^2)
C(11)	−0.1947(2)	0.26667(10)	0.6382(3)	1.49(9)	C(23)	−0.15209(2)	0.4546(1)	0.6723(3)	1.44(9)
C(12)	−0.2275(2)	0.2587(1)	0.7419(3)	1.75(10)	C(24)	−0.1240(1)	0.4923(1)	0.6115(3)	1.95(10)
C(13)	−0.2577(2)	0.2150(1)	0.7633(3)	2.4(1)	C(25)	−0.1650(2)	0.5290(1)	0.5725(3)	2.5(1)
C(14)	−0.2551(2)	0.1793(1)	0.6810(3)	2.5(1)	C(26)	−0.2340(2)	0.5280(1)	0.5943(3)	2.3(1)
C(15)	−0.2223(2)	0.1873(1)	0.5773(3)	2.4(1)	C(27)	−0.2620(1)	0.4903(1)	0.6550(3)	2.0(1)
C(16)	−0.1921(2)	0.2310(1)	0.5559(2)	1.84(10)	C(28)	−0.2210(2)	0.4537(1)	0.6941(3)	1.73(10)
HC(12)	−0.2293(3)	0.2830(1)	0.7982(4)	2.7	HC(24)	−0.0769(1)	0.4930(2)	0.5966(5)	2.9
HC(13)	−0.2801(3)	0.2096(2)	0.8342(3)	3.4	HC(25)	−0.1459(2)	0.5547(1)	0.5310(5)	3.4
HC(14)	−0.2758(3)	0.1495(1)	0.6956(5)	3.5	HC(26)	−0.2619(2)	0.5530(1)	0.5676(5)	3.4
HC(15)	−0.2205(3)	0.1630(1)	0.5210(4)	3.4	HC(27)	−0.3091(1)	0.4897(2)	0.6699(5)	3.0
HC(16)	−0.1697(3)	0.2364(2)	0.4850(3)	2.8	HC(28)	−0.2401(2)	0.4280(1)	0.7355(4)	2.7
C(17)	−0.2165(2)	0.3558(1)	0.5260(3)	1.44(9)	C(29)	−0.0786(2)	0.4250(1)	0.8700(2)	1.5(9)
C(18)	−0.2842(2)	0.3487(1)	0.5517(3)	1.82(10)	C(30)	−0.0505(2)	0.3924(1)	0.9457(3)	2.6(1)
C(19)	−0.3335(1)	0.3756(1)	0.4971(3)	2.4(1)	C(31)	−0.0376(2)	0.4054(1)	1.0588(3)	2.8(1)
C(20)	−0.3150(2)	0.4097(1)	0.4167(3)	2.4(1)	C(32)	−0.0529(2)	0.4510(1)	1.0962(2)	2.3(1)
C(21)	−0.2473(2)	0.4169(1)	0.3910(3)	2.5(1)	C(33)	−0.0811(2)	0.4836(1)	1.0206(3)	2.5(1)
C(22)	−0.1980(1)	0.3899(1)	0.4456(3)	1.97(10)	C(34)	−0.0939(2)	0.4706(1)	0.9074(3)	2.1(1)
HC(18)	−0.2968(2)	0.3254(2)	0.6066(4)	3.8	HC(30)	−0.0400(3)	0.3613(1)	0.9201(5)	3.6
HC(19)	−0.3798(1)	0.3707(2)	0.5146(5)	3.0	HC(31)	−0.0184(3)	0.3831(2)	1.1105(4)	3.8
HC(20)	−0.4212(1)	0.3934(2)	0.4687(6)	3.1	HC(32)	−0.0442(3)	0.4598(2)	1.1734(3)	3.2
HC(21)	−0.2346(3)	0.4402(2)	0.3361(4)	3.4	HC(33)	−0.0915(3)	0.5148(1)	1.0461(4)	3.5
HC(22)	−0.1517(1)	0.3948(2)	0.4280(5)	2.9	HC(34)	−0.1131(3)	0.4929(2)	0.8558(4)	3.1

two equatorial carbonyl ligands by a dppm ligand. Each cluster molecule consists of triangular array of cobalt atoms capped with a face bridging ethylidyne group. The dppm ligand bridges one of the three Co–Co bonds, namely Co(2)–Co(3). The coordination sphere of each of these metal atoms is completed by terminal CO ligands, i.e. three CO ligands around Co(1) and two CO ligands around each of the other two cobalt atoms Co(2) and Co(3). The absence of a bridging carbonyl ligand is confirmed by the absence of absorption around 1800 cm^{-1} in the IR spectrum. In the ^1H NMR spectrum, the two protons of the methylene group are inequivalent. This observation is in good agreement with the equatorial coordination of the dppm ligand as revealed by the crystal structure.

