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CLUSTER CHEMISTRY

XXIV *. X-RAY STRUCTURE OF $H_4Ru_4(CO)_9(PMe_2Ph)[P(OC_6H_4Me\text{-}p)_3]$-$[P(OCH_2)_3CEt]$, A CHIRAL CLUSTER COMPLEX CONTAINING FOUR DIFFERENT LIGANDS

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Summary

The X-ray structure of $H_4Ru_4(CO)_9(PMe_2Ph)[P(OC_6H_4Me\text{-}p)_3][P(OCH_2)_3CEt]$, a chiral cluster complex, has been determined. The complex is triclinic, space group $P\bar{1}$, a 19.812(7), b 14.299(4), c 10.323(4) Å, α 100.09(3), β 98.18(3), γ 102.23(3)°. The unit cell contains an enantiomeric pair of molecules. The Ru_4 core contains two short (av. 2.785 Å) and four long (2.967 Å) Ru–Ru separations with approximate D_{2d} symmetry. Ru–P separations are 2.254(6) Å [to $P(OCH_2)_3CEt$], 2.270(6) Å [to $P(OC_6H_4Me\text{-}p)_3$] and 2.326(7) Å [to PMe_2Ph]; all *P*-donor ligands are *trans* to short Ru–Ru vectors.

Introduction

Interest in chiral cluster molecules has burgeoned recently because of their potential as catalysts for asymmetric syntheses. There are at least three possible sources of chirality in cluster complexes containing *closo*-M_4 cores: (a) the presence of an asymmetric (optically active) ligand; (b) the presence of an asymmetric heterometallic M_4 core; and (c) the attachment of four different ligands to a homometallic core. These are illustrated in Fig. 1. Examples of class (a) have been known for several years, and asymmetric catalysis of several reactions by complexes

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[*] For Part XXIII, see ref. 5.

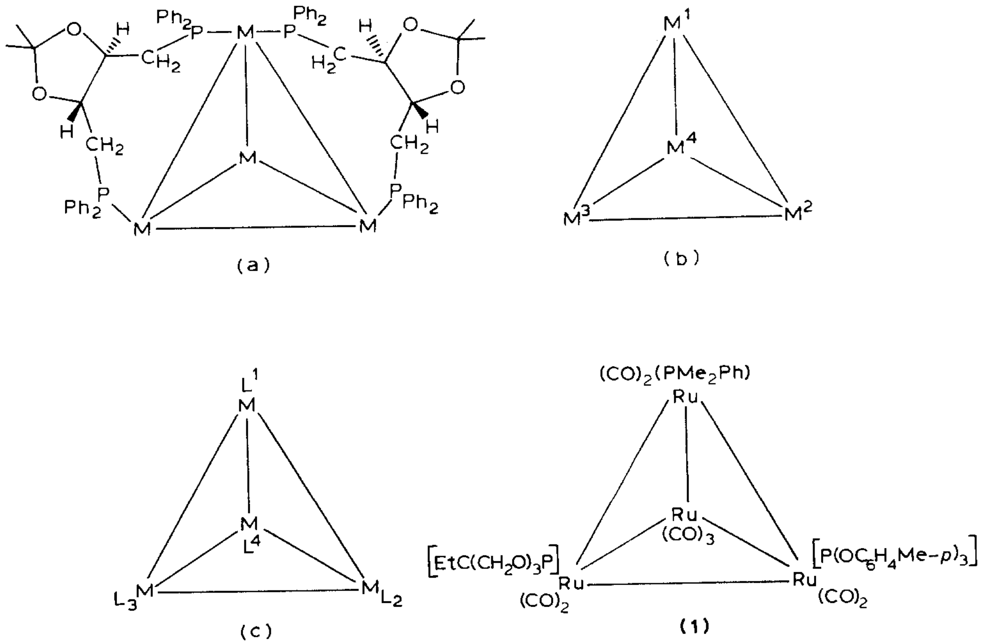
(a) (b) (c) (1)

