

**MIXED-METAL CLUSTER DERIVATIVES OF $\text{Co}_3(\mu_3\text{-CPh})(\text{CO})_9$:
 CRYSTAL STRUCTURES OF $\text{Co}_3(\mu_3\text{-CPh})(\text{CO})_9$, $\text{HFeCo}_2(\mu_3\text{-CPh})(\text{CO})_9$,
 AND $\text{FeCo}_2(\mu\text{-AuPPh}_3)(\mu_3\text{-CPh})(\text{CO})_9$**

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Summary

The compound $\text{Co}_3(\mu_3\text{-CPh})(\text{CO})_9$ (**1**) reacts with $\text{Na}_2[\text{Fe}(\text{CO})_4]$ in tetrahydrofuran to afford the mixed-metal hydride cluster $\text{HFeCo}_2(\mu_3\text{-CPh})(\text{CO})_9$ (**2**) after acid treatment. The structures of **1** and **2** have been determined by X-ray diffraction. The cluster **1** crystallizes in space group $P\bar{1}$ ($Z = 4$) with a 8.034(3), b 15.760(7), c 15.900(7) Å, α 101.11(3), β 100.99(3), γ 100.13(3)°, and the cluster **2** in the space group $C2/c$ ($Z = 8$) with a 14.114(4), b 7.804(3), c 33.844(12) Å, β 96.13(3)°. The two structures are similar, with a M_3 triangle triply bridged by the alkylidyne carbon atom and with three terminal carbonyl ligands bonded to each metal atom. The hydride ligand in **2** could not be located from the difference Fourier maps, but the structure of its gold triphenylphosphine derivative $\text{FeCo}_2(\mu\text{-AuPPh}_3)(\mu_3\text{-CPh})(\text{CO})_9$ (**3**), which was synthesized in toluene by a direct reaction of **2** with $\text{Au}(\text{PPh}_3)\text{Cl}$ in the presence of TiPF_6 , indicates that the hydride ligand is in an edge bridging position. The cluster **3** crystallizes in space group $Pna2_1$ ($Z = 4$) with a 34.617(6), b 8.793(2), c 11.226(2) Å.

Introduction

The widespread interest in metal alkylidyne cluster chemistry, in particular that of cobalt, has afforded a better understanding of the interactions between small organic molecules and metal clusters [1]. The alkylidyne complexes are regarded as useful models for the chemisorption of molecules on metal surfaces and for the catalysis.

Treatment of alkylidynecobalt complexes with metal exchange reagents, organometallic dimethyl arsenide or dinuclear cyclopentadienylmetal carbonyls [2], provides a facile synthetic route to clusters with mixed-metal framework, e.g., reaction of $\text{RCCo}_3(\text{CO})_9$ ($\text{R} = \text{CH}_3$, C_2H_5 , C_6H_5) with $\text{Na}_2\text{Fe}(\text{CO})_4$ has been found to form $\text{RCFeCo}_2(\text{CO})_9\text{H}$ clusters [3]. In these compounds the location of the

hydride ligand could not be deduced from the spectroscopic data, but in view of the electronic similarity to $\text{HFeCo}_2(\text{CO})_9[\text{P}(\text{OCH}_3)_3]$, which has been shown by X-ray [4] and neutron diffraction studies [5] to have the hydride ligand bridging the Co_3 face, a face-bridging position was assumed for the hydride in the $\text{RCFeCo}_2(\text{CO})_9\text{H}$ complexes.

A convenient indirect way of locating a hydride ligand is replacement of the H ligand by an $\text{Au}(\text{PPh}_3)$ group, which has been shown to possess similar bonding characteristics [6]. Investigation of the structures of the gold analogues are appropriate in cases where the location of the hydrogen cannot be determined by X-ray diffraction due to reactive or fluxional nature of the hydride.

The aim of our studies is to investigate the effect of metal exchange on the nonacarbonyl- μ_3 -phenylmethyldynetricobalt cluster (**1**). We report here mixed-metal syntheses involving the complex **1**, and present a full account of structural results that were briefly outlined previously [7].

Experimental

Reagents

Published methods were used to synthesize $\text{Co}_3(\mu_3\text{-CPh})(\text{CO})_9$ [8], $\text{HFeCo}_2(\mu_3\text{-CPh})(\text{CO})_9$ [3] and $\text{Au}(\text{PPh}_3)\text{Cl}$ [9]. Other reagents were obtained from commercial sources. Tetrahydrofuran (THF) was dried and deoxygenated by stirring over Na/benzophenone ketyl and freshly distilled before use. Reactions and manipulations of the reagents were carried out under N_2 up to the stage of chromatographic separations.

