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Stereochemically active lone pairs of electrons in subvalent main fourth-group compounds. The crystal and molecular structures of $\{\eta^5\text{-}C_5H_5Co[P(OC_2H_5)_2O]_3\}_2M^{II}$ (M = Sn, Pb)

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Abstract

The air-stable, mixed main group-transition metal, trinuclear sandwich oxygen tripod 2/1 complexes, $\{\eta^5\text{-}C_5H_5Co[P(OC_2H_5)_2O]_3\}_2M$, (**1**, M = Sn): $C_{34}H_{70}Co_2O_{18}P_6Sn$, *a* 18.871(12), *b* 22.461(12), *c* 12.671(7) Å, *β* 92.53(5)°, monoclinic space group $P2_1/a$, d_{calc} 1.472 g cm^{-3}, $Z = 4$, $R = 9.5\%$: **2** (M = Pb): $C_{34}H_{70}Co_2O_{18}P_6Pb$, *a* 18.787(8), *b* 22.397(9), *c* 12.674(3) Å, *β* 92,01(3)°, monoclinic space group $P2_1/a$, d_{calc} 1.594 g cm^{-3}, $Z = 4$, $R = 7.2\%$, have been subjected to single crystal X-ray analysis. Both complexes show a stereochemically active lone pair at the metal and coordination to two tridentate $\eta^5\text{-}C_5H_5Co[P(OC_2H_5)_2O]_3$ groups. The angles through the MO_6 units are Co–M–Co 149.04(14)° and 150.96(7)° for M = Sn and Pb, respectively. The tilting of the two tripod ligand moieties is reflected in the M–O internuclear distances which range from 2.24(3) to 2.83 (3) Å for M-Sn and 2.40 (2) to 2.66(3) Å for M = Pb, differences of 0.59(3) and 0.26(3) Å, respectively. The average distances are 2.48(3) and 2.51(2) Å for **1** and **2** which are isostructural.

Introduction

After our discovery that in decaphenylstannocene, $[\eta^5\text{-}(C_6H_5)_5C_5]_2Sn^{II}$, the lone pair of electrons is stereochemically inert (S_{10} symmetry) [1], we sought other

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molecular, subvalent main fourth-group compounds in which a similar effect might be observed [2–5]. A likely candidate seemed to be the mixed main group-transition metal trinuclear sandwich, oxygen tripod, 2/1 complexes of tin(II) (**1**) and lead(II), (**2**) [6–8], especially considering our long-standing interest in tin phosphonate derivatives [9–17]. The ^{1}H and ^{31}P NMR spectra are consistent with a symmetrically octahedral MO_6 system. There is no splitting of the ν(P=O) absorption in the infrared spectra of **1** or **2** in pentane as is seen in the spectra of the M = Cu, Hg and V=O complexes [7] with the same ligands. The M = Cu complex is known to exhibit small (4 + 2) deviations from regular O_h geometry despite the location of the Cu atom on a center of symmetry. The electronic spectrum of this complex is in accord with a Jahn–Teller distorted CuO_6 octahedron [18].

The tin-119m Mössbauer spectrum of **1** confirms the presence of divalent tin, but shows a quadropole splitting (QS) of 0.88 mm s^{-1} [6]. Remeasurement of the Mössbauer spectrum gave a resonance line with no resolvable QS which could be fit to a broad singlet. In any case splitting might be expected to arise from the lower than perfect O_h symmetry of the $Sn[OP(OR)_2]_6$ residue (ideally D_{3d}). There are no known, authenticated tin(II)-oxygen structures in which the subvalent lone pair of electrons is stereochemically inert [2], and hence the Mössbauer spectroscopic behavior of such a system is not known [9]. Decaphenylstannocene [1] itself gives only a small QS [5]. The electric-field gradient is presumably oriented down the S_{10} symmetry screw axis [5] as in ferrocene.

Thus we hoped to find the sought after tin(II)-oxygen example of a stereochemically inert lone pair of electrons in $\{\eta^5\text{-}C_5H_5Co[P(OC_2H_5)_2O]_3\}_2M^{II}$ where M = Sn, or in its M = Pb homologue. Regular O_h symmetry would demand equal M–O and M–Co distances, a linear Co–M–Co axis, parallel η^5-cyclopentadiene rings and similarity of equivalent O–M–O angles. Unfortunately, we were to be disappointed.

Experimental

A modified synthesis of the title compound where M = Sn (**1**) [6], and Pb (**2**) [7], showed better reproducibility than previous methods and yielded crystals suitable for structure determination.

Bis[(η^5-cyclopentadienyl)tris(diethylphosphito-P)cobalt-O,O′,O″]tin(II) (1)

The sodium salt, $Na\{\eta^5\text{-}C_5H_5Co[P(OC_2H_5)_2O]_3\}$ [8], (1.74 mmol) was dissolved in a minimum of distilled water to give a clear, yellow solution. Tin(II) chloride dihydrate (0.87 mmol) was added with vigorous stirring. A light-yellow precipitate formed and was separated by centrifugation and washed with distilled water. The methylene chloride extract of **1** from an aqueous suspension was withdrawn with a syringe and evaporated. The solid residue was dissolved in pentane, filtered through a membrane and crystallized by slow evaporation of the solvent, yield 480 mg (46%). A second recrystallization from the mother liquor combined to give a total yield of ca. 70–80%.

Bis[(η^5-cyclopentadienyl)tris(diethylphosphito-P)cobalt-O,O′,O″]lead(II) (2)

From $Na\{\eta^5\text{-}C_5H_5Co[P(OC_2H_5)_2O]_3\}$ [8] (1.00 mmol) and lead(II) acetate (0.5 mmol) as described for **1**. Recrystallization from hexane yielded 463 mg (83% yield).

The tin-199m Mössbauer spectrum of **1**, recorded at 77 K on a Ranger-Engineering spectrometer using $Ca^{119m}SnO_3$ as source and standard reference material for zero velocity gave isomer shift (IS) = 4.03 + 0.03; $\Gamma = 1.45 + 0.03$ mm s^{-1}. There was no detectable signal at ambient temperature. Velocity calibration was based upon β-tin and natural iron foils.