The value of the non-bridged Co–Co bonds of 2.468(1) Å is in close agreement with the average value of 2.467 Å in $(\mu_3\text{-}CCH_3)Co_3(CO)_9$, [14] while the bridged bond Co(2)–Co(3) of 2.486(1) Å is significantly longer. Such a lengthening may reflect an increase in electron density in the σ^*-antibonding orbital of Co(2) and Co(3) when carbonyl groups are replaced by poorer π acceptor phosphorus ligands. Such a feature has previously been observed in the related trinuclear cobalt cluster $(\mu_3\text{-}CCH_3)Co_3(CO)_6(P(OMe)_3)_3$ [14] in which the average Co–Co bond length is

(Continued on p. 438)

TABLE 4

SELECTED BOND LENGTHS (Å) FOR $(\mu_3\text{-}CCH_3)Co_3(CO)_7\text{-}\mu\text{-}dppm$

Co–Co				
Co(1)–Co(2)	2.468(1)	non-bridged	Co(2)–Co(3)	2.486(1)
Co(1)–Co(3)	2.468(1)			bridged by dppm
Co–C (carbonyl groups)				
Axial			*Equatorial*	
Co(1)–C(1)	1.829(6)		Co(1)–C(2)	1.775(6)
Co(2)–C(4)	1.834(6)		Co(1)–C(3)	1.771(6)
Co(3)–C(6)	1.807(6)		Co(2)–C(5)	1.763(6)
			Co(3)–C(7)	1.771(6)
	1.823 av.			1.770 av.
Co–C (μ_3-CCH_3 group)				
Co(1)–C(8)	1.954(5)		Co(3)–C(8)	1.860(6)
Co(2)–C(8)	1.887(5)			1.900 av.
C–O (carbonyl groups)				
C(1)–O(1)	1.127(8)		C(5)–O(5)	1.139(7)
C(2)–O(2)	1.135(7)		C(6)–O(6)	1.139(7)
C(3)–O(3)	1.142(7)		C(7)–O(7)	1.140(7)
C(4)–O(4)	1.123(7)			
			1.135 av.	
P–C				
P(1)–C(10)	1.838(5)		P(2)–C(10)	1.839(5)
P(1)–C(11)	1.840(5)		P(2)–C(23)	1.836(5)
P(1)–C(17)	1.839(5)		P(2)–C(29)	1.839(5)
				1.839 av.
Co(2)–P(1)	2.194(2)		C(8)–C(9)	1.506(8)
Co(3)–P(2)	2.196(2)			