Reaction of $\text{HFeCo}_2(\mu_3\text{-CPh})(\text{CO})_9$ with $\text{Au}(\text{PPh}_3)\text{Cl}$

A toluene solution (10 ml) of $\text{Au}(\text{PPh}_3)\text{Cl}$ (200 mg, 0.40 mmol) and TiPF_6 (140 mg, 0.40 mmol) was treated with the mixed-metal hydride cluster $\text{HFeCo}_2(\mu_3\text{-CPh})(\text{CO})_9$ (206 mg, 0.40 mmol) in toluene (10 ml). The mixture was stirred under nitrogen for 1.5 h at 0°C then for 1 h at room temperature. Toluene was then evaporated off in vacuo, and the residue was extracted with hexane until the extract was colourless. A chromatographic separation of the extract on silica gel gave, on elution with hexane, the red-brown band of $\text{Co}_3(\mu_3\text{-CPh})(\text{CO})_9$, followed by the green band of $\text{Fe}_3(\text{CO})_{12}$. Two dark fractions remained at the top of the column. The first such fraction was extracted with methanol from the silica gel and identified as $\text{HFeCo}_2(\mu_3\text{-CPh})(\text{CO})_9$. The second dark fraction (41 mg) was extracted with CH_2Cl_2 , and purified by crystallization from hexane/ CH_2Cl_2 (5/1). IR (hexane) ν (CO): 2070w, 2050m, 2037s, 2021s, 2007m, 1998sh, 1960w(br), 1930w(br) cm^{-1} .

X-ray crystal structure determination

Brown crystals of $\text{Co}_3(\mu_3\text{-CPh})(\text{CO})_9$ and $\text{HFeCo}_2(\mu_3\text{-CPh})(\text{CO})_9$ were obtained by slow evaporation of hexane solutions at -20 and 10°C , respectively. Black crystals of $\text{FeCo}_2(\mu\text{-AuPPh}_3)(\mu_3\text{-CPh})(\text{CO})_9$ was obtained by evaporation of a hexane/ CH_2Cl_2 solution at 10°C . Crystals of **1**, **2** and **3** suitable for X-ray analysis were mounted on a Nicolet R3m diffractometer, and accurate lattice parameters were determined using 16–25 reflections in the range of $15.9 < 2\theta < 27.6^\circ$ with graphite monochromatized Mo-K_α X-radiation; the data are summarized in Table

TABLE 1

CRYSTALLOGRAPHIC DATA FOR $\text{Co}_3(\mu_3\text{-CPh})(\text{CO})_9$ (1), $\text{HFeCo}_2(\mu_3\text{-CPh})(\text{CO})_9$ (2) AND $\text{FeCo}_2(\mu\text{-AuPPh}_3)(\mu_3\text{-CPh})(\text{CO})_9$ (3)

	1	2	3
Formula	$\text{C}_{16}\text{H}_5\text{Co}_3\text{O}_9$	$\text{C}_{16}\text{H}_6\text{Co}_2\text{FeO}_9$	$\text{C}_{34}\text{H}_{20}\text{AuCo}_2\text{FeO}_9\text{P}$
Formula weight	518.01	515.93	974.18
Crystal system	Triclinic	Monoclinic	Orthorhombic
Space group	$P\bar{1}$	$C2/c$	$Pna2_1$
$a(\text{\AA})$	8.034(3)	14.114(4)	34.617(6)
$b(\text{\AA})$	15.760(7)	7.804(3)	8.793(2)
$c(\text{\AA})$	15.900(7)	33.844(12)	11.226(2)
$\alpha(\text{deg})$	101.11(3)	90	90
$\beta(\text{deg})$	100.99(3)	96.13(3)	90
$\gamma(\text{deg})$	100.13(3)	90	90
$V(\text{\AA}^3)$	1892(1)	3707(2)	3417(1)
Z	4	8	4
$D_{\text{calc}}(\text{g cm}^{-3})$	1.82	1.85	1.89
Crystal(mm)	$0.25 \times 0.35 \times 0.40$	$0.20 \times 0.25 \times 0.40$	$0.10 \times 0.25 \times 0.40$
Radiation	Mo- K_α	Mo- K_α	Mo- K_α
2θ -limits	5–55	5–55	5–50
Unique data	8713	4208	3184
Data, $I > 3\sigma(I)$	4765	3006	1952
$\mu(\text{Mo-}K_\alpha)(\text{cm}^{-1})$	26.4	25.9	57.4
R	0.044	0.089	0.048
R_w	0.046	0.094	0.047
$w = 1.0/(\sigma^2(F) + gF^2)$	$g = 0.00044$	$g = 0.00084$	$g = 0.00083$

1. Intensities were corrected for background, polarization and Lorentz factors. Empirical absorption corrections were made from ψ -scan data. The structures were solved by direct methods and subsequent Fourier syntheses. The structures were routinely refined by least-squares calculations of the SHELXTL program package [10] with initially isotropic and then anisotropic thermal parameters for non-hydrogen atoms, except that for 1 and 3, where the phenyl rings were refined as rigid groups with individual isotropic temperature factors. The hydrogen atoms of the phenyl rings were placed at calculated positions (C–H 0.96 Å). The hydride ligand of 2 could not be located from difference maps. All possible combinations of iron and cobalt atoms in the mixed-metal clusters of 2 and 3 were included in the structure determinations and the best fits were considered as the correct structures. For 3 the values of R and R_w for the two alternative absolute structures were effectively the same. For all three analyses the final difference maps showed no significant features. The atomic coordinates with isotropic temperature factors are listed in Tables 2–4 for the clusters 1–3. Full lists of bond lengths and angles, thermal parameters, and structure factors are available from the authors.