Data collection and structure determination

Crystals of $\{\eta^5\text{-}C_5H_5Co[P(OC_2H_5)_2O]_3\}_2M^{II}$, $C_{34}H_{70}Co_2O_{18}P_6M$, (**1**, M = Sn; **2**, M = Pb) were sealed in capillaries and mounted on a Syntex P3 automated diffractometer. Unit cell dimensions (Table 1) were determined by least-squares refinement of the best angular positions for fifteen independent reflections ($2\theta >$ 15°) during normal crystal alignment procedures using monochromated Mo-K_α radiation ($\lambda = 0.71069$ Å). Data, 7978 points (**1**), 11840 (**2**), were collected at ambient temperature using a variable scan rate, a θ–2θ scan mode and a scan width of 1.2° below K_{α_1} and 1.2° above K_{α_2} to a maximum 2θ value of 50°. Backgrounds were measured at each side of the scan for a combined time equal to the total scan time. The intensities of three standard reflections were remeasured after every 97 reflections. The intensities of these reflections showed less than 8% variation; therefore, corrections for decomposition were deemed unnecessary. Data were corrected for Lorentz, polarization and background effects. After removal of redundant and space group forbidden data, 1966 (**1**), 3905 (**2**) reflections were considered observed $I > 3.0\sigma(I)$. The structures were solved by direct methods using MULTAN 80 to locate the heavy atoms. Successive least-squares/difference-Fourier cycles allowed location of the remainder of the heavy atoms [20].

Table 1

Crystal Data for $\{\eta^5\text{-}C_5H_5Co[P(OC_2H_5)_2O]_3\}_2M^{II}$ where M = Sn, Pb [a]

	1 (M = Sn)	**2** (M = Pb)
Formula	$C_{34}H_{70}Co_2O_{18}P_6Sn$	$C_{34}H_{70}Co_2O_{18}P_6Pb$
f_w, daltons	1189.3	1277.8
a, Å	18.871(12)	18.787(8)
b, Å	22.461(12)	22.397(9)
c, Å	12.671(7)	12.674(3)
β, deg	92.53(5)	92.01(3)
V, Å^3	5365.7(52)	5329.4(34)
$F(000)$	2448	2576
μ(Mo-K_α), cm^{-1}	13.08	40.27
λ(Mo-K_α), Å	0.71069	0.71069
ρ_{calc}, g cm^{-3}	1.472	1.592
Z	4	4
Obsd reflctn	1966	3905
R	9.5%	7.2%
R_w	9.7%	
Space group	$P2_1/a$	$P2_1/a$
Cryst dimens, mm	0.15×0.15×0.3	0.2×0.2×0.2

[a] Estimated standard deviations in parentheses.

Table 2

Positional parameters for $\{\eta^5\text{-}C_5H_5Co[P(OC_2H_5)_2O]_3\}_2Sn^{II}$, $C_{34}H_{70}Co_2O_{18}P_6Sn$ (1) [a]

Atom	*x*	*y*	*z*
Sn(1)	0.1713(2)	0.0452(2)	0.7531(3)
Co(1)	0.1409(3)	−0.1475(3)	0.7465(5)
Co(2)	0.3158(3)	0.1977(3)	0.7739(5)
P(11)	0.1475(8)	−0.0924(6)	0.8889(11)
P(12)	0.2247(8)	−0.0959(7)	0.6770(11)
P(13)	0.0608(8)	−0.0894(7)	0.6729(11)
P(21)	0.2914(8)	0.1463(7)	0.6318(12)
P(22)	0.3201(8)	0.1189(7)	0.8714(12)
P(23)	0.2046(7)	0.2144(6)	0.8035(12)
O(11)	0.1429(18)	−0.0271(12)	0.8848(24)
O(111)	0.2209(23)	−0.1100(16)	0.9536(30)
O(112)	0.0892(21)	−0.1172(14)	0.9648(25)
O(12)	0.2394(15)	−0.0321(12)	0.7106(25)
O(121)	0.3005(16)	−0.1300(15)	0.7040(31)
O(122)	0.2216(24)	−0.1011(17)	0.5542(28)
O(13)	0.0779(19)	−0.0280(14)	0.6517(26)
O(131)	0.0415(23)	−0.1238(17)	0.5628(34)
O(132)	−0.0142(17)	−0.0965(17)	0.7307(39)
O(21)	0.2490(18)	0.0926(15)	0.6333(23)
O(211)	0.2668(24)	0.1854(18)	0.5408(30)
O(212)	0.3672(20)	0.1286(21)	0.5843(32)
O(22)	0.2681(16)	0.0721(14)	0.8614(22)
O(221)	0.3240(23)	0.1382(19)	0.9939(30)
O(222)	0.3957(16)	0.0893(18)	0.8677(32)
O(23)	0.1524(16)	0.1687(14)	0.7836(25)
O(231)	0.1982(19)	0.2396(15)	0.9193(28)
O(232)	0.1818(17)	0.2725(15)	0.7306(30)
C(1111)	0.2853(41)	−0.0765(37)	1.0001(62)
C(1112)	0.3146(59)	−0.0875(53)	1.0757(90)
C(1121)	0.0635(30)	−0.0835(27)	0.9547(46)
C(1122)	0.0016(33)	−0.1101(28)	0.9061(49)
C(1211)	0.3651(36)	−0.1116(28)	0.6687(49)
C(1212)	0.4209(30)	−0.1451(28)	0.7227(46)
C(1221)	0.2100(31)	−0.0530(32)	0.4867(49)
C(1222)	0.2432(41)	−0.0559(37)	0.3842(63)
C(1311)	0.0038(33)	−0.0944(29)	0.4894(52)
C(1312)	0.0032(33)	−0.1363(32)	0.3880(53)
C(1321)	−0.0564(30)	−0.0567(28)	0.7572(45)
C(1322)	−0.1244(38)	−0.0671(33)	0.8054(57)
C(2111)	0.1999(48)	0.1936(38)	0.5104(68)
C(2112)	0.1791(47)	0.1747(44)	0.4150(77)
C(2121)	0.3695(43)	0.0984(36)	0.4820(60)
C(2122)	0.4340(55)	0.0663(44)	0.4829(76)
C(2211)	0.3145(41)	0.0963(35)	1.0854(61)
C(2212)	0.3708(66)	0.1082(51)	1.1677(93)
C(2221)	0.4099(36)	0.0348(32)	0.8151(51)
C(2222)	0.4861(48)	0.0238(40)	0.8213(66)
C(2311)	0.1678(38)	0.2140(33)	1.0127(56)
C(2312)	0.1060(39)	0.2514(36)	1.0415(59)
C(2321)	0.1090(27)	0.2889(25)	0.7211(43)
C(2322)	0.0897(43)	0.3405(41)	0.6492(65)