Fig. 1. Three sources of chirality in M_4 cluster complexes: (a) use of an optically active ligand, e.g. $H_4Ru_4(CO)_8[(-)\text{-diop}]_2$; (b) presence of a heterometallic $M^1M^2M^3M^4$ core, e.g. $MoFeCo(\mu_3\text{-}S)(CO)_8(\eta\text{-}C_5H_5)$; (c) presence of four different ligands, e.g. complex **1**.

such as $H_4Ru_4(CO)_8[(-)\text{-diop}]_2$ [(−)-diop = (−)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane] has been shown to occur [1]. The synthesis [2] and resolution [3] of complexes such as $MoFeCo(\mu_3\text{-}S)(CO)_8(\eta\text{-}C_5H_5)$, i.e. class (b), have been achieved by Vahrenkamp's group.

Until recently, the formation of chiral cluster complexes containing an M_4 core, to each atom of which is coordinated a different ligand (other coordination positions being occupied by CO groups), was a challenge which awaited a suitable synthetic approach. We have described the radical ion-initiated substitution of metal cluster carbonyls which affords multi-substituted clusters in stepwise fashion [4,5], and we have further shown that it is possible to introduce different ligands sequentially [5]. If the cluster complex contains a *closo*-M_4 core, syntheses of chiral clusters containing $M_4L^1L^2L^3L^4$ moieties should be possible. These would consitute examples of class (c), which might be considered to be intermediate between classes (a) and (b). We first showed that this approach could succeed with the synthesis of $H_4Ru_4(CO)_9(PMe_2Ph)[P(OMe)_2Ph][P(OMe)_3]$ [5]. It was naturally of interest to confirm that each entering ligand became attached to a different metal atom. It has proved difficult to obtain these complexes as well-formed crystals; indeed, many were obtained as oils, which may be taken as an indication of the presence of enantiomeric mixtures. We were successful with the complex $H_4Ru_4(CO)_9(PMe_2Ph)[P(OC_6H_4Me\text{-}p)_3][P(OCH_2)_3CEt]$ (**1**), however, and the X-ray structure of this molecule is described below.

TABLE 1

NON-HYDROGEN ATOM COORDINATES

(Primed atoms are components of disordered species. Populations 0.45, 0.30, 0.25 respectively for singly, doubly, and triply primed components of the disordered ligand on Ru(1); for the terminal carbon, two components only were resolved with populations 0.56, 0.44.)

