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SYNTHESIS AND CHARACTERISATION OF $H_3Ru_3Co(CO)_{10}(dppe)$ AND $HRuCo_3(CO)_{10}(dppe)$

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Summary

Ligand replacement of $H_3Ru_3Co(CO)_{12}$ and $HRuCo_3(CO)_{12}$ by dppe (dppe = $Ph_2PCH_2CH_2PPh_2$) has been studied. The following crystal structures are reported: (i) $H_3Ru_3Co(CO)_{10}$(dppe), orthorhombic, space group *Pbca*, *a* 18.609(7), *b* 19.524(6), *c* 20.889(5) Å, $Z = 8$; (ii) $HRuCo_3(CO)_{10}$(dppe), monoclinic, space group $P2_1/n$, *a* 15.15(2), *b* 11.380(4), *c* 21.792(8) Å, β 98.02(7)°, $Z = 4$. The phosphorus ligand chelates one Ru atom in $H_3Ru_3Co(CO)_{10}$(dppe) and is axially coordinated to two Co atoms in $HRuCo_3(CO)_{10}$(dppe). The former complex, unlike the parent cluster $H_3Ru_3Co(CO)_{12}$, has two carbonyls bridging Ru–Co bonds. The molecule contains also the first crystallographically observed edge-bridging Ru(μ-H)Co linkage.

Introduction

Phosphorus donor ligands are common in mononuclear metal complexes and in metal cluster compounds, and their effects on the properties of organometallic compounds have been extensively studied [1]. In metal clusters carbonyl ligands can often be easily replaced by tertiary phosphines or phosphites [2,3]. Mixed metal clusters afford many different sites for these reactions and the structures of the products are not easily predictable. Ligand substitution also often gives isomers. The effects of ligand substitution on the other ligands are usually restricted to minor distortions. However, there are cases in which the positions of hydride ligands are changed by ligand substitution [4–6]. Introduction of several phosphine ligands, as in $Ru_3(CO)_8(PPh(OMe)_2)_4$, can also result in movement of carbonyls from terminal to bridging positions [7].

In connection with our catalytic studies we have prepared two dppe derivatives of Ru-Co mixed metal clusters, $H_3Ru_3Co(CO)_{10}$(dppe), (**1**) and $HRuCo_3(CO)_{10}$(dppe)

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(2). Crystal structures and NMR spectra of these compounds reveal two modes of coordination of the dppe ligand, and in **1** a strong influence on the other ligands.

Experimental

Reagents

The complexes $H_3Ru_3Co(CO)_{12}$ [8] and $HRuCo_3(CO)_{12}$ [9] were prepared by published procedures. Other reagents and solvents were obtained from commercial sources and used without further purification. Tetrahydrofuran (THF) was dried and deoxygenated over Na benzophenone ketyl and freshly distilled before use. Other solvents were deoxygenated by bubbling N_2 through them. Reactions and manipulations were carried out under N_2 up to the stage of chromatographic separation.

Syntheses

$H_3Ru_3Co(CO)_{10}(dppe)$. A solution of 275 mg (0.39 mmol) $H_3Ru_3Co(CO)_{12}$ and 156 mg (0.39 mmol) dppe in 30 ml of deoxygenated tetrahydrafuran (thf) was stirred at room temperature for 1 h after a few μl of $Ph_2O^{\cdot -}$ catalyst in THF solution had been added to speed up the reaction [3]. The THF was evaporated off and the product was separated by chromatography on silica gel. Hexane elution gave a yellow fraction and elution with CH_2Cl_2/hexane (1/1) gave the red complex sought. Yield 285 g (70%). IR (CH_2Cl_2): 2082vs, 2048vs, 2012vs, 1860w, 1825w.

$HRuCo_3(CO)_{10}(dppe)$. A solution of 90 mg (0.15 mmol) $HRuCo_3(CO)_{12}$ and 59 mg (0.15 mmol) dppe was dissolved in 30 ml THF and the mixture was stirred at room temperature for 1 h after addition of the $Ph_2O^{\cdot -}$ catalyst, The THF was evaporated off and the residue was chromatographed on silica gel with CH_2Cl_2/hexane (1/1) mixture as eluent. A small red band was followed by a red band of the desired complex, Yield 70 mg (47%), IR (CH_2Cl_2): 2069vs, 2020vs, 2005vs, 1970m, 1940w, 1840s. (This was followed by a green fraction, and CH_2Cl_2 then eluted a red fraction, which is probably the disubstituted cluster.)

X-Ray crystallography

Crystals were grown by slow evaporation from saturated CH_2Cl_2/hexane solutions. The data were collected on a Nicolet R3m diffractometer. Accurate cell parameters were obtained from 22 centered reflections in the 2θ-range 25–26° for **1** and 20–25° for **2**. Intensities were corrected for background, polarisation, and Lorenz effects. Empirical absorption corrections were made from ψ-scan data.