TABLE 5

SELECTED BOND ANGLES (deg.) FOR (μ_3-CCH$_3$)Co$_3$(CO)$_7$-μ-dppm

Around Co(1)			
C(1)–Co(1)–C(2)	102.7(3)	C(2)–Co(1)–Co(3)	149.5(2)
C(1)–Co(1)–C(3)	106.5(3)	C(3)–Co(1)–C(8)	99.7(2)
C(1)–Co(1)–C(8)	140.8(3)	C(3)–Co(1)–Co(2)	147.9(2)
C(1)–Co(1)–Co(2)	98.7(2)	C(3)–Co(1)–Co(3)	95.1(2)
C(1)–Co(1)–Co(3)	100.2(2)	C(8)–Co(1)–Co(2)	48.8(2)
C(2)–Co(1)–C(3)	97.3(3)	C(8)–Co(1)–Co(3)	48.1(2)
C(2)–Co(1)–C(8)	102.3(3)	Co(2)–Co(1)–Co(3)	69.49(3)
C(2)–Co(1)–Co(2)	96.2(2)		
Around Co(2)			
P(1)–Co(2)–C(4)	99.9(2)	C(4)–Co(2)–Co(3)	108.9(2)
P(1)–Co(2)–C(5)	99.4(2)	C(5)–Co(2)–C(8)	93.4(2)
P(1)–Co(2)–C(8)	104.6(2)	C(5)–Co(2)–Co(1)	96.9(2)
P(1)–Co(2)–Co(1)	151.73(4)	C(5)–Co(2)–Co(3)	141.4(2)
P(1)–Co(2)–Co(3)	93.76(4)	C(8)–Co(2)–Co(1)	51.2(2)
C(4)–Co(2)–C(5)	104.4(3)	C(8)–Co(2)–Co(3)	48.0(2)
C(4)–Co(2)–C(8)	146.8(3)	Co(1)–Co(2)–Co(3)	59.75(3)
C(4)–Co(2)–Co(1)	98.3(2)		
Around Co(3)			
P(2)–Co(3)–C(6)	104.0(2)	C(6)–Co(3)–Co(2)	95.7(2)
P(2)–Co(3)–C(7)	94.1(2)	C(7)–Co(3)–C(8)	104.4(3)
P(2)–Co(3)–C(8)	101.4(2)	C(7)–Co(3)–Co(1)	99.4(2)
P(2)–Co(3)–Co(1)	151.88(5)	C(7)–Co(3)–Co(2)	152.2(2)
P(2)–Co(3)–Co(2)	98.37(5)	C(8)–Co(3)–Co(1)	51.4(2)
C(6)–Co(3)–C(7)	105.3(3)	C(8)–Co(3)–Co(2)	48.9(2)
C(6)–Co(3)–C(8)	139.1(2)	Co(1)–Co(2)–Co(3)	59.76(3)
C(6)–Co(3)–Co(1)	96.2(3)		
Around P(1)			
Co(2)–P(1)–C(10)	111.1(2)	C(10)–P(1)–C(11)	104.0(2)
Co(2)–P(1)–C(11)	115.5(2)	C(10)–P(1)–C(17)	102.1(2)
Co(2)–P(1)–C(17)	120.0(2)	C(11)–P(1)–C(17)	102.4(2)
Around P(2)			
Co(3)–P(2)–C(10)	110.4(2)	C(10)–P(2)–C(23)	106.7(2)
Co(3)–P(2)–C(23)	116.7(2)	C(10)–P(2)–C(29)	101.6(2)
Co(3)–P(2)–C(29)	118.0(2)	C(23)–P(2)–C(29)	101.7(2)
Around C(8)			
Co(1)–C(8)–C(9)	123.7(4)	Co(1)–C(8)–Co(2)	79.9(2)
Co(2)–C(8)–C(9)	131.6(4)	Co(1)–C(8)–Co(3)	80.6(2)
Co(3)–C(8)–C(9)	137.2(4)	Co(2)–C(8)–Co(3)	83.1(2)
Co–C–O (terminal carbonyls)			
Co(1)–C(1)–O(1)	179.0(8)	Co(2)–C(5)–O(5)	176.3(5)
Co(1)–C(2)–O(2)	178.8(7)	Co(3)–C(6)–O(6)	176.7(6)
Co(1)–C(3)–O(3)	177.4(6)	Co(3)–C(7)–O(7)	179.9(6)
Co(2)–C(4)–O(4)	177.5(5)		
			177.9av.
P(1)–C(10)–P(2)	107.6(3)		

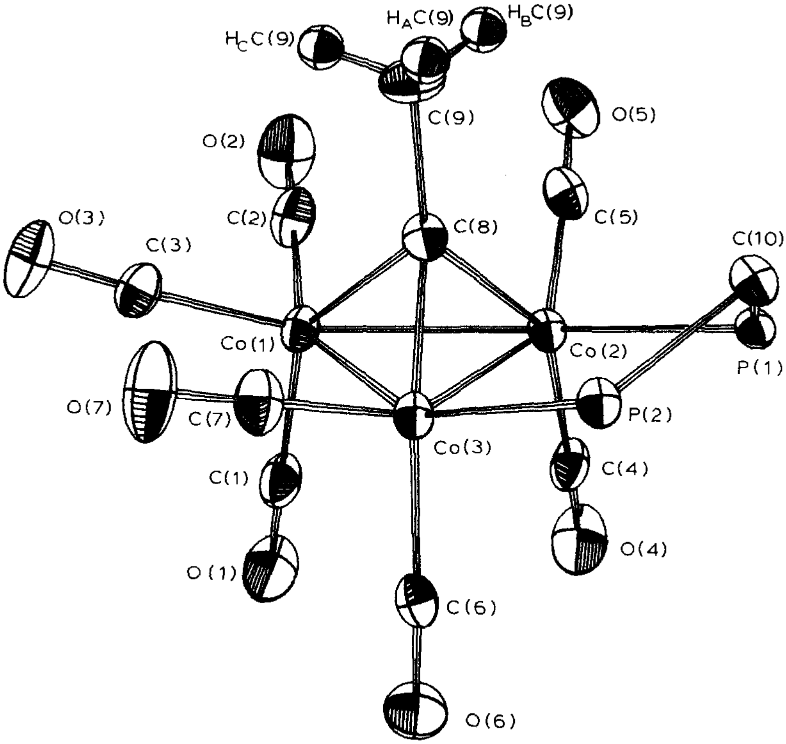


Fig. 1. Perspective view of the complex (μ_3-CCH$_3$)Co$_3$(CO)$_7$-μ-dppm (II). Phenyl rings around the phosphorus atoms have been omitted for clarity. All atoms are represented by thermal vibrations ellipsoid drawn to encompass 50% of the electron density.