Table 2 (continued)

Atom	x	y	z
C(1)	0.1472(25)	−0.2282(22)	0.6584(37)
C(2)	0.1999(23)	−0.2279(20)	0.7442(35)
C(3)	0.1617(27)	−0.2250(23)	0.8366(40
C(4)	0.0927(24)	−0.2215(21)	0.8151(35)
C(5)	0.0795(30)	−0.2237(26)	0.7023(45)
C(6)	0.3458(29)	0.2804(25)	0.8368(45)
C(7)	0.3941(37)	0.2352(34)	0.8688(55)
C(8)	0.4210(33)	0.2124(29)	0.7801(56)
C(9)	0.3961(34)	0.2352(30)	0.6953(53)
C(10)	0.3396(31)	0.2821(27)	0.7281(50)

[a] Estimated standard deviations in parentheses.

Refinement [21] of scale-factor, positional and anisotropic thermal parameters for all non-hydrogen atoms were carried out to convergence (excepting the carbon atoms of **1** which were refined isotropically). Hydrogen positional parameters were not determined. The final cycle of refinement [function minimized $\Sigma(|F_o| - |F_c|)^2$] led to a final agreement factor [$R = 9.5\%$, $R_w = 9.7\%$ (**2**); $R = (\Sigma ||F_o| - |F_c|| / \Sigma |F_o|) \times 100$]. Anomalous dispersion corrections were made for Sn, Co, and P (**1**); Pb, Co, and P (**2**). Scattering factors were taken from ref. 22.

Unit weights were used throughout for **2**. For **1** a weighting scheme was applied to down-weight the intensities of the high-intensity reflections. The validity of this

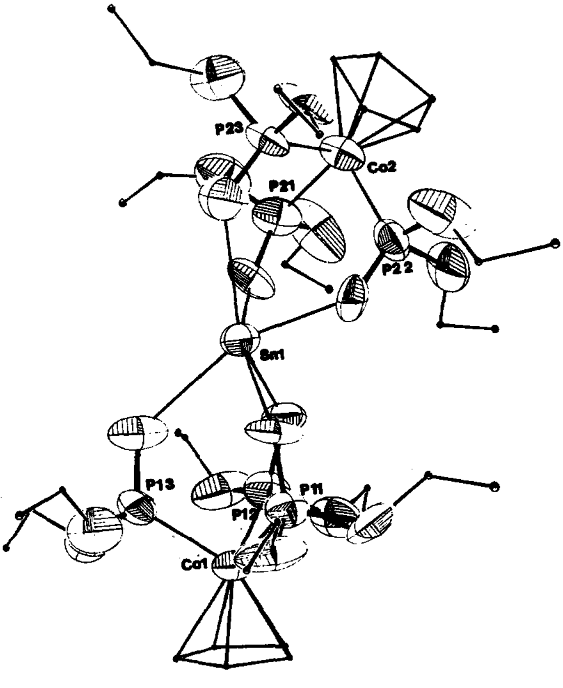

Fig. 1. $\{\eta^5\text{-}C_5H_5Co[P(OC_2H_5)_2O]_3\}_2Sn^{II}$ showing the atomic numbering for the Co and P atoms.

Table 3

Positional parameters for $\{\eta^5\text{-}C_5H_5Co[P(OC_2H_5)_2O]_3\}_2Pb^{II}$, $C_{34}H_{70}Co_2O_{18}P_6Pb$ (**2**) [a]