Atom	*x*	*y*	*z*
Ru(1)	0.12432(9)	0.8701(1)	0.2244(2)
C(13)	0.1728(10)	0.9349(16)	0.3927(22)
O(13)	0.1971(8)	0.9731(12)	0.5042(16)
C(14)	0.1218(11)	0.9874(14)	0.1693(22)
O(14)	0.1197(9)	1.0597(10)	0.1384(19)
P(a)	0.0137(3)	0.8456(4)	0.2641(6)
O(a1′)	−0.018(1)	0.741(2)	0.286(2)
O(a1″)	−0.034(2)	0.732(3)	0.224(4)
O(a1‴)	−0.010(3)	0.763(4)	0.339(5)
O(a2′)	−0.004(1)	0.919(2)	0.382(3)
O(a2″)	−0.002(2)	0.865(3)	0.428(4)
O(a2‴)	−0.010(2)	0.939(2)	0.342(3)
O(a3′)	−0.041(1)	0.861(2)	0.142(2)
O(a3″)	−0.032(2)	0.909(3)	0.231(5)
O(a3‴)	−0.047(2)	0.816(3)	0.115(5)
C(a1′)	−0.095(3)	0.707(4)	0.289(5)
C(a1″)	−0.111(3)	0.713(4)	0.237(5)
C(a1‴)	−0.084(2)	0.735(3)	0.339(5)
C(a2′)	−0.075(2)	0.900(3)	0.397(4)
C(a2″)	−0.075(3)	0.851(4)	0.458(5)
C(a2‴)	−0.089(3)	0.927(5)	0.355(7)
C(a3′)	−0.115(2)	0.840(2)	0.149(3)
C(a3″)	−0.107(3)	0.883(4)	0.221(6)
C(a3‴)	−0.121(4)	0.793(5)	0.127(7)
C(a4)	−0.121(1)	0.810(1)	0.297(2)
C(a5)	−0.203(1)	0.793(2)	0.306(2)
C(a6′)	−0.215(2)	0.768(3)	0.420(4)
C(a6″)	−0.236(4)	0.684(5)	0.273(7)
Ru(2)	0.24174(8)	0.8435(1)	0.1157(2)
C(23)	0.2963(12)	0.9257(16)	0.2691(21)
O(23)	0.3333(8)	0.9799(12)	0.3594(17)
C(24)	0.2379(10)	0.9469(14)	0.0276(22)
O(24)	0.2335(8)	1.0071(11)	−0.0290(18)
P(b)	0.3267(3)	0.7859(4)	0.0252(6)
O(b1)	0.3047(6)	0.6749(9)	−0.0393(14)
C(b11)	0.3423(10)	0.6202(14)	−0.1108(21)
C(b12)	0.3979(18)	0.5961(27)	−0.0541(31)
C(b13)	0.4332(19)	0.5342(26)	−0.1327(30)
C(b14)	0.4113(14)	0.5026(16)	−0.2601(22)
C(b141)	0.4525(15)	0.4349(19)	−0.3396(32)
C(b15)	0.3548(16)	0.5246(21)	−0.3190(26)
C(b16)	0.3173(15)	0.5825(20)	−0.2437(27)
O(b2)	0.4052(6)	0.8055(11)	0.1126(14)
C(b21)	0.4183(11)	0.7948(16)	0.2505(18)
C(b22)	0.3853(11)	0.7134(17)	0.2845(24)
C(b23)	0.4057(12)	0.7105(18)	0.4213(27)
C(b24)	0.4559(13)	0.7903(21)	0.5145(24)
C(b241)	0.4811(17)	0.7902(29)	0.6572(31)
C(b25)	0.4882(14)	0.8677(20)	0.4633(24)

TABLE I (continued)

Atom	*x*	*y*	*z*
C(b26)	0.4693(12)	0.8755(18)	0.3307(25)
O(b3)	0.3529(8)	0.8230(10)	−0.1037(14)
C(b31)	0.3658(11)	0.9202(15)	−0.1205(25)
C(b32)	0.4091(10)	0.9949(15)	−0.0158(22)
C(b33)	0.4208(11)	1.0897(17)	−0.0437(22)
C(b34)	0.3907(11)	1.1085(17)	−0.1598(23)
C(b341)	0.4016(13)	1.2120(19)	−0.1869(31)
C(b35)	0.3497(13)	1.0333(17)	−0.2611(24)
C(b36)	0.3387(12)	0.9353(18)	−0.2473(21)
Ru(3)	0.10366(8)	0.7108(1)	−0.0162(2)
C(31)	0.1272(9)	0.6032(13)	−0.1124(19)
O(31)	0.1388(7)	0.5403(10)	−0.1846(13)
C(32)	0.0132(10)	0.6375(13)	−0.0088(16)
O(32)	−0.0404(7)	0.5921(9)	−0.0060(13)
P(c)	0.0629(3)	0.7654(4)	−0.2049(6)
C(c11)	−0.0204(10)	0.6875(15)	−0.3071(19)
C(c12)	−0.0791(10)	0.6959(16)	−0.2540(24)
C(c13)	−0.1428(12)	0.6303(23)	−0.3308(30)
C(c14)	−0.1474(19)	0.5606(26)	−0.4570(40)
C(c15)	−0.0910(21)	0.5638(17)	−0.4849(28)
C(c16)	−0.0254(16)	0.6198(17)	−0.4273(21)
C(c21)	0.0409(13)	0.8843(15)	−0.1747(26)
C(c31)	0.1222(14)	0.7728(23)	−0.3276(24)
Ru(4)	0.16619(8)	0.6836(1)	0.2287(2)
C(41)	0.1958(11)	0.5771(13)	0.1456(22)
O(41)	0.2126(8)	0.5095(10)	0.0904(16)
C(42)	0.0793(10)	0.6011(13)	0.2489(18)
O(42)	0.0296(7)	0.5541(10)	0.2608(14)
C(43)	0.2143(10)	0.6893(15)	0.4030(20)
O(43)	0.2447(8)	0.6926(13)	0.5090(14)
"Solvent" molecules			
O(1)	0.288(1)	0.244(2)	0.122(3)
O(2)	0.312(1)	0.225(2)	0.298(3)
O(3)	0.347(1)	0.407(2)	0.306(3)
O(4)	0.390(2)	0.338(3)	0.199(4)
O(5)	0.321(3)	0.373(4)	0.096(5)