The structures were solved by direct methods with the SHELXTL program package [10]. The organic hydrogen atoms were placed in ideal positions. In **1** the peaks of the cluster hydrogen atoms could be clearly seen in difference Fourier maps after the remainder of the structure was refined anisotropically. Isotropic refinement of these hydrogen atoms was also possible. Their positions could also be deduced from the lengthening of the corresponding metal–metal bonds.

In the case of **2** the hydrogen atom could not be located directly. However, its position was deduced by comparison with the structures of other compounds of the same type. After the anisotropic refinement for non-hydrogen atoms with rigid organic hydrogen atoms and isotropic refinement of the cluster hydrides (compound **1**), the refinements converged to $R = 0.031$ and $R_w = 0.032$ for **1** and $R = 0.065$ and $R_w = 0.044$ for **2**.

Infrared spectroscopy

Infrared spectra were recorded on a Perkin–Elmer 297 infrared spectrometer using 0.5 mm NaCl solution cells.

NMR spectroscopy

The ^{31}P NMR spectra were recorded (in 10 mm NMR tubes) with a Bruker AM-250 spectrometer using $CDCl_3$ as solvent at ambient temperature. Broad band decoupling was used to remove the $^1H-^{31}P$ couplings. The shifts are relative to external 85% H_3PO_4, contained in a coaxial tube.

The ^1H NMR spectra were recorded (5 mm tubes) in $CDCl_3$ solutions at room temperature. The chemical shifts are relative to TMS.

Results and discussion

The mixed metal clusters $H_3Ru_3Co(CO)_{12}$ and $HRuCo_3(CO)_{12}$ react readily with dppe to form $H_3Ru_3Co(CO)_{10}(dppe)$ and $HRuCo_3(CO)_{10}(dppe)$.

Because clusters of this type offer several different sites for coordination of the new ligand, their structures are not easily predictable. Some ligands, such as hydride, prefer to bond to certain metals, but no clear preference between ruthenium and cobalt has been observed for tertiary phosphines. In the examples discussed here the bidentate dppe ligand coordinates to one ruthenium atom in **1** and two cobalt atoms in **2**.

Crystal structures

The numbering schemes for the compounds are shown in Figs. 1 and 2. Crystallographic data are listed in Table 1 and the atomic coordinates in Table 2. Selected

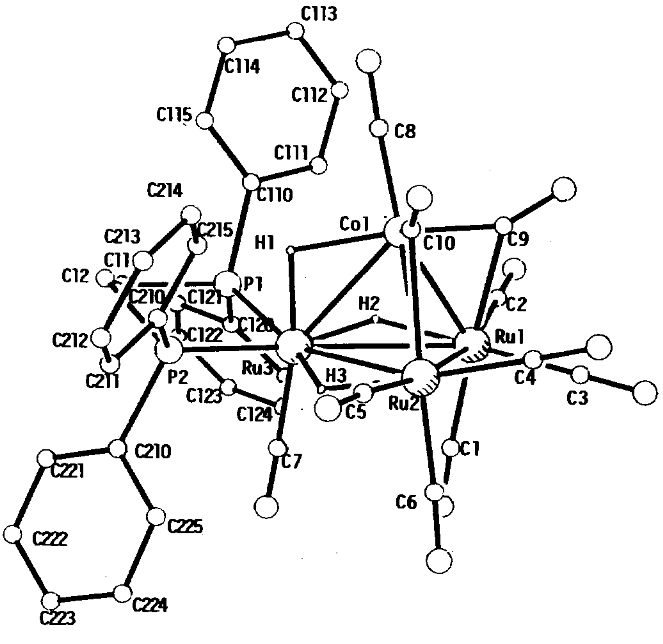

Fig. 1. Structure and numbering scheme for $H_3Ru_3Co(CO)_{10}(dppe)$.

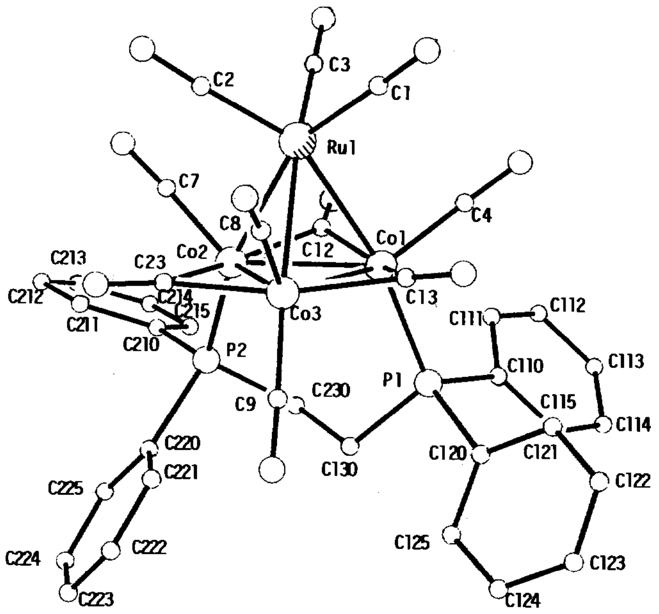

Fig. 2. Structure and numbering scheme for $HRuCo_3(CO)_{10}(dppe)$.