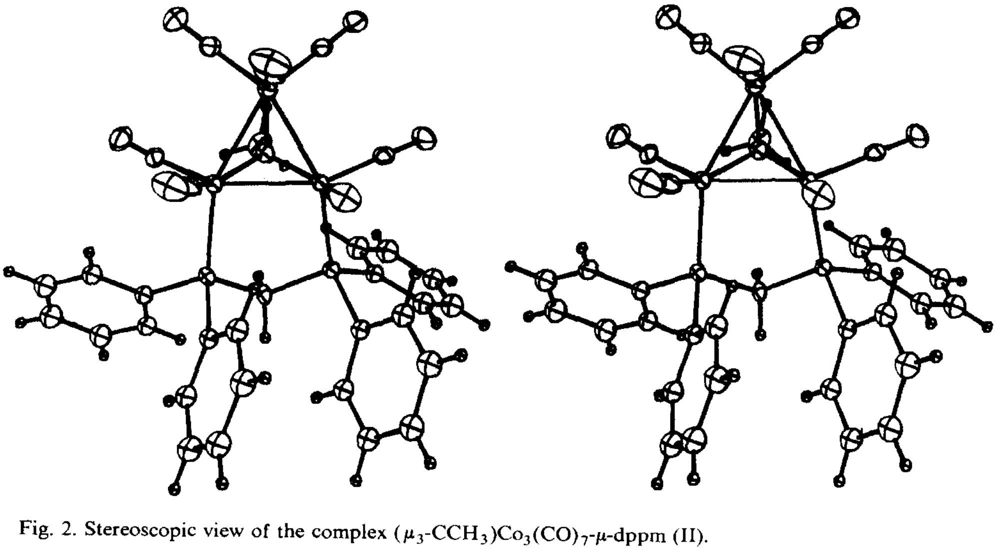


Fig. 2. Stereoscopic view of the complex (μ_3-CCH$_3$)Co$_3$(CO)$_7$-μ-dppm (II).

TABLE 6

A SELECTION OF BEST PLANES AND DIHEDRAL ANGLES FOR (μ_3-CCH$_3$)Co$_3$(CO)$_7$-μ-dppm

Atoms defining the plane	Plane	Equation of the best plane	Distances of atoms (Å) to the best plane
Co(1), Co(2), Co(3)	1	$2.757x - 12.472y + 10.329z - 1.400 = 0$	P(1), 0.397; P(2), 0.704; C(10), 1.435
P(1), P(2), C(10)	2	$-16.132x + 14.743y - 2.970z - 5.400 = 0$	
Co(2), Co(3), P(1), P(2)	3	$7.102x - 14.541y + 9.073z + 0.174 = 0$	Co(2), 0.040; Co(3), −0.039; P(1), −0.111 P(2), 0.116; C(10), 0.704; Co(1), 0.535
C(11), C(12), C(13), C(14), C(15), C(16)	4	$16.920x - 9.464y + 4.642z + 2861 = 0$	
C(17), C(18), C(19), C(20), C(21), C(22)	5	$-1.175x - 19.314y - 8.464z + 11.067 = 0$	
C(23), C(24), C(25), C(26), C(27), C(28)	6	$-2.976x - 13.930y - 9.983z + 12.584 = 0$	
C(29), C(30), C(31), C(32), C(33), C(34)	7	$18.156x + 8.621y - 3.047z + 0.428 = 0$	

Dihedral angles

Plane	Plane	Angle (deg.)	Plane	Plane	Angle (deg.)
1	2	55.2	4	7	54.9
1	3	14.6	5	6	14.3
2	3	40.6	5	7	94.2
4	5	96.3	6	7	93.7
4	6	107.7			

TABLE 7

SIGNED CONFORMATIONAL (TORSION) ANGLES (deg.) FOR $(\mu_3\text{-CCH}_3)\text{Co}_3(\text{CO})_7\text{-}\mu\text{-dppm}$ WITHIN THE FIVE-MEMBERED CHELATE RING