Atom	*x*	*y*	*z*
Pb(1)	0.3281(1)	0.0473(0)	0.2483(1)
Co(1)	0.3624(2)	−0.1468(2)	0.2498(3)
Co(2)	0.1857(2)	0.2031(2)	0.2387(3)
P(11)	0.3534(4)	−0.0929(3)	0.1076(6)
P(12)	0.2754(5)	−0.1000(4)	0.3227(7)
P(13)	0.4402(5)	−0.0867(4)	0.3247(7)
P(21)	0.2079(4)	0.1495(4)	0.3778(7)
P(22)	0.1747(4)	0.1250(4)	0.1363(7)
P(23)	0.2972(4)	0.2133(3)	0.2049(7)
O(11)	0.3595(12)	−0.0252(8)	0.1063(15)
O(111)	0.2786(14)	−0.1089(10)	0.0436(19)
O(112)	0.4127(13)	−0.1164(9)	0.0295(17)
O(12)	0.2568(10)	−0.0381(8)	0.2874(16)
O(121)	0.2015(11)	−0.1371(9)	0.2993(22)
O(122)	0.2859(15)	−0.1033(10)	0.4525(17)
O(13)	0.4234(11)	−0.0229(8)	0.3443(17)
O(131)	0.4610(17)	−0.1176(10)	0.4367(21)
O(132)	0.5148(12)	−0.0902(11)	0.2575(24)
O(21)	0.2505(13)	0.0925(9)	0.3791(15)
O(211)	0.2437(16)	0.1911(11)	0.4770(17)
O(212)	0.1311(12)	0.1318(11)	0.4265(20)
O(22)	0.2283(10)	0.0772(9)	0.1358(15)
O(221)	0.1645(14)	0.1472(11)	0.0157(18)
O(222)	0.0969(10)	0.0957(10)	0.1540(24)
O(23)	0.3485(8)	0.1640(7)	0.2221(17)
O(231)	0.3030(12)	0.2382(11)	0.0859(21)
O(232)	0.3253(11)	0.2697(9)	0.2757(20)
C(1111)	0.2318(27)	−0.0699(23)	−0.0105(50)
C(1112)	0.1875(33)	−0.0781(25)	−0.0654(51)
C(1121)	0.4403(23)	−0.0859(17)	−0.0512(32)
C(1122)	0.4949(23)	−0.1043(20)	−0.1018(37)
C(1211)	0.1312(22)	−0.1185(19)	0.3170(52)
C(1212)	0.0792(22)	−0.1554(24)	0.2875(48)
C(1221)	0.2687(42)	−0.0586(25)	0.5190(41)
C(1222)	0.2645(41)	−0.0523(24)	0.6125(43)
C(1311)	0.4911(24)	−0.0885(17)	0.5208(31)
C(1312)	0.5041(24)	−0.1255(18)	0.6027(33)
C(1321)	0.5638(28)	−0.0475(22)	0.2445(40)
C(1322)	0.6245(24)	−0.0614(21)	0.1920(43)
C(2111)	0.3098(25)	0.1845(30)	0.5198(41)
C(2112)	0.3354(34)	0.1829(31)	0.6006(36)
C(2121)	0.1262(25)	0.0950(27)	0.5167(42)
C(2122)	0.0645(32)	0.0778(36)	0.5336(57)
C(2211)	0.1733(39)	0.1091(25)	−0.0789(40)
C(2212)	0.1184(62)	0.1075(30)	−0.1280(71)
C(2221)	0.0803(23)	0.0388(17)	0.1952(53)
C(2222)	0.0128(23)	0.0199(23)	0.1714(62)
C(2311)	0.3379(27)	0.2149(25)	−0.0017(39)
C(2312)	0.3910(32)	0.2408(29)	−0.0442(51)
C(2321)	0.3994(15)	0.2857(17)	0.2801(45)
C(2322)	0.4099(24)	0.3375(24)	0.3442(48)

Table 3 (continued)

Atom	x	y	z
C(1)	0.3702(53)	−0.2239(18)	0.3420(41)
C(2)	0.3141(29)	−0.2286(14)	0.2642(60)
C(3)	0.3406(29)	−0.2247(12)	0.1612(42)
C(4)	0.4135(35)	−0.2179(15)	0.1771(47)
C(5)	0.4304(30)	−0.2171(17)	0.2776(77)
C(6)	0.1591(21)	0.2861(16)	0.1807(50)
C(7)	0.1122(22)	0.2491(18)	0.1431(31)
C(8)	0.0806(16)	0.2288(16)	0.2308(31)
C(9)	0.1038(22)	0.2450(17)	0.3202(34)
C(10)	0.1664(23)	0.2899(18)	0.2952(48)

[a] Estimated standard deviations in parentheses.

weighting scheme was established by the observation that average values of weight F for intensity data divided into 20 equally populated groups based on magnitude of F did not differ by more than a factor of two. Final difference Fourier maps showed no intensity of interpretable level.

Results

Crystal data are listed in Table 1, positional parameters in Tables 2 and 3 for **1** and **2**, respectively, and selected bond angles and distances for both **1** and **2** in Table 6. Listings of thermal parameters in Tables 4 and 5 for **1** and **2**, respectively, the complete bond angles and distances for both **1** and **2** in Table 7, and the

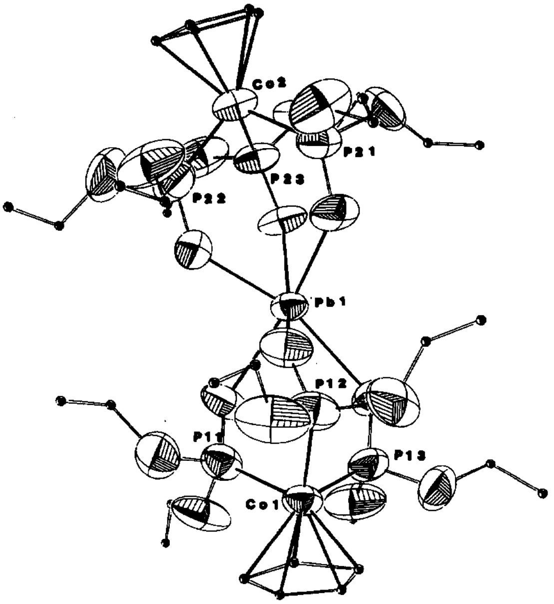

Fig. 2. $\{\eta^5\text{-}C_5H_5Co[P(OC_2H_5)_2O]_3\}_2Pb^{II}$ showing the atomic numbering for the Co and P atoms.

Table 4

Thermal parameters for $\{\eta^5\text{-}C_5H_5Co[P(OC_2H_5)_2O]_3\}_2Sn^{II}$, $C_{34}H_{70}Co_2O_{18}P_6Sn$ (1) [a]