TABLE 1

CRYSTALLOGRAPHIC DATA

Formula	$H_3Ru_3Co(CO)_{10}(dppe)$	$HRuCo_3(CO)_{10}(dppe)$
Formula weight	1043.7	957.4
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbca*	$P2_1/n$
a (Å)	18.609(7)	15.15(2)
b (Å)	19.524(6)	11.380(4)
c (Å)	20.889(5)	21.792(8)
α (°)	90	90
β (°)	90	98.02(7)
γ (°)	90	90
V (Å^3)	7590	3720
Z	8	4
D_{calcd} (g cm^{-3})	1.83	1.71
Crystal dimensions (mm)	0.8 × 0.5 × 0.4	0.4 × 0.2 × 0.1
Radiation	Mo-K_α	Mo-K_α
Monochromator	graphite	graphite
2θ limits	5–50	3–45
No. of refl. measured	6689	4878
No. of unique data [a]	5232	2940
μ(Mo-K_α) (cm^{-1})	17.3	19.0
R [b]	0.031	0.065
R_w [c]	0.032	0.044

[a] $|F| > 5\sigma(|F|)$. [b] $R = \Sigma||F_0| - |F_c||/\Sigma|F_0|$. [c] Weight $= 1/(\sigma^2(F)+0.005F^2)$.

bond lengths and angles are given in Tables 3–6. The ligand geometry of **1** differs from that of the parent cluster. One of the hydrides bridges a Ru–Co edge and the cobalt atom has only one terminal carbonyl with two carbonyls semibridging Ru–Co bonds, whereas solid $H_3RuCo(CO)_{12}$ contains only terminal carbonyls and all the hydride ligands bridge Ru–Ru edges [8]. The formation and stability of these bridges is not unexpected, since in solution $H_3Ru_3Co(CO)_{12}$ co-exists along with an isomer containing one semibridging carbonyl and one bridging hydride on Ru–Co edges [8]. The $Ru_3Co(CO)_{13}^-$ anion has also bridging carbonyls in Ru–Co bonds and only one terminal carbonyl bound to the cobalt atom [11]. The bridging carbonyls in **1** have stronger bonds to Co(1), as indicated by the bond angles (Ru(1)–C(9)–O(9) 130.0, Ru(2)–C(10)–O(10) 126.1, Co(1)–C(9)–O(9) 148.0 and Co(1)–C(10)–O(10) 156.7°) and the metal–carbon bond lengths (Ru(1)–C(9) 2.239, Ru(2)–C(10) 2.448, Co(1)–C(9) 1.795, Co(1)–C(10) 1.753 Å). In $Ru_3Co(CO)_{13}^-$ the bridging carbonyls are symmetrical, and have rather similar Ru–C(bridge)–O (141–143°) and Co–C(bridge)–O (140–142°) bond angles. The average values for Ru–C(bridge) and Co–C(bridge) bond lengths are 2.164 and 1.856 Å, respectively. The presence of semibridges in **1** is reasonable since on the assumption that a hydride contributes 1/2 electrons to each metal Co(1) would have 18 1/2 electrons with three terminal carbonyls and only 16 1/2 electrons with two symmetrically bridging carbonyls. C(9) is almost coplanar with Ru(1), Ru(3) and Co(1) (at a distance of 0.248 Å from the plane), whereas C(10) is nearly in an eclipsed position. In $Ru_3Co(CO)_{13}^-$ all the bridging carbonyls are in the same plane as a Ru_2Co triangle.

The three terminal ligands of each Ru atom are slightly rotated, apparently to minimize the steric interactions, so that the distances of C(2), C(3), C(4), C(5), P(2) and P(1) from the Ru(1)–Ru(2)–Ru(3) plane are 0.471, −0.337, 0.487, 0.104, 0.114 and 0.687 Å, respectively. $Ru_3Co(CO)_{13}^-$ shows a more distinct rotation of this kind; C(8) is nearly coplanar with Ru(1), Ru(2) and Co(1) (distance 0.113 Å) is not far from being *trans* to Ru(2) (Ru(2)–Co(1)–C(8) angle is 161.3°).