Experimental

Complex **1** was obtained from $H_4Ru_4(CO)_{12}$ by three successive radical ion-initiated substitutions, as described earlier [6]. Bright yellow crystals were obtained from benzene/light petroleum mixtures, and the X-ray specimen was selected from the first batch isolated.

Crystallography

$C_{44}H_{47}O_{15}P_3Ru_4$ *, $M = 1313$, Triclinic, space group $P\bar{1}$ (C_i^1, No. 2), a 19.812(7), b 14.299(4), c 10.323(4) Å, α 100.09(3), β 98.18(3), γ 102.23(3)°, U 2764(2) Å^3, D_m

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* Formula, M, D_c, μ exclude consideration of solvent.

1.66, D_c ($Z = 2$) 1.58 g cm^{-3}. $F(000) = 1304$. Monochromatic Mo-K_α radiation, λ 0.71069 Å, μ(Mo) 11.2 cm^{-1}. Specimen: 0.20 × 0.10 × 0.05 mm. T 295(1) K.

Structure determination. A unique data set was measured to the limit $2\theta_{max} = 40°$ using a Syntex $P\bar{1}$ four-circle diffractometer in conventional $2\theta/\theta$ scan mode, yielding 6020 independent reflections, 3121 of which with $I > 3\sigma(I)$ were considered "observed" and used in the solution and (basically) 9 × 9 block diagonal least squares refinement after absorption correction. Because of the small crystal size and limited data available in consequence, anisotropic thermal parameters were refined only for the $Ru_4(CO)_9P_3$ molecular core, and the non-disordered ligand fragments. Disorder was evident in one of the phosphine ligands and also in the presence of peaks in difference maps computed at a late stage which were then modelled in terms of oxygen atoms, there being no chemically sensible connectivity. As they comprised a relatively small contribution to the scattering and many were affected by disorder, ligand hydrogen atoms were neglected. At convergence residuals R, R' were 0.057, 0.066, reflection weights being $(\sigma^2(F_0) + 0.0005(F_0)^2)^{-1}$. Neutral complex scattering factors were used [7]; computation used the X-RAY 76 program

TABLE 2

RUTHENIUM ENVIRONMENTS

(The entries in the first column of the matrix are the ruthenium–ligand distances (Å). Other entries are the angles subtended by the atoms at the head of the relevant row and column (degrees))

Ru(1)	r(Ru–X)	Ru(3)	Ru(4)	C(13)	C(14)	P(a)
Ru(2)	2.790(3)	61.72(5)	62.06(7)	96.4(7)	95.2(7)	161.4(2)
Ru(3)	2.977(3)		55.85(6)	149.9(7)	109.0(6)	99.9(1)
Ru(4)	2.961(3)			96.6(8)	156.3(7)	106.4(2)
C(13)	1.84(2)				92.3(10)	99.6(7)
C(14)	1.87(2)					93.6(7)
P(a)	2.254(6)					