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sn(1)	59(2)	40(2)	64(2)	0(2)	3(1)	1(2)
Co(1)	67(5)	33(4)	51(4)	0(3)	7(4)	1(3)
Co(2)	58(5)	54(4)	70(5)	−14(3)	18(4)	−18(4)
P(11)	77(12)	47(10)	48(9)	−5(8)	8(9)	−2(8)
P(12)	88(12)	58(11)	55(10)	−10(8)	13(8)	−10(9)
P(13)	93(13)	47(11)	64(11)	−14(9)	−23(9)	−8(9)
P(21)	97(13)	66(11)	65(11)	−19(10)	26(10)	6(9)
P(22)	46(11)	78(12)	74(12)	−18(9)	−11(8)	−10(9)
P(23)	56(10)	49(9)	80(10)	−24(7)	4(8)	−20(8)
O(11)	130(30)	19(21)	58(23)	−17(18)	24(21)	−10(16)
O(111)	144(42)	73(31)	107(31)	47(28)	−30(29)	34(25)
O(112)	181(39)	47(23)	50(23)	−11(23)	37(25)	5(19)
O(12)	65(24)	31(23)	96(27)	0(16)	17(20)	11(18)
O(121)	50(26)	75(27)	155(36)	−14(19)	26(24)	4(25)
O(122)	217(47)	62(28)	74(26)	27(28)	29(29)	5(23)
O(13)	131(33)	49(25)	77(26)	−5(21)	26(23)	7(19)
O(131)	154(42)	83(32)	151(42)	13(28)	−94(33)	−17(29)
O(132)	23(25)	115(33)	261(53)	−3(22)	37(29)	25(36)
O(21)	107(31)	78(27)	43(21)	−26(23)	6(20)	−43(21)
O(211)	117(39)	113(38)	114(33)	−20(29)	20(28)	−5(29)
O(212)	90(32)	225(53)	128(35)	−63(32)	70(28)	103(36)
O(22)	61(24)	74(27)	40(20)	7(20)	−19(17)	20(18)
O(221)	198(44)	104(35)	99(34)	−46(31)	12(31)	−32(28)
O(222)	27(23)	105(32)	177(40)	−6(21)	−16(23)	−24(30)
O(23)	74(27)	78(26)	88(27)	6(20)	5(21)	−2(21)
O(231)	109(30)	78(28)	100(30)	−29(23)	0(23)	−68(24)
O(232)	63(26)	80(27)	147(34)	−1(21)	39(24)	12(26)
C(1111)	162(32)					
C(1112)	260(53)					
C(1121)	92(19)					
C(1122)	114(22)					
C(2211)	108(22)					
C(1212)	111(20)					
C(1221)	110(21)					
C(1222)	185(32)					
C(1321)	107(20)					
C(1322)	156(29)					
C(1311)	113(21)					
C(1312)	129(24)					
C(2111)	142(33)					
C(2112)	204(39)					
C(2121)	170(30)					
C(2122)	217(42)					
C(2211)	151(28)					
C(2212)	273(56)					
C(2221)	118(23)					
C(2222)	190(35)					
C(2311)	149(28)					
C(2312)	174(30)					
C(2321)	86(17)					
C(2322)	181(33)					

Table 4 (continued)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	70(15)					
C(2)	59(13)					
C(3)	81(17)					
C(4)	64(14)					
C(5)	105(20)					
C(6)	81(17)					
C(7)	132(24)					
C(8)	110(21)					
C(9)	108(21)					
C(10)	104(20)					

[a] Estimated standard deviations in parentheses. Anisotropic thermal parameters in the form: $\exp[-2\pi^2(U_{11}h^2a^{\star 2} + U_{22}k^2b^{\star 2} + U_{33}l^2c^{\star 2} + 2U_{12}hka^{\star}b^{\star} + 2U_{13}hla^{\star}c^{\star} + 2U_{23}klb^{\star}c^{\star})] \times 10^3$; isotropic thermal parameters $\times 10^3$.

structure factors are available in the supplementary material. The molecular geometry and labeling schemes for **1** and **2** are given in Figs. 1 and 2, respectively.

Discussion

The 2/1 complexes of the trinuclear tripod ligand, η^5-$C_5H_5Co[P(OC_2H_5)_2O]_3$, crystallize with the tripod ligand providing tridentate coordination to the metal via ligation of the three phosphonyl oxygen atoms.

Disorder in the positions of the ethyl carbons of **1** and **2** is apparent in the associated internuclear distances and angles and in the thermal parameters. Because of the lack of observed data for **1**, refinement of carbon-atom positions was limited to positional and isotropic thermal parameters. For **2** the availability of more data allowed anisotropic refinement of all atoms. Details of structure not involving alkyl groups agree for the two complexes which crystallize in cells of identical space group symmetry and similar size and may be regarded as isostructural. Positional parameters for **1** and **2** are related by $1/2-x$, y, $1-z$.

Octahedral symmetry at the tin and lead atoms in **1** and **2**, respectively, requires linearity of the Co–M–Co system, equivalence of the M–O and M–Co distances, appropriate O_h O–M–O angles and parallel orientation of the η^5-cyclopentadienyl rings. Complexes **1** and **2** fail to meet any of these criteria.

The Co–M–Co angle is 149.04(14)° for **1** and 150.96(7)° for **2**. Each tripod ligand shows three different M–O distances. In **1** the six M–O distances lie in the range 2.24(3) to 2.83(3) Å, a difference of Δ 0.59(3) Å. The corresponding values for **2** are 2.40(2) to 2.66(2) Å (Δ 0.24(2) Å). Each ligand displays one short, one intermediate and one long M–O distance. The averages of the M–O distances are similar for **1** (2.48(3)) and **2** (2.52(2) Å).

Examination of intra- and inter-ligand O–M–O angles shows that the coordination geometry cannot be described as pentagonal bipyramidal, capped trigonal prismatic capped octahedral or trigonal base-trigonal base, common seven coordinated geometries. Intraligand O–M–O angles in the two structures are acute, 75.7(10)–79.5(7)°, whereas interligand O–M–O angles show a range, 79.5(11)–159.5(6)°. In **1** the *trans*-O–M–O angles are 157.5(10), 153.8(11) and 150.5(10)°. The corresponding angles in **2** are 159.5(6), 155.2(7) and 153.2(6)°.

Table 5

Anisotropic thermal parameters for $\{\eta^5\text{-}C_5H_5Co[P(OC_2H_5)_2O]_3\}_2Pb^{II}$, $C_{34}H_{70}Co_2O_{18}P_6Pb$ (**2**) [a]