Results and discussion

The $\text{Co}_3(\mu_3\text{-CR})(\text{CO})_9$ complexes can be prepared in various ways [11,12]. $\text{Co}_3(\mu_3\text{-CPh})(\text{CO})_9$ was obtained in 50% yield from $\text{Co}_2(\text{CO})_8$ and PhCCl_3 . The overall geometry of 1 is shown in Fig. 1. There is a triangular array of cobalt atoms

(Continued on p. 98)

TABLE 2
 ATOM COORDINATES ($\times 10^4$) AND TEMPERATURE FACTORS ($\text{\AA}^2 \times 10^3$) FOR $\text{Co}_3(\mu_3\text{-CPh})(\text{CO})_9$

Atom	x	y	z	U^a	Atom	x	y	z	U^a
Co(1)	3829(1)	5147(1)	2759(1)	49(1)	Co(4)	4736(1)	1252(1)	8294(1)	44(1)
Co(2)	823(1)	5110(1)	2012(1)	46(1)	Co(5)	2333(1)	131(1)	8453(1)	46(1)
Co(3)	2183(1)	3868(1)	1549(1)	44(1)	Co(6)	1747(1)	1111(1)	7450(1)	55(1)
O(11)	6370(10)	4281(5)	3606(5)	157(4)	O(41)	6609(7)	2099(4)	7177(4)	105(3)
O(12)	3970(9)	6402(4)	4385(4)	137(3)	O(42)	7586(6)	488(3)	9024(4)	93(3)
O(13)	5824(7)	6213(3)	1794(4)	96(3)	O(43)	4806(7)	2694(3)	9807(3)	88(2)
O(21)	61(9)	6502(4)	3273(4)	117(3)	O(51)	4320(6)	-1051(3)	9181(3)	82(2)
O(22)	-2783(6)	4169(3)	1310(4)	94(2)	O(52)	-925(7)	-1194(4)	7778(4)	116(3)
O(23)	1538(7)	6116(3)	683(3)	86(2)	O(53)	1611(7)	1143(3)	10065(3)	84(2)
O(31)	-925(7)	2488(3)	691(4)	98(3)	O(61)	-1329(10)	-65(5)	6247(6)	205(5)
O(32)	4395(7)	2641(3)	1936(4)	96(3)	O(62)	2673(8)	2138(4)	6203(4)	106(3)
O(33)	3212(7)	4417(3)	16(3)	85(2)	O(63)	531(8)	2422(4)	8646(4)	117(3)
C(11)	5413(10)	4623(5)	3253(5)	82(3)	C(41)	5871(8)	1779(4)	7605(4)	64(3)
C(12)	3913(10)	5933(4)	3743(5)	80(3)	C(42)	6470(8)	785(4)	8743(4)	60(3)
C(13)	5041(8)	5804(4)	2152(4)	63(3)	C(43)	4796(8)	2156(4)	9229(4)	56(2)

C(21)	386(9)	5956(4)	2795(4)	70(3)	C(51)	3553(8)	-591(4)	8890(4)	56(2)
C(22)	-1371(8)	4533(4)	1579(4)	60(3)	C(52)	321(9)	-682(4)	8027(4)	71(3)
C(23)	1256(8)	5730(4)	1192(4)	58(2)	C(53)	1871(8)	757(4)	9454(4)	58(2)
C(31)	263(8)	3025(4)	1019(4)	60(3)	C(61)	-186(11)	413(6)	6739(6)	114(5)
C(32)	3558(8)	3128(4)	1791(4)	60(3)	C(62)	2325(9)	1750(4)	6695(4)	66(3)
C(33)	2839(8)	4202(4)	604(4)	56(2)	C(63)	973(9)	1919(5)	8182(5)	76(3)
C(70)	1729(7)	4321(3)	2658(3)	43(2)	C(80)	3193(7)	272(3)	7438(3)	44(2)
C(71A) ^a	1189(12)	3941(5)	3366(6)	55(3)	C(81A) ^b	3575(11)	-345(6)	6728(5)	43(8)
C(72A) ^b	685(12)	4437(5)	4061(6)	80(4)	C(82A) ^b	4849(11)	-827(6)	6897(5)	48(3)
C(73A) ^b	179(12)	4040(5)	4712(6)	100(5)	C(83A) ^b	5221(11)	-1393(6)	6202(5)	66(4)
C(74A) ^b	177(12)	3147(5)	4667(6)	110(6)	C(84A) ^b	4319(11)	-1477(6)	5338(5)	71(6)
C(75A) ^b	681(12)	2651(5)	3972(6)	165(9)	C(85A) ^b	3044(11)	-994(6)	5170(5)	83(4)
C(76A) ^b	1187(12)	3048(5)	3321(6)	130(7)	C(86A) ^b	2672(11)	-428(6)	5865(5)	65(4)
C(71B) ^b	1083(10)	3819(6)	3268(6)	40(2)	C(81B) ^b	3596(16)	-369(8)	6707(7)	65(13)
C(72B) ^b	2151(10)	3896(6)	4094(6)	121(6)	C(82B) ^b	4209(16)	-1096(8)	6914(7)	87(5)
C(73B) ^b	1552(10)	3432(6)	4680(6)	149(8)	C(83B) ^b	4691(16)	-1680(8)	6274(7)	133(8)
C(74B) ^b	-115(10)	2891(6)	4441(6)	84(4)	C(84B) ^b	4560(16)	-1537(8)	5428(7)	114(10)
C(75B) ^b	-1184(10)	2813(6)	3616(4)	94(5)	C(85B) ^b	3947(16)	-810(8)	5220(7)	70(4)
C(76B) ^b	-585(10)	3277(6)	3029(6)	79(4)	C(86B) ^b	3465(16)	-226(8)	5860(7)	61(3)

^a Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor. ^b Site occupancy factor 0.5.