Ru(2)	r(Ru–X)	Ru(3)	Ru(4)	C(23)	C(24)	P(b)
Ru(1)	2.790(3)	62.24(6)	61.80(6)	87.6(8)	90.7(7)	167.1(2)
Ru(3)	2.962(2)		55.92(6)	147.6(7)	98.8(5)	108.3(1)
Ru(4)	2.968(3)			100.7(7)	148.4(6)	106.0(2)
C(23)	1.84(2)				92.9(9)	99.3(8)
C(24)	1.88(2)					99.8(7)
P(b)	2.270(6)					

Ru(3)	r(Ru–X)	Ru(2)	Ru(4)	C(31)	C(32)	P(c)
Ru(1)	2.977(3)	56.04(5)	61.79(6)	152.4(6)	99.4(5)	108.8(2)
Ru(2)	2.962(2)		62.15(6)	103.6(5)	151.2(5)	108.0(2)
Ru(4)	2.781(3)			93.0(6)	94.3(5)	168.8(1)
C(31)	1.86(2)				93.3(8)	94.8(6)
C(32)	1.89(2)					93.3(6)
P(c)	2.326(7)					

Ru(4)	r(Ru–X)	Ru(2)	Ru(3)	C(41)	C(42)	C(43)
Ru(1)	2.961(3)	56.14(6)	62.36(6)	151.0(7)	100.6(6)	108.7(7)
Ru(2)	2.968(3)		61.93(6)	101.4(7)	150.0(6)	109.8(6)
Ru(3)	2.781(3)			91.7(7)	91.5(6)	170.0(6)
C(41)	1.86(2)				92.4(8)	95.7(9)
C(42)	1.93(2)					94.9(8)
C(43)	1.89(2)					

TABLE 3

CARBONYL GEOMETRIES

Carbonyl	r(C–O) (Å)	Angle Ru–C–O (°)
13	1.17(2)	173(2)
14	1.14(3)	178(2)
23	1.15(2)	175(2)
24	1.13(3)	177(2)
31	1.15(2)	172(2)
32	1.13(2)	179(2)
41	1.17(3)	178(2)
42	1.10(2)	180(3)
43	1.16(3)	179(2)

system [8] implemented by S.R. Hall on a Perkin–Elmer 3240 computer.

Atom labelling is given in Fig. 2; about each ruthenium atom Ru(m), the carbonyl CO(mn) lies trans to Ru(n). Phosphine ligands a,b,c are attached to Ru(1,2,3) respectively.

In Tables 1–3 the final parameters for the non-hydrogen atoms, the ruthenium environments and the carbonyl geometries are given.