The hydride bridged Ru–Ru bonds (av. 3.004 Å) are longer than the corresponding three bonds in $H_3Ru_3Co(CO)_{12}$ (av. 2.898 Å). This differ distinctly from the unbridged Ru(1)–Ru(2) bond (2.830 Å). The hydride-bridged Ru–Co bond (2.748 Å) is also longer than the others (av. 2.670 Å) and than the Ru–Co bonds in $H_3Ru_3Co(CO)_{12}$ (av. 2.675 Å).

An Ru–Co edge bridging hydride ligand is not common, but have been indicated by NMR spectroscopic studies for $RuCoH(Cl)(PPh_2)(CO)_4(PPh_3)_2$ [11] and $H_3Ru_3Co(CO)_{12}$ [8] in solution.

A similar change of hydride positions with respect to the parent cluster can be seen in $H_4Ru_4(CO)_{10}$(dppe) [4–6]. Three hydride ligands are bound to the same (more basic) Ru bearing the phosphine ligand. A common feature of tetranuclear clusters $H_4Ru_4(CO)_{10}$(dppe) [4–6], $H_4Ru_4(CO)_{10}(PPh_3)_2$ [13], $H_4Ru_4(CO)_{11}(P(OMe)_3)$ [14], $H_2FeRu_3(CO)_{12}(PR_3)$ [15], $H_2FeRu_3(CO)_{11}(PR_3)_2$ [15], $HFeCo_3(CO)_9(POMe_3)_3$ [16], $HFeCo_3(CO)_{10}(PPh_3)_2$ [17], $HRuCo_3(CO)_{10}(PPh_3)_2$ [18]. $HRuRh_3(CO)_{10}(PPh_3)_2$ [18], $H_2Ru_2Rh_2(CO)_{11}(PPh_3)$ [19] and $H_2Os_3Pt(CO)_{10}(P(C_6H_{11})_3)$ [20] is the presence of a hydride and a phosphorus ligand *cis* to each other on the same metal. Although this is not the case for one of the three isomers of $H_2Ru_4(CO)_{12}(P(OMe)_3)$ [15], it can be speculated that the unusual Ru(μ-H)Co hydride in **1** arises from the presence of two phosphine ligands in *cis* position.

$HRuCo_3(CO)_{10}$(dppe) closely resembles $HRuCo_3(CO)_{10}(PPh_3)_2$. The geometry

(Continued on p. 194)