Pb(1)	59(0)	38(0)	73(0)	4(0)	0(0)	−1(0)
Co(1)	75(2)	38(2)	68(2)	2(1)	8(2)	0(1)
Co(2)	54(2)	55(2)	94(3)	13(1)	13(2)	15(2)
P(11)	90(5)	57(5)	71(5)	−4(4)	11(4)	−2(4)
P(12)	93(6)	51(4)	100(6)	−4(4)	31(4)	1(4)
P(13)	101(6)	44(5)	98(6)	7(4)	−20(5)	2(4)
P(21)	77(5)	66(5)	83(6)	15(4)	21(4)	6(4)
P(22)	69(5)	73(5)	104(6)	7(4)	−19(4)	6(5)
P(23)	64(4)	46(4)	104(6)	9(3)	17(4)	15(4)
O(11)	140(19)	51(11)	72(13)	0(11)	32(13)	−11(9)
O(111)	149(22)	62(14)	122(19)	−19(14)	−43(16)	−7(13)
O(112)	164(21)	58(13)	106(17)	0(13)	79(16)	−9(12)
O(12)	83(13)	55(13)	115(16)	−9(10)	20(11)	−5(11)
O(121)	95(16)	63(14)	202(27)	−26(12)	53(17)	−6(15)
O(122)	213(28)	92(17)	69(15)	13(18)	57(16)	12(13)
O(13)	106(16)	48(11)	107(17)	6(11)	−33(13)	7(11)
O(131)	251(32)	65(16)	113(20)	19(18)	−94(21)	−1(15)
O(132)	65(15)	88(18)	218(29)	14(13)	17(17)	−11(18)
O(21)	159(21)	75(15)	75(14)	52(14)	44(13)	43(11)
O(211)	223(28)	90(19)	67(18)	45(18)	−3(18)	−31(14)
O(212)	96(17)	130(21)	147(22)	19(15)	38(15)	63(18)
O(22)	81(13)	76(13)	78(14)	11(10)	−15(10)	−7(11)
O(221)	169(24)	110(19)	98(18)	22(17)	−41(16)	38(15)
O(222)	50(13)	92(17)	264(32)	2(12)	−28(16)	3(19)
O(23)	51(11)	43(10)	140(18)	10(8)	8(11)	12(11)
O(231)	114(19)	118(19)	161(23)	40(15)	56(17)	73(17)
O(232)	85(14)	67(13)	174(23)	−1(12)	38(15)	−31(14)
C(1111)	171(45)	139(46)	289(69)	47(35)	120(45)	−91(45)
C(1112)	266(69)	166(51)	270(71)	21(47)	170(58)	−38(48)
C(1121)	177(39)	90(28)	153(36)	−15(26)	125(33)	−17(25)
C(1122)	135(37)	139(38)	185(44)	−1(29)	92(35)	−39(33)
C(1211)	94(32)	87(31)	422(85)	−18(25)	12(42)	−7(42)
C(1212)	92(31)	202(52)	298(70)	−68(34)	14(37)	−20(49)
C(1221)	414(99)	138(46)	100(39)	90(54)	53(53)	−20(37)
C(1222)	449(99)	103(37)	132(42)	13(52)	45(55)	−29(40)
C(1311)	194(43)	91(29)	90(28)	−29(28)	0(24)	
C(1312)	184(41)	101(31)	127(36)	−55(28)	−66(31)	40(27)
C(1321)	168(44)	123(36)	206(49)	−33(36)	96(39)	26(38)
C(1322)	118(34)	135(43)	223(55)	21(30)	27(35)	14(37)
C(2111)	149(42)	338(83)	155(51)	0(47)	−70(37)	115(54)
C(2112)	304(73)	372(87)	104(35)	220(68)	−71(41)	−71(46)
C(2121)	160(40)	247(64)	207(55)	39(41)	58(37)	154(50)
C(2122)	200(58)	347(8)	279(84)	−29(63)	119(57)	102(78)
C(2211)	391(84)	141(46)	127(41)	39(51)	155(48)	−54(35)
C(2212)	712(90)	129(54)	313(11)	−56(81)	335(21)	−15(61)
C(2221)	149(36)	45(27)	435(89)	−11(25)	−18(45)	37(38)
C(2222)	99(31)	164(50)	507(11)	−87(32)	−9(47)	−54(58)
C(2311)	165(44)	207(56)	151(43)	84(41)	56(35)	7(39)
C(2312)	195(56)	231(65)	259(70)	22(47)	166(54)	76(53)
C(2321)	42(18)	83(28)	346(67)	−12(17)	−12(27)	25(35)
C(2322)	117(38)	158(47)	307(72)	−46(34)	−37(40)	109(48)

Table 5 (continued)

C(1)	358(2)	21(22)	107(39)	−9(39)	−15(50)	9(21)
C(2)	214(55)	14(15)	242(63)	−34(23)	177(54)	−40(27)
C(3)	122(34)	10(15)	230(56)	−7(18)	−21(37)	−20(20)
C(4)	178(51)	24(20)	162(47)	29(24)	21(40)	−19(26)
C(5)	131(43)	20(20)	285(87)	27(23)	−59(52)	14(39)
C(6)	74(27)	50(23)	307(71)	22(19)	0(39)	37(35)
C(7)	154(35)	143(35)	129(33)	124(30)	14(27)	31(27)
C(8)	76(22)	112(29)	176(37)	80(21)	37(23)	−28(25)
C(9)	146(36)	108(30)	174(40)	104(28)	30(30)	4(28)
C(10)	112(31)	76(29)	324(68)	80(25)	145(43)	115(38)

[a] Estimated standard deviations in parentheses. Anisotropic thermal parameters in the form: $\exp[-2\pi^2(U_{11}h^2a^{\star 2} + U_{22}k^2b^{\star 2} + U_{33}l^2c^{\star 2} + 2U_{12}hka^{\star}b^{\star} + 2U_{13}hla^{\star}c^{\star} + 2U_{23}klb^{\star}c^{\star})] \times 10^3$.

The planes of the η^5-cyclopentadienyl rings are not parallel (angle between planes of rings in **1**, 43.23°; in **2**, 43.24°). The non-bonded distances between the terminal cobalt atoms are 8.745(8) for **1** and 8.78(4) Å for **2**, with the individual M–Co distances in **1** being 4.366(8) and 4.379(8) and, in **2** 4.392(4) and 4.397(4) Å.