TABLE 3
ATOM COORDINATES ($\times 10^4$) AND TEMPERATURE FACTORS ($\text{\AA}^2 \times 10^3$) FOR $\text{HfFeCo}_2(\mu_3\text{-CPh})(\text{CO})_9$

Atom	x	y	z	U^a	Atom	x	y	z	U^a
Fe	3809(1)	1234(2)	4136(1)	33(1)	C(13)	4042(7)	2981(16)	4493(3)	53(4)
Co(1)	2033(1)	1236(2)	4127(1)	35(1)	C(21)	1923(7)	-528(16)	4460(3)	51(4)
Co(2)	2807(1)	2957(2)	3639(1)	34(1)	C(22)	818(8)	1234(16)	3921(4)	59(4)
O(11)	5655(6)	1339(17)	3826(3)	99(5)	C(23)	1922(7)	2960(14)	4477(3)	46(3)
O(12)	4318(8)	-1545(15)	4703(4)	103(5)	C(31)	1754(8)	3268(13)	3304(3)	48(3)
O(13)	4211(7)	3998(12)	4712(3)	83(4)	C(32)	3692(8)	3222(14)	3303(3)	52(3)
O(21)	1821(8)	-1669(12)	4653(3)	81(4)	C(33)	2875(7)	5064(11)	3872(3)	40(3)
O(22)	23(6)	1277(17)	3789(4)	97(5)	C(1)	2815(6)	409(12)	3704(2)	35(3)
O(23)	1864(7)	4018(12)	4703(3)	72(3)	C(2)	2703(8)	-711(12)	3362(3)	48(3)
O(31)	1085(7)	3392(14)	3093(3)	84(4)	C(3)	3504(11)	-1333(21)	3195(4)	83(6)
O(32)	4265(7)	3289(14)	3093(3)	80(4)	C(4)	3406(18)	-2371(22)	2872(4)	115(9)
O(33)	2931(6)	6344(10)	4029(2)	61(3)	C(5)	2510(20)	-2870(18)	2698(4)	133(11)
C(11)	4955(8)	1311(16)	3939(3)	55(4)	C(6)	1737(16)	-2330(22)	2860(4)	115(9)
C(12)	4084(8)	-502(16)	4477(4)	58(4)	C(7)	1817(11)	-1234(19)	3188(4)	77(5)

^a Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

TABLE 4
ATOM COORDINATES ($\times 10^4$) AND TEMPERATURE FACTORS ($\text{\AA}^2 \times 10^3$) FOR $\text{FeCo}_2(\mu\text{-AuPPh}_3)(\mu_3\text{-CPh})(\text{CO})_9$

Atom	x	y	z	U^a	Atom	x	y	z	U^a
Au	3841(1)	1096(1)	2500	51(1)	C(2)	3265(3)	-726(18)	-1390(15)	52(5)
Co(1)	3406(1)	1635(3)	591(3)	43(1)	C(3)	2908(3)	-1096(18)	-1884(15)	67(7)
Co(2)	2937(1)	-382(4)	1174(3)	56(1)	C(4)	2879(3)	-1430(18)	-3096(15)	94(11)
Fe	3637(1)	-1131(4)	1090(3)	45(1)	C(5)	3208(3)	-1394(18)	-3813(15)	65(6)
P	4177(2)	2132(6)	4035(4)	41(2)	C(6)	3566(3)	-1024(18)	-3318(15)	78(8)
O(11)	4119(4)	2617(22)	-592(19)	93(8)	C(7)	3594(3)	-690(18)	-2107(15)	57(6)
O(12)	2864(5)	3146(21)	-1021(14)	77(6)	C(41)	4553(3)	3429(18)	3555(14)	54(5)
O(13)	3235(5)	3903(22)	2437(22)	109(8)	C(42)	4452(3)	4484(18)	2680(14)	72(6)
O(21)	2254(5)	717(26)	-37(16)	92(8)	C(43)	4725(3)	5529(18)	2272(14)	84(8)
O(22)	2729(6)	-3642(25)	1199(32)	146(13)	C(44)	5099(3)	5518(18)	2739(14)	84(8)
O(23)	2829(5)	546(29)	3660(14)	107(10)	C(45)	5199(3)	4463(18)	3613(14)	69(7)
O(31)	4439(5)	-848(25)	303(21)	108(9)	C(46)	4926(3)	3418(18)	4021(14)	57(6)
O(32)	3615(6)	-4093(20)	-66(19)	102(8)	C(51)	4431(4)	701(18)	4937(10)	48(5)
O(33)	3684(6)	-2386(23)	3559(14)	101(8)	C(52)	4596(4)	-538(18)	4350(10)	63(6)
C(11)	3839(7)	2217(28)	-148(22)	70(9)	C(53)	4797(4)	-1638(18)	4995(10)	92(9)
C(12)	3091(7)	2580(25)	-396(20)	55(8)	C(54)	4833(4)	-1500(18)	6228(10)	83(8)
C(13)	3341(7)	2973(29)	1802(23)	71(9)	C(55)	4668(4)	-261(18)	6816(10)	78(8)
C(21)	2515(6)	332(27)	434(21)	61(8)	C(56)	4467(4)	839(18)	6170(10)	56(6)
C(22)	2803(7)	-2376(39)	1230(38)	120(15)	C(61)	3899(4)	3183(17)	5093(14)	47(5)
C(23)	2873(7)	187(41)	2743(20)	96(13)	C(62)	4054(4)	4450(17)	5667(14)	61(6)
C(31)	4124(6)	-899(25)	661(20)	57(8)	C(63)	3848(4)	5165(17)	6576(14)	83(8)
C(32)	3613(7)	-2939(29)	381(22)	70(9)	C(64)	3487(4)	4613(7)	6912(14)	83(8)
C(33)	3666(6)	-1808(29)	2652(28)	71(8)	C(65)	3331(4)	3347(17)	6338(14)	84(8)
C(1)	3316(4)	-372(25)	-115(16)	40(6)	C(66)	3537(4)	2632(17)	5429(14)	60(6)