TABLE 2

ATOMIC COORDINATES AND TEMPERATURE FACTORS (Å^2 × 10^3) FOR $H_3Ru_3Co(CO)_{10}(dppe)$ AND $HRuCo_3(CO)_{10}(dppe)$

Atom	x	y	z	U^a
$H_3Ru_3Co(CO)_{10}(dppe)$				
Ru(1)	0.2009(1)	0.4747(1)	0.2242(1)	38(1)
Ru(2)	0.1409(1)	0.4789(1)	0.3486(1)	39(1)
Ru(3)	0.1222(1)	0.3501(1)	0.2728(1)	32(1)
Co(1)	0.0591(1)	0.4735(1)	0.2436(1)	42(1)
P(1)	0.0890(1)	0.2782(1)	0.1905(1)	36(1)
P(2)	0.0532(1)	0.2802(1)	0.3356(1)	37(1)
O(1)	0.3353(2)	0.3929(2)	0.2568(2)	80(2)
O(2)	0.2237(2)	0.4781(2)	0.0804(2)	71(1)
O(3)	0.2816(2)	0.6070(2)	0.2478(2)	87(2)
O(4)	0.1542(2)	0.6342(2)	0.3567(2)	79(2)
O(5)	0.0644(2)	0.4598(2)	0.4765(2)	79(2)
O(6)	0.2834(2)	0.4454(2)	0.4091(2)	84(2)
O(7)	0.2561(2)	0.2683(2)	0.3036(2)	67(1)
O(8)	−0.0663(3)	0.4822(2)	0.1635(3)	110(2)
O(9)	0.1030(2)	0.5949(2)	0.1781(3)	93(2)
O(10)	−0.0194(2)	0.5474(2)	0.3390(2)	80(2)
C(1)	0.2838(3)	0.4223(2)	0.2467(2)	52(2)
C(2)	0.2163(3)	0.4750(2)	0.1339(2)	48(2)
C(3)	0.2508(3)	0.5583(3)	0.2401(2)	61(2)
C(4)	0.1509(3)	0.5768(2)	0.3530(2)	53(2)
C(5)	0.0899(3)	0.4679(2)	0.4283(2)	53(2)
C(6)	0.2314(3)	0.4589(2)	0.3844(3)	53(2)
C(7)	0.2068(2)	0.2991(2)	0.2910(2)	43(1)
C(8)	−0.0160(3)	0.4762(3)	0.1933(3)	66(2)
C(9)	0.1059(3)	0.5417(3)	0.2039(3)	58(2)
C(10)	0.0223(3)	0.5149(2)	0.3105(3)	56(2)
C(11)	0.0393(3)	0.2053(2)	0.2246(2)	47(1)
C(12)	−0.0039(2)	0.2296(2)	0.2830(2)	46(1)
C(110)	0.0293(2)	0.3142(2)	0.1297(2)	42(1)
C(111)	0.0579(3)	0.3569(3)	0.0837(3)	61(2)
C(112)	0.0141(3)	0.3872(3)	0.0378(3)	74(2)
C(113)	−0.0581(3)	0.3763(3)	0.0387(3)	78(2)
C(114)	−0.0869(3)	0.3325(3)	0.0838(3)	76(2)
C(115)	−0.0438(3)	0.3026(3)	0.1294(3)	58(2)
C(120)	0.1580(2)	0.2357(2)	0.1424(2)	41(1)
C(121)	0.1405(3)	0.1776(2)	0.1065(2)	55(2)
C(122)	0.1939(3)	0.1435(3)	0.0751(3)	67(2)
C(123)	0.2629(3)	0.1638(3)	0.0767(3)	66(2)
C(124)	0.2807(3)	0.2224(3)	0.1101(3)	60(2)
C(125)	0.2284(3)	0.2585(3)	0.1428(2)	51(2)
C(210)	−0.0111(2)	0.3182(2)	0.3911(2)	43(1)
C(211)	−0.0186(3)	0.2968(2)	0.4538(2)	61(2)
C(212)	−0.0677(3)	0.3261(3)	0.4939(3)	73(2)
C(213)	−0.1110(3)	0.3783(3)	0.4709(3)	69(2)
C(214)	−0.1049(3)	0.4002(3)	0.4098(3)	63(2)
C(215)	−0.0552(3)	0.3702(2)	0.3701(3)	53(2)
C(220)	0.1041(2)	0.2202(2)	0.3844(2)	42(1)
C(221)	0.0987(3)	0.1504(2)	0.3769(2)	52(2)
C(222)	0.1429(3)	0.1064(3)	0.4119(3)	64(2)
C(223)	0.1914(3)	0.1335(3)	0.4538(3)	66(2)
C(224)	0.1971(3)	0.2028(3)	0.4618(3)	65(2)

TABLE 2 (continued)