The tilting of the cyclopentadienyl rings along with the observed interligand angles and distribution of the short M–O bonds suggests the existence of the lone

Table 6

Selected bond angles (°) and distances (Å) for $\{\eta^5\text{-}C_5H_5Co[P(OC_2H_5)_2O]_3\}_2M^{II}$, $C_{34}H_{70}Co_2O_{18}P_6M$ [a]

	1 (M = Sn)	**2** (M = Pb)
M–O(11)	2.40(3)	2.51(2)
M–O(12)	2.24(3)	2.40(2)
M–O(13)	2.69(3)	2.64(2)
M–O(21)	2.40(3)	2.46(2)
M–O(22)	2.32(3)	2.41(2)
M–O(23)	2.83(3)	2.66(2)
O(11)–M–O(12)	78.0(11)	77.3(6)
O(11)–M–O(13)	76.0(10)	76.9(6)
O(11)–M–O(21)	153.8(11)	155.2(7)
O(11)–M–O(22)	87.6(11)	85.1(6)
O(11)–M–O(23)	122.3(10)	120.4(6)
O(12)–M–O(13)	77.4(10)	78.8(6)
O(12)–M–O(21)	79.5(11)	80.8(7)
O(12)–M–O(22)	84.2(11)	85.1(6)
O(12)–M–O(23)	150.5(10)	153.2(6)
O(13)–M–O(21)	111.9(10)	110.0(7)
O(13)–M–O(22)	157.5(10)	159.5(6)
O(13)–M–O(23)	125.5(9)	122.8(5)
O(21)–M–O(22)	76.8(10)	79.5(7)
O(21)–M–O(23)	75.7(10)	76.8(6)
O(22)–M–O(23)	76.3(10)	76.4(6)
Co(1)–M	4.366(8)	4.392(4)
Co(2)–M	4.379(8)	4.397(4)
Co(1)–M–Co(2)	149.04(14)	150.96(7)

[a] Estimated standard deviations in parentheses.

Table 7

Bond angles (°) and distances (Å) for $\{\eta^5\text{-}C_5H_5Co[P(OC_2H_5)_2O]_3\}_2M^{II}$, $C_{34}H_{70}Co_2O_{18}P_6M$ [a]

	1 (M = Sn)	2 (M = Pb)		1 (M = Sn)	2 (M = Pb)
Bond lengths			O(112)–C(1121)	1.38(7)	1.35(5)
M–O(11)	2.40(3)	2.51(2)	O(121)–C(1211)	1.38(7)	1.41(5)
M–O(12)	2.24(3)	2.40(2)	O(122)–C(1221)	1.39(8)	1.35(6)
M–O(13)	2.69(3)	2.64(2)	O(131)–C(1311)	1.32(8)	1.36(5)
M–O(21)	2.40(3)	2.46(2)	O(132)–C(1321)	1.38(8)	1.34(6)
M–O(22)	2.32(3)	2.41(2)	O(211)–C(2111)	1.32(10)	1.34(6)
M–O(23)	2.83(3)	2.66(2)	O(212)–C(2121)	1.46(9)	1.42(6)
			O(221)–C(2211)	1.51(9)	1.49(6)
O(11)–M–O(12)	78.0(11)	77.3(6)	O(222)–C(2221)	1.42(8)	1.42(5)
O(11)–M–O(13)	76.0(10)	76.9(6)	O(231)–C(2311)	1.46(8)	1.41(6)
O(11)–M–O(21)	153.8(11)	155.2(7)	O(232)–C(2321)	1.42(6)	1.44(4)
O(11)–M–O(22)	87.6(11)	85.1(6)	C(1111)–C(1112)	1.11(14)	1.08(8)
O(11)–M–O(23)	122.3(10)	120.4(6)	C(1121)–C(1122)	1.47(9)	1.30(6)
O(12)–M–O(13)	77.4(10)	78.8(6)	C(1211)–C(1212)	1.44(9)	1.32(6)
O(12)–M–O(21)	79.5(11)	80.8(7)	C(1221)–C(1222)	1.46(10)	1.20(8)
O(12)–M–O(22)	84.2(11)	85.1(6)	C(1311)–C(1312)	1.59(9)	1.34(6)
O(12)–M–O(23)	150.5(10)	153.2(6)	C(1321)–C(1322)	1.46(9)	1.38(7)
O(13)–M–O(21)	111.9(10)	110.0(7)	C(2111)–C(2112)	1.32(13)	1.12(7)
O(13)–M–O(22)	157.5(10)	159.5(6)	C(2121)–C(2122)	1.42(13)	1.25(8)
O(13)–M–O(23)	125.5(9)	122.8(5)	C(2211)–C(2212)	1.32(13)	1.25(8)
O(21)–M–O(22)	76.8(10)	79.5(7)	C(2221)–C(2222)	1.46(11)	1.36(6)
O(21)–M–O(23)	75.7(10)	76.8(6)	C(2311)–C(2312)	1.50(11)	1.29(8)
O(22)–M–O(23)	76.3(10)	76.4(6)	C(2321)–C(2322)	1.51(10)	1.43(7)
			C(1)–C(2)	1.44(6)	1.42(10)
P(11)–O(11)	1.47(3)	1.62(2)	C(2)–C(3)	1.40(7)	1.42(9)
P(12)–O(12)	1.52(3)	1.50(2)	C(3)–C(4)	1.32(7)	1.38(8)
P(13)–O(13)	1.44(4)	1.48(2)	C(4)–C(5)	1.44(7)	1.30(11)
P(21)–O(21)	1.45(4)	1.51(2)	C(5)–C(1)	1.42(8)	1.43(11)
P(22)–O(22)	1.44(3)	1.47(2)	C(6)–C(7)	1.41(9)	1.29(6)
P(23)–O(23)	1.44(3)	1.48(2)	C(7)–C(8)	1.35(10)	1.36(6)
Co(1)–P(11)	2.19(1)	2.170(9)	C(8)–C(9)	1.26(9)	1.25(6)
Co(1)–P(12)	2.18(2)	2.173(10)	C(9)–C(10)	1.57(9)	1.59(6)
Co(1)–P(13)	2.18(2)	2.180(9)	C(10)–C(6)	1.38(8)	1.46(9)
Co(2)–P(21)	2.17(2)	2.161(9)			
Co(2)–P(22)	2.16(2)	2.184(10)	*Bond angles*		
Co(2)–P(23)	2.18(2)	2.165(8)	P(11)–Co(1)–P(12)	90.0(6)	92.7(3)
Co(1)–C(1)	2.14(5)	2.09(4)	P(11)–Co(1)–P(13)	91.6(6)	92.8(3)
Co(1)–C(2)	2.12(4)	2.06(4)	P(12)–Co(1)–P(13)	90.6(6)	91.2(4)
Co(1)–C(3)	2.11(5)	2.11(4)	P(21)–Co(2)–P(22)	92.3(6)	92.9(4)
Co(1)–C(4)	2.10(5)	2.09(5)	P(21)–Co(2)–P(23)	93.7(6)	93.4(3)
Co(1)–C(5)	2.13(6)	2.05(5)	P(22)–Co(2)–P(23)	93.1(6)	92.2(3)
Co(2)–C(6)	2.09(6)	2.05(4)	Co(1)–P(11)–O(11)	122(1)	124.0(8)
Co(2)–C(7)	2.04(7)	2.08(4)	Co(1)–P(12)–O(12)	121(1)	119.4(9)
Co(2)–C(8)	2.01(6)	2.06(3)	Co(1)–P(13)–O(13)	120(2)	121.5(9)
Co(2)–C(9)	2.03(7)	2.10(4)	Co(2)–P(21)–O(21)	122(1)	124.5(9)
Co(2)–C(10)	2.04(6)	2.11(4)	Co(2)–P(22)–O(22)	123(1)	122.4(9)
P(11)–O(111)	1.62(4)	1.64(3)	Co(2)–P(23)–O(23)	120(2)	121.5(8)
P(11)–O(112)	1.59(4)	1.60(2)	P(11)–O(11)–M	133(2)	128(1)
P(12)–O(121)	1.64(4)	1.64(2)	P(12)–O(12)–M	134(2)	132(1)
P(12)–O(122)	1.56(4)	1.65(2)	P(13)–O(13)–M	130(2)	130(1)
P(13)–O(131)	1.62(4)	1.62(3)	P(21)–O(21)–M	137(2)	132(1)
P(13)–O(132)	1.63(4)	1.67(3)	P(22)–O(22)–M	139(2)	136(1)
P(21)–O(211)	1.51(4)	1.68(2)	P(23)–C(23)–M	129(2)	131(1)