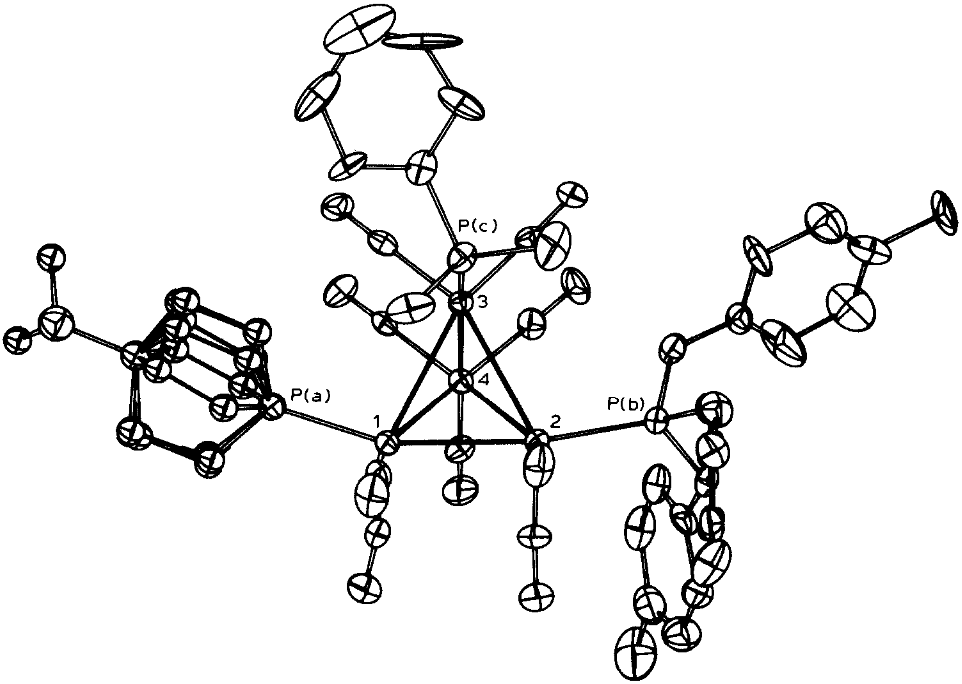

Fig. 2. Molecular projection of $H_4Ru_4(CO)_9(PMe_2Ph)[P(OC_6H_4Me\text{-}p)_3][P(OCH_2)_3CEt]$ (**1**).