Atom	x	y	z	U^{a}
C(225)	0.1541(3)	0.2458(3)	0.4271(2)	57(2)
H(1)	0.0375(31)	0.3830(32)	0.2578(28)	103(20)
H(2)	0.1543(28)	0.3998(28)	0.2132(25)	83(17)
H(3)	0.1278(23)	0.3923(24)	0.3448(21)	57(14)
$HRuCo_3(CO)_{10}(dppe)$				
Ru(1)	0.3705(1)	0.7268(1)	0.2590(1)	39(1)
Co(1)	0.4722(1)	0.8893(1)	0.3181(1)	33(1)
Co(2)	0.4580(1)	0.8832(1)	0.2020(1)	34(1)
Co(3)	0.5447(1)	0.7259(1)	0.2660(1)	39(1)
P(1)	0.5736(2)	1.0252(2)	0.3523(1)	34(1)
P(2)	0.5253(2)	1.0438(2)	0.1726(1)	34(1)
O(1)	0.3320(5)	0.5686(7)	0.3640(4)	83(3)
O(2)	0.3103(5)	0.5565(7)	0.1546(4)	86(3)
O(3)	0.1864(5)	0.8382(7)	0.2495(4)	78(4)
O(4)	0.3550(5)	0.9033(6)	0.4116(3)	69(3)
O(7)	0.3108(5)	0.8682(7)	0.1025(3)	78(3)
O(8)	0.5153(6)	0.4755(7)	0.2608(4)	94(4)
O(9)	0.7389(4)	0.7258(7)	0.2783(4)	83(3)
O(12)	0.3387(4)	1.0492(6)	0.2521(3)	45(2)
O(13)	0.5445(4)	0.6970(6)	0.3998(3)	57(3)
O(23)	0.5299(5)	0.6997(6)	0.1287(3)	72(3)
C(1)	0.3469(7)	0.6283(9)	0.3254(4)	55(4)
C(2)	0.3356(7)	0.6199(9)	0.1939(5)	55(4)
C(3)	0.2558(8)	0.7961(9)	0.2532(4)	50(4)
C(4)	0.4009(6)	0.8984(8)	0.3738(4)	44(3)
C(7)	0.3676(7)	0.8737(9)	0.1426(4)	51(4)
C(8)	0.5194(7)	0.5762(10)	0.2623(5)	65(4)
C(9)	0.6628(7)	0.7252(9)	0.2746(4)	53(4)
C(12)	0.3936(6)	0.9791(8)	0.2564(4)	37(3)
C(13)	0.5300(5)	0.7481(7)	0.3531(4)	39(3)
C(23)	0.5168(6)	0.7525(10)	0.1715(5)	52(4)
C(110)	0.5356(6)	1.1504(7)	0.3940(4)	37(3)
C(111)	0.4509(7)	1.1926(8)	0.3787(5)	52(4)
C(112)	0.4224(8)	1.2899(10)	0.4078(5)	66(5)
C(113)	0.4773(8)	1.3465(9)	0.4544(5)	67(5)
C(114)	0.5605(8)	1.3032(9)	0.4701(5)	67(5)
C(115)	0.5908(7)	1.2088(8)	0.4412(4)	51(4)
C(120)	0.6727(6)	0.9722(8)	0.4043(4)	43(3)
C(121)	0.6585(7)	0.9241(9)	0.4598(4)	53(4)
C(122)	0.7304(9)	0.8868(10)	0.5014(5)	66(5)
C(123)	0.8147(9)	0.8972(10)	0.4888(5)	71(5)
C(124)	0.8295(7)	0.9446(10)	0.4328(5)	74(5)
C(125)	0.7583(7)	0.9829(10)	0.3894(5)	67(5)
C(210)	0.4561(6)	1.1343(8)	0.1151(4)	41(3)
C(211)	0.4351(7)	1.0866(9)	0.0559(4)	52(4)
C(212)	0.3853(8)	1.1509(11)	0.0096(5)	77(5)
C(213)	0.3560(8)	1.2618(10)	0.0215(5)	83(5)
C(214)	0.3750(8)	1.3068(11)	0.0794(5)	87(5)
C(215)	0.4261(7)	1.2416(10)	0.1263(5)	70(5)
C(220)	0.6311(6)	1.0306(8)	0.1407(4)	35(3)
C(221)	0.6383(7)	0.9385(9)	0.1601(4)	48(4)
C(222)	0.7690(7)	0.9310(10)	0.1393(5)	60(4)
C(223)	0.7955(7)	1.0120(10)	0.0998(5)	60(4)

TABLE 2 (continued)

Atom	x	y	z	U [a]
C(224)	0.7383(7)	1.1004(10)	0.0790(5)	59(4)
C(225)	0.6568(7)	1.1099(9)	0.0993(4)	46(4)
C(130)	0.6233(6)	1.0973(8)	0.2903(4)	44(4)
C(230)	0.5570(6)	1.1503(8)	0.2361(4)	40(3)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U tensor.

of the carbonyl groups is not affected by the phosphorus ligand. Although the crystallographic data did not allow a direct location of the hydride, a comparison of the cluster geometry with that of $HRuRh_3(CO)_{10}(PPh_3)_2$, $HFeCo_3(CO)_{10}(PPh_3)_2$ and $HRuCo_3(CO)_{10}(PPh_3)_2$ suggests that the hydrogen atom is bound to the three cobalt atoms. Indirect support for this proposal is provided by the hydrogen-induced distortions of the axial and equatorial ligands of the Co(3)-triangle as well as by the metal–metal bond lengths. The Ru–Co–C equatorial carbonyl angles (Table 6) are small enough to exclude the possibility of edge-bridging hydride in Ru–Co bonds. The observed values in $H_2Ru_2Co_2(CO)_{12}$ (111.2°) [21] and $H_2Ru_2Rh_2(CO)_{12}$ (110.7 and 115.8°) [22] are much higher.

The Ru–Co bonds (av. 2.626 Å) are slightly shorter than in $HRuCo_3(CO)_{10}(PPh_3)_2$ (av. 2.646 Å) [15], whereas the average Co–Co bond lengths are the same (2.514 Å) in both.

The average Co–Co–C axial ligand angle (113.9°) (Table 5) lies between the corresponding values for the compounds with a face-bridging hydride