^a Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

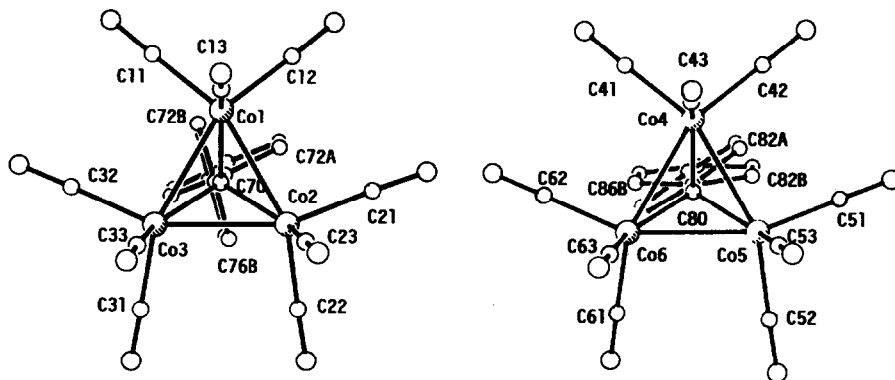


Fig. 1. The structure of $\text{Co}_3(\mu_3\text{-CPh})(\text{CO})_9$ (**1**).

capped by the $\mu_3\text{-CPh}$, and each Co atom contains one axial and two equatorial terminal CO ligands. Free rotation of the phenyl group about the C–C axis is facilitated by the 3-fold symmetry of the $\text{Co}_3(\text{CO})_9\text{C}$ fragment, in fact the cluster exhibits crystallographic disorder, the asymmetric unit containing two clusters each with two main orientations of the phenyl ring. These orientations depend on each other, as shown e.g. by short intermolecular contacts of $\text{C}(73\text{A})\cdots\text{C}(73\text{A})'$ 3.068 Å and $\text{C}(85\text{B})\cdots\text{C}(85\text{B})''$ 3.080 Å.

The Co–Co (average 2.466 Å) and Co– C_{ap} (average 1.906 Å) distances (Table 5) are in the range found in $\text{Co}_3(\mu_3\text{-CH})(\text{CO})_9$ [13], in $\text{Co}_3(\mu_3\text{-CCH}_3)(\text{CO})_9$ [14] and in $\text{Co}_3(\mu_3\text{-CC}_3\text{H}_5)(\text{CO})_9$ [15]. The axial metal–carbonyl distances (average 1.831 Å) are about 0.05 Å longer than the corresponding equatorial distances (average 1.782 Å), and are in good agreement with observations on related species.

An attempt to increase the size of the $\text{Co}_3(\mu_3\text{-CPh})(\text{CO})_9$ cluster by using $\text{Na}_2\text{Fe}(\text{CO})_4$ as the metalating agent resulted in formation of $\text{HFeCo}_2(\mu_3\text{-CPh})(\text{CO})_9$ (**2**) [3]. The X-ray crystallographic study of this mixed-metal cluster revealed the structure illustrated in Fig. 2. It consists of a similar M_3C trigonal-pyramidal core as **1**. The cluster is derived from **1** by replacing one $\text{Co}(\text{CO})_3$ fragment by a $\text{Fe}(\text{CO})_3$ group and adding a hydrogen. This change resulted in longer metal–metal distances (2.473–2.503 Å) than those in **1** (2.464–2.471 Å). The metal–apical carbon distances, which range from 2.001 (Co(2)–C(1)) to 2.020 Å (Fe–C(1)), are significantly longer than those in **1** (1.898–1.913 Å), suggesting that the π system of the phenyl ring may be alleviating the electron deficiency at the apical carbon by π donation [11,16]. The $\text{C}_{\text{ap}}\text{--C}_{\text{Ph}}$ bond length (1.446 Å) is indeed 0.03 Å shorter than that in **1** (average 1.480 Å), in $[\text{Co}_3(\mu_3\text{-CPh})(\text{CO})_8]_2\text{dppe}$ (1.488 Å) [17], in $\text{Co}_2\text{Mo}(\mu_3\text{-CPh})\text{Cp}(\text{CO})_8$ (1.49 Å) [18] and in $\text{Ni}_2\text{Mo}(\mu_3\text{-CPh})\text{Cp}_3(\text{CO})_2$ (1.47 Å) [19] but near the value of 1.456 Å found in $(\mu\text{-H})\text{Os}_3(\mu_3\text{-CPh})(\text{CO})_{10}$ in which one of the Os– C_{ap} bond lengths (2.586 Å) is 0.55 Å longer than the others [20]. The IR results support this conclusion, too, some CO bands being shifted to lower wave numbers owing to back donation of electron density from the metal triangle to carbonyl ligands.