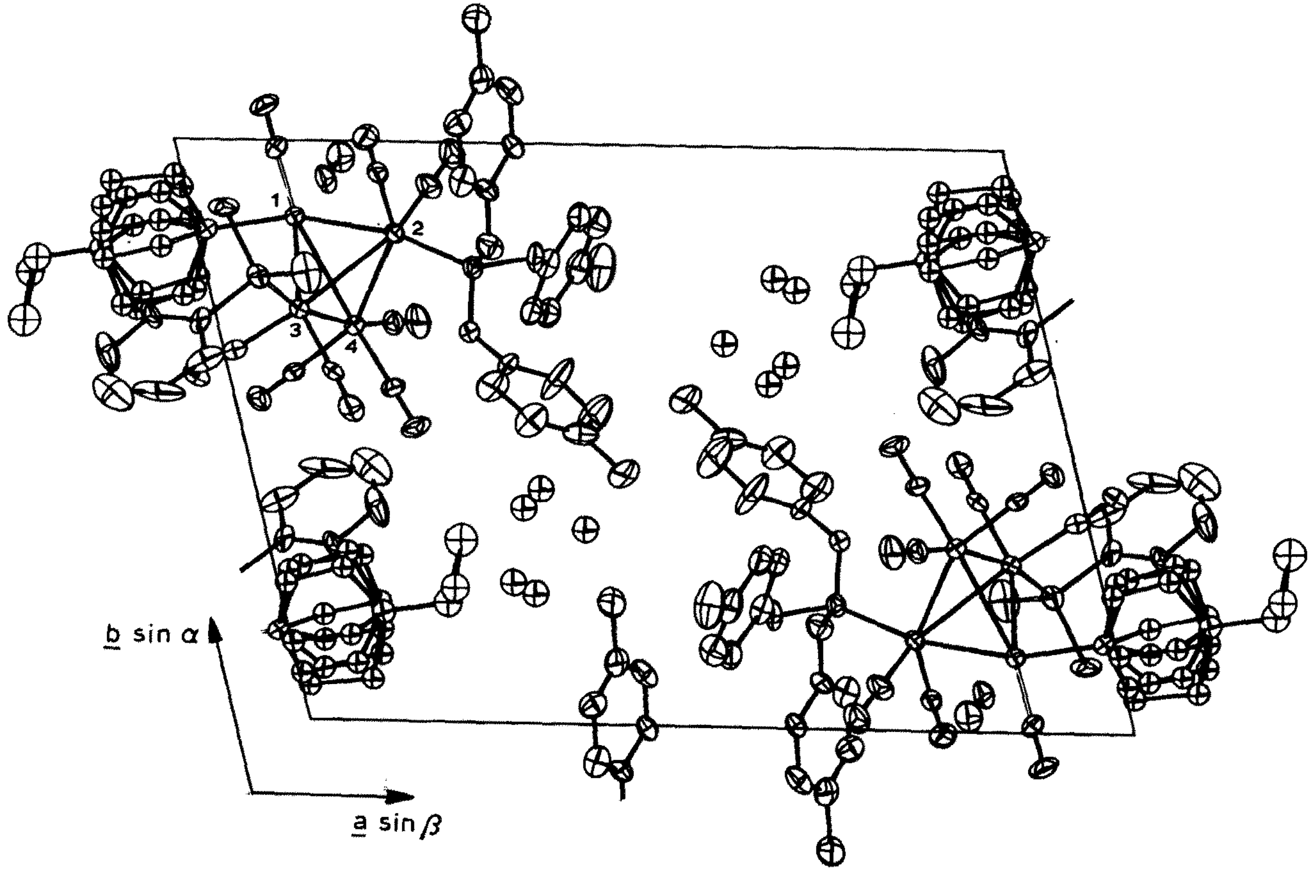

Fig. 3. Unit cell contents of **1** projected down *c*. In this and Fig. 2, non-hydrogen atoms are shown with 20% thermal ellipsoids.

Description of structure

Crystals of complex **1** contain discrete molecules of the cluster separated by normal Van der Waals distances. The unit cell (Fig. 3) contains two molecules, which are necessarily an enantiomeric pair. In Fig. 2. the molecular projection of complex 1 is shown.

As expected, the cluster contains a central Ru_4 unit with the now familiar two short [2.781(3), 2.790(3) Å]/four long [2.961(3), 2.962(2), 2.968(3), 2.977(3) Å] set of Ru–Ru separations as found in $H_4Ru_4(CO)_{12}$ [9] and $H_4Ru_4(CO)_{10}(PPh_3)_2$ [9,10] for example. We make the usual assumption that the four hydrogen atoms, which were not located in the refinement, bridge the four long bonds. The average Ru–Ru distances (2.785, 2.967 Å) compare well with those found in $H_4Ru_4(CO)_{10}(PPh_3)_2$ (2.772, 2.966 Å) [9,10]. The disposition of the hydrogen atoms gives the H_4Ru_4 core D_{2d} symmetry, the phosphorus donor ligands all being *trans* to the non-bridged Ru–Ru bonds.

The CO ligands all occupy terminal positions, and are staggered with respect to the Ru–Ru edges, as expected from a simple consideration of the location of available orbitals on the ML_3 fragments from which the cluster can be assembled [11]. The phosphorus-donor ligands are attached in a manner which results in minimum steric interference with each other. The tertiary phosphine is attached to Ru(3), the aryl phosphite to Ru(2), and the constrained phosphite ester to Ru(1). The Ru–P distances are respectively, 2.326(7), 2.270(6) and 2.254(6) Å, values entirely similar with others described earlier (e.g., 2.330 Å in $Ru_3(CO)_9(PMe_3)_3$ [12], 2.265(2) and 2.330(1) Å in $Ru_3(CO)_{10}[P(OMe)_3]_2$ [12], 2.380(6) in $Ru_3(CO)_{11}(PPh_3)$ [13], or 2.359(4) Å in $H_4Ru_4(CO)_{10}(PPh_3)_2$ [9]), and in accord with the better π-accepting properties of phosphite ligands compared with tertiary phosphines.

Conclusions

We have synthesised and determined the structure of a cluster complex which derives its chirality from the presence of four different ligands (CO, PMe_2Ph, $P(OCH_2)_3CEt$ and $P(OC_6H_4Me\text{-}p)_3$), one on each metal atom of an approximately tetrahedral M_4 core. Unlike the chiral clusters made by Vahrenkamp, the asymmetry of the molecule is not revealed by NMR studies of the PMe_2Ph ligand. Further studies on these aspects and the possible resolution of complex **1** are in hand.

Acknowledgements

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