TABLE 3

SELECTED BOND LENGTHS (Å) FOR $H_3Ru_3Co(CO)_{10}(dppe)$

Ru(1)–Ru(2)	2.830(1)	Ru(1)–Ru(3)	3.015(1)
Ru(2)–Ru(3)	2.993(1)	Ru(1)–Co(1)	2.669(1)
Ru(2)–Co(1)	2.670(1)	Ru(3)–Co(1)	2.748(1)
Ru(1)–C(1)	1.910(5)	Ru(1)–C(2)	1.907(5)
Ru(1)–C(3)	1.907(5)	Ru(1)–C(9)	2.239(5)
Ru(2)–C(4)	1.922(5)	Ru(2)–C(5)	1.929(5)
Ru(2)–C(6)	1.885(6)	Ru(2)–C(10)	2.448(5)
Ru(3)–C(7)	1.901(4)	Ru(3)–P(1)	2.303(1)
Ru(3)–P(2)	2.288(1)	Co(1)–C(8)	1.750(6)
Co(1)–C(9)	1.795(5)	Co(1)–C(10)	1.753(5)
P(1)–C(11)	1.841(4)	P(1)–C(110)	1.827(5)
P(1)–C(120)	1.831(4)	P(2)–C(12)	1.819(5)
P(2)–C(210)	1.826(5)	P(2)–C(220)	1.818(4)
O(1)–C(1)	1.137(6)	O(2)–C(2)	1.128(6)
O(3)–C(3)	1.122(7)	O(4)–C(4)	1.125(6)
O(5)–C(5)	1.123(6)	O(6)–C(6)	1.127(7)
O(7)–C(7)	1.127(5)	O(8)–C(8)	1.130(8)
O(9)–C(9)	1.171(6)	O(10)–C(10)	1.167(6)
Ru(1)–H(2)	1.72(6)	Ru(2)–H(3)	1.71(5)
Ru(3)–H(1)	1.73(6)	Ru(3)–H(2)	1.69(5)
Ru(3)–H(3)	1.72(4)	Co(1)–H(1)	1.84(6)

TABLE 4

SELECTED BOND LENGTHS (Å) FOR $HRuCo_3(CO)_{10}(dppe)$

Ru–Co(1)	2.626(1)	Ru–Co(2)	2.631(1)
Ru–Co(3)	2.622(1)	Co(1)–Co(2)	2.508(2)
Co(1)–Co(3)	2.511(2)	Co(2)–Co(3)	2.522(2)
Ru–C(1)	1.903(10)	Ru–C(2)	1.887(10)
Ru–C(3)	1.896(11)	Co(1)–P(1)	2.233(3)
Co(1)–C(4)	1.737(9)	Co(1)–C(12)	1.954(9)
Co(1)–C(13)	1.935(8)	Co(2)–P(2)	2.229(3)
Co(2)–C(7)	1.752(9)	Co(2)–C(12)	1.966(9)
Co(2)–C(23)	1.900(11)	Co(3)–C(8)	1.746(11)
Co(3)–C(9)	1.772(10)	Co(3)–C(13)	1.958(9)
Co(3)–C(23)	2.064(10)	P(1)–C(110)	1.827(9)
P(1)–C(120)	1.852(9)	P(1)–C(130)	1.828(9)
P(2)–C(210)	1.834(9)	P(2)–C(220)	1.839(9)
P(2)–C(230)	1.853(9)	O(1)–C(1)	1.130(13)
O(2)–C(2)	1.145(12)	O(3)–C(3)	1.149(14)
O(4)–C(4)	1.152(12)	O(7)–C(7)	1.139(12)
O(8)–C(8)	1.148(14)	O(9)–C(9)	1.144(12)
O(12)–C(12)	1.147(11)	O(13)–C(13)	1.167(11)
O(23)–C(23)	1.151(13)		

($HRuCo_3(CO)_{10}(PPh_3)_2$ (123.3°) and $H_2Ru_2Co_2(CO)_{12}$ (114.5°) [21]) and non-hydrogen compounds (($PPN)(RuCo_3(CO)_{12}$ (113.1°) [9] and $Co_4(CO)_{12}$ (105.1°) [23]). The large difference between **2** and $HRuCo_3(CO)_{10}(PPh_3)_2$ is apparently due to the