The longest M–M bond (Fe–Co(1) 2.503 Å) is suggested to be H-bridged. We could not locate the hydrogen atom from our data, and a method [21] based on low angle reflection data also failed to give significant results. The geometry around the

TABLE 5

SELECTED BOND LENGTHS (Å) FOR $\text{Co}_3(\mu_3\text{-CPh})(\text{CO})_9$ (1), $\text{HFeCo}_2(\mu_3\text{-CPh})(\text{CO})_9$ (2) AND $\text{FeCo}_2(\mu\text{-AuPPh}_3)(\mu_3\text{-CPh})(\text{CO})_9$ (3)

<i>$\text{Co}_3(\mu_3\text{-CPh})(\text{CO})_9$ (1)</i>					
Co(1)–Co(2)	2.466(1)	Co(1)–Co(3)	2.471(1)	Co(2)–Co(3)	2.465(1)
Co(4)–Co(5)	2.464(1)	Co(4)–Co(6)	2.467(1)	Co(5)–Co(6)	2.464(1)
Co(1)–C(70)	1.900(5)	Co(2)–C(70)	1.913(6)	Co(3)–C(70)	1.898(6)
Co(4)–C(80)	1.910(4)	Co(5)–C(80)	1.908(6)	Co(6)–C(80)	1.908(6)
Co(1)–C(11)	1.777(8)	Co(1)–C(12)	1.780(7)	Co(1)–C(13)	1.829(7)
Co(2)–C(21)	1.772(7)	Co(2)–C(22)	1.772(6)	Co(2)–C(23)	1.822(7)
Co(3)–C(31)	1.790(5)	Co(3)–C(32)	1.786(7)	Co(3)–C(33)	1.823(7)
Co(4)–C(41)	1.786(7)	Co(4)–C(42)	1.783(7)	Co(4)–C(43)	1.838(6)
Co(5)–C(51)	1.782(6)	Co(5)–C(52)	1.799(6)	Co(5)–C(53)	1.841(6)
Co(6)–C(61)	1.775(8)	Co(6)–C(62)	1.784(7)	Co(6)–C(63)	1.830(8)
<i>$\text{HFeCo}_2(\mu_3\text{-CPh})(\text{CO})_9$ (2)</i>					
Fe–Co(1)	2.503(2)	Fe–Co(2)	2.476(2)	Co(1)–Co(2)	2.473(2)
Fe–C(1)	2.020(8)	Co(1)–C(1)	2.005(9)	Co(2)–C(1)	2.001(10)
Fe–C(11)	1.816(11)	Fe–C(12)	1.795(13)	Fe–C(13)	1.829(12)
Co(1)–C(21)	1.797(12)	Co(1)–C(22)	1.781(11)	Co(1)–C(23)	1.811(11)
Co(2)–C(31)	1.786(10)	Co(2)–C(32)	1.787(12)	Co(2)–C(33)	1.822(9)
<i>$\text{FeCo}_2(\mu\text{-AuPPh}_3)(\mu_3\text{-CPh})(\text{CO})_9$ (3)</i>					
Fe–Co(1)	2.621(4)	Fe–Co(2)	2.512(4)	Co(1)–Co(2)	2.492(4)
Fe–C(1)	1.872(18)	Co(1)–C(1)	1.959(21)	Co(2)–C(1)	1.953(17)
Fe–Au	2.615(3)	Co(1)–Au	2.661(3)	Au–P	2.272(5)
Fe–C(31)	1.764(22)	Fe–C(32)	1.779(26)	Fe–C(33)	1.854(31)
Co(1)–C(11)	1.789(25)	Co(1)–C(12)	1.764(23)	Co(1)–C(13)	1.812(26)
Co(2)–C(21)	1.793(23)	Co(2)–C(22)	1.815(34)	Co(2)–C(23)	1.844(23)
P–C(41)	1.811(15)	P–C(51)	1.838(15)	P–C(61)	1.788(15)
Au–C(13)	2.515(25)	Au–C(33)	2.629(25)		

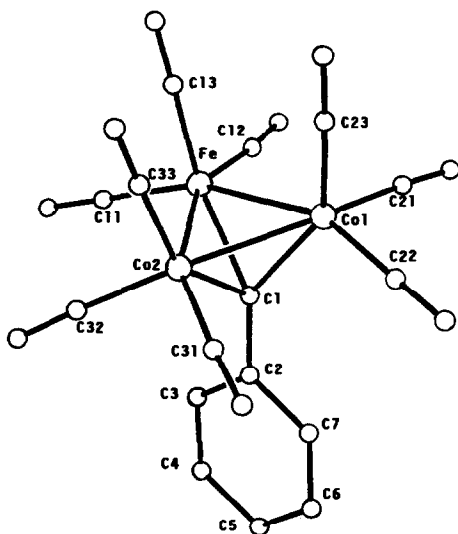


Fig. 2. The structure of $\text{HFeCo}_2(\mu_3\text{-CPh})(\text{CO})_9$ (2).