C(10)–P(2)–Co(3)–Co(2)	15.9(2)
P(2)–Co(3)–Co(2)–P(1)	8.46(6)
Co(3)–Co(2)–P(1)–C(10)	−32.3(2)
Co(2)–P(1)–C(10)–P(2)	48.0(3)
P(1)–C(10)–P(2)–Co(3)	−39.4(3)

2.484 Å. It is noteworthy that the dppm ligand adopts a geometry which leads to an envelope form for the five-membered ring Co(2)–Co(3)–P(2)–C(10)–P(1) as revealed by (i) the torsion angle P(2)–Co(3)–Co(2)–P(1) of 8.46° [15]; (ii) the distance of C(10) to the best plane through Co(2), Co(3), P(1), P(2) of 0.704 Å (see Tables 6 and 7). The dihedral angle describing the envelope form is 40.6°. The adoption of an envelope form is probably related to the presence of a face-bridging carbon atom which induces eclipsed atoms as does the face-bridging oxygen atom in $\text{Ru}_3\text{O}(\text{CO})_6(\text{dpam})_2$ [16]. Significantly, in the absence of such face-bridging atoms the preferred conformation for dppm or the related arsine ligand (dpam) seems to be a half chair as found in $\text{Ru}_3(\text{CO})_{10}(\text{dppm})$ [17] or $\text{Ru}_3(\text{CO})_8(\text{dppm})_4$ [4]. The apical methyl group is slightly bent away from the dppm ligand towards Co(1), as can be seen from the angles of the type C(9)–C(8)–Co (see Table 5). A similar feature was previously reported for the $(\mu_3\text{-CCH}_3)\text{Co}_3(\text{CO})_8\text{P}(\text{C}_6\text{H}_5)_3$ cluster [18].

As for the Co–CO bond lengths, the mean value of 1.770 Å for the equatorial groups is significantly shorter than that of 1.823 Å observed for the axial groups. They cannot be compared with those found in the unsubstituted related cluster $(\mu_3\text{-CCH}_3)\text{Co}_3(\text{CO})_9$ [14], where the mean value is 1.80 Å for all the Co–CO bond lengths, because of the poor quality of the relevant data. Nevertheless the IR spectrum showed a decrease of ν(CO) frequencies in comparison with $(\mu_3\text{-CCH}_3)\text{Co}_3(\text{CO})_9$. The two mean values (1.770 and 1.823 Å) are in relatively good agreement with those reported for the cluster $(\mu_3\text{-CCH}_3)\text{Co}_3(\text{CO})_8\text{P}(\text{C}_6\text{H}_5)_3$ i.e. 1.79 Å for the Co–CO axial bonds and 1.74 Å for the Co–CO equatorial bonds [18].

Catalytic tests

In a preliminary exploration of the catalytic abilities of the dppm cluster we looked at catalysis of hydroformylation of 1-pentene since the analogous cluster $(\mu_3\text{-CPh})\text{Co}_3(\text{CO})_9$ is reported to be as an effective hydroformylation catalyst [9]. The unsubstituted cluster was a poor hydroformylation catalyst. When it was used under the same conditions as those described by Pittman (130°C, see Experimental section) after 24 h only traces of aldehydes were detected. Moreover fragmentation of I is observed whereas the analogous cluster $(\mu_3\text{-CPh})\text{Co}_3(\text{CO})_9$ is recovered inchanged after depressurisation [9]. On the other hand, use of the substituted cluster $(\mu_3\text{-CCH}_3)\text{Co}_3(\text{CO})_7\text{-}\mu\text{-(dppm)}$ (II), with the same work-up, gives 2-methylpentanal and -hexanal in a total yield of 22% after 24 h. The selectivity (2-methylpentanal/-hexanal) is 1.37, with a turnover of about 80. After depressurisation cluster II cannot be recovered in high yields, showing that there is substantial decomposition. However at lower temperature, i.e. 110°C, cluster II is still active, the catalytic reaction being only slightly slower and can be recovered unchanged (as indicated by IR spectra) in high yields. Although recovery of II after many catalytic cycles does not establish unambiguously that II is the true catalyst, our results show that the replacement of two CO groups in I by a dppm ligand increases the rate of the hydroformylation reaction and seems to suppress or completely eliminate the cluster fragmentation.

Conclusion

This work provides additional evidence of the values of using bridging diphosphines as a mean of stabilizing and activating clusters for catalysis. Moreover, the results suggest that use of a dissymmetric bridging diphosphine (R_2-$PCH_2PR'_2$) could provide a potentially useful approach to the synthesis of tetrahedric-type chiral clusters in which the asymmetry is a basic skeletal property of the cluster [19].

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