TABLE 5

SELECTED BOND ANGLES (°) FOR $H_3Ru_3Co(CO)_{10}(dppe)$

Ru(2)–Ru(1)–C(1)	96.2(1)	Ru(3)–Ru(2)–C(1)	82.9(1)
Co(1)–Ru(1)–C(1)	139.1(1)	Ru(2)–Ru(1)–C(2)	165.3(1)
Ru(3)–Ru(1)–C(2)	114.1(1)	Co(1)–Ru(1)–C(2)	107.4(1)
Ru(2)–Ru(1)–C(3)	90.4(2)	Ru(3)–Ru(1)–C(3)	150.2(2)
Co(1)–Ru(1)–C(3)	117.6(2)	Ru(2)–Ru(1)–C(9)	81.1(1)
Ru(3)–Ru(1)–C(9)	98.8(1)	Co(1)–Ru(1)–C(9)	41.8(1)
Ru(1)–Ru(2)–C(4)	92.0(1)	Ru(3)–Ru(2)–C(4)	150.7(1)
Co(1)–Ru(2)–C(4)	97.7(1)	Ru(1)–Ru(2)–C(5)	169.7(1)
Ru(3)–Ru(2)–C(5)	107.9(1)	Co(1)–Ru(2)–C(5)	115.2(2)
Ru(1)–Ru(2)–C(6)	90.4(2)	Ru(3)–Ru(2)–C(6)	98.0(1)
Co(1)–Ru(2)–C(6)	145.8(2)	Ru(1)–Ru(2)–C(10)	93.8(1)
Ru(3)–Ru(2)–C(10)	88.0(1)	Co(1)–Ru(2)–C(10)	39.8(1)
Ru(1)–Ru(3)–P(1)	111.8(1)	Ru(2)–Ru(3)–P(1)	159.7(1)
Co(1)–Ru(3)–P(1)	104.7(1)	Ru(1)–Ru(3)–P(2)	161.3(1)
Ru(2)–Ru(3)–P(2)	105.3(1)	Co(1)–Ru(3)–P(2)	114.2(1)
Ru(1)–Ru(3)–C(7)	95.1(1)	Ru(2)–Ru(3)–C(7)	103.7(1)
Co(1)–Ru(3)–C(7)	149.0(1)	Ru(1)–Co(1)–C(8)	134.3(2)
Ru(2)–Co(1)–C(8)	161.3(2)	Ru(3)–Co(1)–C(8)	120.1(2)
Ru(1)–Co(1)–C(9)	56.2(2)	Ru(2)–Co(1)–C(9)	94.2(2)
Ru(3)–Co(1)–C(9)	123.1(2)	Ru(1)–Co(1)–C(10)	120.2(2)
Ru(2)–Co(1)–C(10)	63.3(2)	Ru(3)–Co(1)–C(10)	113.3(2)
Ru(3)–P(1)–C(11)	108.5(1)	Ru(3)–P(2)–C(12)	107.8(1)
Ru(3)–P(1)–C(110)	105.1(2)	Ru(3)–P(1)–C(120)	119.8(1)
Ru(3)–P(2)–C(210)	119.3(1)	Ru(3)–P(2)–C(220)	114.4(2)

TABLE 6

SELECTED BOND ANGLES (°) FOR $HRuCo_3(CO)_{10}(dppe)$

Co(3)-Ru-C(1)	104.4(1)	Co(2)-Ru-C(1)	156.5(3)
Co(1)-Ru-C(1)	101.6(3)	Co(3)-Ru-C(2)	102.5(3)
Co(2)-Ru-C(2)	100.9(3)	Co(1)-Ru-C(2)	155.0(3)
Co(3)-Ru-C(3)	155.6(3)	Co(2)-Ru-C(3)	101.8(3)
Co(1)-Ru-C(3)	102.1(3)	Ru-Co(3)-C(8)	77.7(4)
Co(2)-Co(3)-C(9)	120.1(3)	Co(1)-Co(3)-C(9)	117.0(3)
Ru-Co(2)-C(7)	85.0(3)	Co(3)-Co(2)-P(2)	121.1(1)
Co(1)-Co(2)-P(2)	106.8(1)	Ru-Co(1)-C(4)	90.3(3)
Co(3)-Co(1)-P(1)	109.9(1)	Co(2)-Co(1)-P(1)	108.3(1)
Co(1)-P(1)-C(110)	117.1(3)	Co(1)-P(1)-C(120)	116.1(3)
Co(1)-P(1)-C(130)	113.5(3)	Co(2)-P(2)-C(210)	114.6(3)
Co(2)-P(2)-C(220)	119.9(3)	Co(2)-P(2)-C(230)	113.7(3)

different steric requirements of dppe on the one hand and two PPh_3 ligands on the other.

In the $^{31}P\{^1H\}$ NMR spectrum of **1** a singlet at 71.4 ppm can be seen at room temperature. Its chemical shift corresponds closely to the values for the geminal isomer of $H_4Ru_4(CO)_{10}(dppe)$ (70.2 and 63.0 ppm). In the hydride region two ^1H signals can be seen: a relatively sharp singlet at -16.6 ppm (Ru-H-Ru) and a broader one at -14.2 ppm (Ru-H-Co), in an intensity ratio of 2/1. The former signal was split at lower temperatures, but the resolution was not adequate for further analysis of these couplings.

For **2** the $^{31}P\{^1H\}$ NMR spectrum shows a very broad signal at 28 ppm, the broadening being caused by the quadrupolar ($I = 7/2$) ^{59}Co nuclei; in the ^{31}P spectrum of $Co_4(CO)_{10}(dppe)$ there are peaks at 25.9 and 30.4 ppm [24]. A broad resonance at 20.2 ppm can be seen in the ^1H NMR spectrum of **2**.

The NMR spectra are thus consistent with the crystal structures.

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