TABLE 6

SELECTED BOND ANGLES (°) FOR $\text{Co}_3(\mu_3\text{-CPh})(\text{CO})_9$ (1), $\text{HFeCo}_2(\mu_3\text{-CPh})(\text{CO})_9$ (2) AND $\text{FeCo}_2(\mu\text{-AuPPh}_3)(\mu_3\text{-CPh})(\text{CO})_9$ (3)

<i>Co₃(μ₃-CPh)(CO)₉ (1)</i>			
C(13)–Co(1)–Co(2)	100.4(2)	C(23)–Co(2)–Co(1)	99.7(2)
C(13)–Co(1)–Co(3)	100.3(2)	C(23)–Co(2)–Co(3)	98.7(2)
C(13)–Co(1)–C(70)	143.6(2)	C(23)–Co(2)–C(70)	141.9(3)
C(13)–Co(1)–C(11)	102.2(4)	C(23)–Co(2)–C(21)	99.6(3)
C(13)–Co(1)–C(12)	103.2(3)	C(23)–Co(2)–C(22)	103.2(3)
C(11)–Co(1)–C(12)	95.5(3)	C(21)–Co(2)–C(22)	95.9(3)
C(43)–Co(4)–Co(5)	99.6(2)	C(53)–Co(5)–Co(4)	98.8(2)
C(43)–Co(4)–Co(6)	98.9(2)	C(53)–Co(5)–Co(6)	100.2(2)
C(43)–Co(4)–C(80)	142.4(3)	C(53)–Co(5)–C(80)	142.8(3)
C(43)–Co(4)–C(41)	104.5(3)	C(53)–Co(4)–C(51)	101.5(3)
C(43)–Co(4)–C(42)	101.5(3)	C(53)–Co(5)–C(52)	100.1(3)
C(41)–Co(4)–C(42)	95.7(3)	C(51)–Co(5)–C(52)	96.0(3)
C(33)–Co(3)–Co(1)	101.1(2)		
C(33)–Co(3)–Co(2)	98.0(2)		
C(33)–Co(3)–C(70)	142.7(2)		
C(33)–Co(3)–C(31)	101.2(3)		
C(33)–Co(3)–C(32)	102.5(3)		
C(31)–Co(3)–C(32)	96.1(3)		
C(63)–Co(6)–Co(4)	101.7(2)		
C(63)–Co(6)–Co(5)	98.1(3)		
C(63)–Co(6)–C(80)	143.1(3)		
C(63)–Co(6)–C(61)	104.1(3)		
C(63)–Co(6)–C(62)	100.1(3)		
C(61)–Co(6)–C(62)	97.2(4)		
<i>HFeCo₂(μ₃-CPh)(CO)₉ (2)</i>			
C(13)–Fe–Co(1)	96.7(3)	C(23)–Co(1)–Fe	98.6(3)
C(13)–Fe–Co(2)	95.4(4)	C(23)–Co(1)–Co(2)	96.2(3)
C(13)–Fe–C(1)	141.1(4)	C(23)–Co(1)–C(1)	143.0(4)
C(13)–Fe–C(11)	96.5(5)	C(23)–Co(1)–C(22)	96.3(5)
C(13)–Fe–C(12)	97.9(5)	C(23)–Co(1)–C(21)	98.0(5)
C(11)–Fe–C(12)	96.9(5)	C(21)–Co(1)–C(22)	95.8(5)
C(33)–Co(2)–Fe	101.3(3)		
C(33)–Co(2)–Co(1)	101.9(3)		
C(33)–Co(2)–C(1)	148.1(4)		
C(33)–Co(2)–C(31)	98.8(4)		
C(33)–Co(2)–C(32)	99.4(5)		
C(31)–Co(2)–C(32)	99.9(5)		
<i>FeCo₂(μ-AuPPh₃)(μ₃-CPh)(CO)₉ (3)</i>			
C(13)–Co(1)–Fe	118.7(8)	C(33)–Fe–Co(1)	121.1(8)
C(13)–Co(1)–Co(2)	100.6(8)	C(33)–Fe–Co(2)	95.8(7)
C(13)–Co(1)–C(1)	150.3(10)	C(33)–Fe–C(1)	146.0(8)
C(13)–Co(1)–C(12)	95.1(11)	C(33)–Fe–C(32)	98.0(11)
C(13)–Co(1)–C(11)	105.4(11)	C(33)–Fe–C(31)	104.1(10)
C(12)–Co(1)–C(11)	95.3(11)	C(32)–Fe–C(31)	91.5(11)
Co(2)–Co(1)–Au	91.7(1)	Co(2)–Fe–Au	92.3(1)
Co(1)–C(13)–O(13)	166.0(22)	Fe–C(33)–O(33)	172.2(23)
C(23)–Co(2)–Co(1)	97.9(10)		
C(23)–Co(2)–Fe	102.9(7)		
C(23)–Co(2)–C(1)	141.9(9)		
C(23)–Co(2)–C(22)	101.5(17)		
C(23)–Co(2)–C(21)	104.4(11)		
C(22)–Co(2)–C(21)	98.4(12)		
Co(1)–C(13)–Au	73.9(8)		
Fe–C(33)–Au	68.9(8)		

metal atoms in **2** is similar to that in **1** (Fig. 2 and Table 6) except that the axial carbonyl ligands on Fe and Co(1) are slightly bent towards the axial carbonyl ligand of Co(2). This is not unexpected, since the $\text{HFeCo}_2(\mu_3\text{-CPh})(\text{CO})_9$ cluster is acidic and is readily deprotonated on basic silica gel during chromatography. The compound can, indeed, be regarded as an $\text{FeCo}_2(\mu_3\text{-CPh})(\text{CO})_9^{\delta-} \text{H}^{\delta+}$ system. The $\text{FeCo}_2(\mu_3\text{-CPh})(\text{CO})_9^-$ fragment is isoelectronic with **1**, and hence no significant rehybridization of **1** will take place on formation of **2** [26]. The protonic nature of the hydrogen in **2** is also supported by the rather low field chemical shift (–8.5 ppm) of the ^1H resonance of **2**. The broad form of the resonance at 25°C is presumably due to coupling with a quadrupolar cobalt and/or to the fluxional nature of the hydride ligand.

In view of the protonic and fluxional nature of the hydrogen in **2** an indirect way of location of the hydrogen was considered necessary and so the hydrogen ligand was replaced by an isolobal $\text{Au}(\text{PPh}_3)$ moiety. Reaction of **2** with $\text{Au}(\text{PPh}_3)\text{Cl}$ afforded $\text{FeCo}_2(\mu\text{-AuPPh}_3)(\mu_3\text{-CPh})(\text{CO})_9$ (**3**) in moderate yield. The overall geometry of **3** is shown in Fig. 3. The complex consists of a trigonal-pyramidal FeCo_2C core with one edge of the metal triangle bridged by the AuPPh_3 group. The FeCo_2

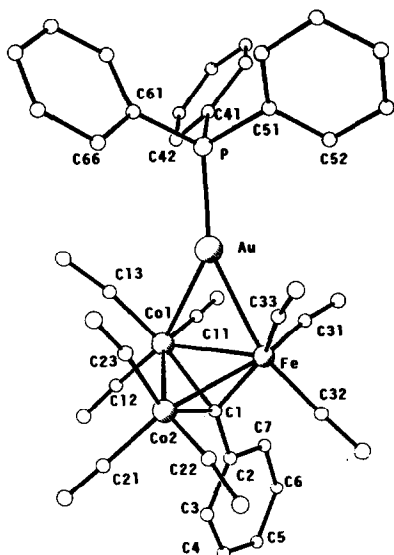


Fig. 3. The structure of $\text{FeCo}_2(\mu\text{-AuPPh}_3)(\mu_3\text{-CPh})(\text{CO})_9$ (**3**).

triangle of **3** is larger than the equivalent part of **2**. The longest distance ($\text{Fe-Co}(1)$ 2.621 Å) is Au-bridged. The metal–apical carbon distances are significantly shorter than the corresponding distances in **2**, the $\text{Fe-C}(1)$ distance being remarkably short, 1.872 Å. The $\text{Au}(\text{PPh}_3)$ ligand presumably encourages a strong apical carbon–metal interaction in complex **3**. This effect is fairly large at the iron, which also forms a short Fe-Au distance of 2.615 Å. The Co-Au bond length of 2.661 Å is comparable to a Au-Fe distance of 2.677 Å in $\text{RuFeCo}(\mu\text{-AuPPh}_3)(\mu_3\text{-PMe})(\text{CO})_9$ [22] but 0.16 Å longer than the terminal Au-Co bond length in $\text{Co}(\text{CO})_4\text{AuPPh}_3$ [23], and 0.05 Å shorter than the mean triply-bridging distances in $\text{FeCo}_3(\mu_3\text{-AuPPh}_3)(\text{CO})_{12}$ [6] and in $\text{RuCo}_3(\mu_3\text{-AuPPh}_3)(\text{CO})_{12}$ [24].

Short $\text{Au}\cdots\text{C}$ separations involving Au and the axial carbonyls on $\text{Co}(1)$ and Fe are observed (2.515 and 2.629 Å, respectively) with the carbonyl ligands deviating slightly from linearity ($\text{Co}(1)\text{-C}(13)\text{-O}(13)$ 166.0° and $\text{Fe-C}(33)\text{-O}(33)$ 172.2°). Similar interactions have been found with clusters containing Au or Cu [24,25], but it is not clear whether these interactions represent semibridging or result from steric effects in the solid state [26]. The IR spectrum of **3** in the CO stretching region shows two weak broad bands at 1960 and 1930 cm^{-1} , respectively, obviously due to very weakly semibridging carbonyls.

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