Table 7 (continued)

	1 (M = Sn)	**2** (M = Pb)		**1** (M = Sn)	**2** (M = Pb)
P(21)–O(212)	1.62(4)	1.64(2)			
P(22)–O(221)	1.61(2)	1.61(3)	Co(1)–M	4.366(8)	4.392(4)
P(22)–O(222)	1.56(4)	1.62(2)	Co(2)–M	4.379(8)	4.397(4)
P(23)–O(231)	1.58(4)	1.62(3)			
O(111)–C(111)	1.52(9)	1.40(6)	Co(1)–M–Co(2)	149.04(14)	150.96(7)

[a] Estimated standard deviations in parentheses.

pair slightly displaced from the O(23)–M–O(13) plane and *trans* to a vector between the M–O(22) and M–O(12) bonds. This is consistent with the expectations that the presence of the tightly held lone pair will require more space in the coordination sphere than bonding electrons and that the bonds *trans* to the lone pair will be shortened. Examination of Table 6 reveals the O(13)–Sn–O(23) angle to be the largest of the non-*trans* angles at 125.5(9)° and the distances d(Sn–O(23)) and d(Sn–O(13)) to be the longest and next longest such distances in the molecule at 2.83(3) and 2.69(3) Å, respectively.

The situation for the more symmetrical **2** is similar. Here the O(13)–Pb–O(23) angle seems closest to the location of the lone pair, and its value of 122.8(5)° is larger than any other non-*trans*-angle. Likewise, the d(Pb–O(23)) and d(Pb–O(13)) distances are the longest and next longest ones in the molecule at 2.66(2) and 2.64(2) Å, respectively.

Solid-state structures for two homologues of the title compounds are available in which M = Co and Cu [18]. The former contains two crystallographically independent molecules in a crystal which suffers from disorder of the phosphonate $O{=}P(OCH_3)_2$ groups and librations of the η^5-C_5H_5 rings. The geometry about the central Co atom is O_h within the limits of the disorder, occupancy factors and experimental error. The latter, has the Cu atom on a center of symmetry in each of the two independent molecules in the unit cell. Unusually high temperature factors, especially for carbon and oxygen atoms of the ethoxy groups, indicate disorder. In both the M = Co and Cu structures the two cyclopentadienyl rings are parallel, with the Co–M–Co axes linear, and the two terminal Co atoms equivalent. The M = Cu complex exhibits small deviations from regular O_h symmetry, with the coordination at the Cu best described as 4 + 2. The electronic spectrum corroborates the lowered CuO_6 symmetry. Both complexes undergo reversible phase transitions below room temperature (M = Co, 228 K; M = Cu, 204 K) and $\Delta H = 10.7$ and 8.57 kJ mol^{-1}, respectively. The M = Pb analogue (**2**) shows small irregularities in the heat capacity, C_p, at 200–250 K, possibly a second-order transition [18].

The 2/1 complexes of the trinuclear tripod ligand with divalent ions are the analogues of a $(C_7H_{13})_2E$ hydrocarbon (where E is a divalent cation) derivative, heterospirobicyclo[2.2.2]octane, which presumably would adopt the O_h geometry at E if that element is neither subject to Jahn–Teller distortion nor is a subvalent, main-group atom. It is interesting that this organic molecule exhibits the same kind of temperature-dependent flexibility [23].

A wide range of hexanitro complexes of the first-row transition metal ions of the general formula $M_2PbM'(NO_2)_6$ where M = K, Rb, Cs, Tl and M′ = Co, Ni, Cu crystallize in the cubic $Fm3$ phase with both the $M'(NO_2)_6$ and Pb^{II} ions with m^3

symmetry (T_h). The lead(II) atom is at the center of the 12 nitrito oxygen atoms in cubic symmetry. The powder ESR spectra consist of single isotropic lines as expected. These materials undergo reversible phase transitions at low temperature to less-symmetrical forms which give anisotropic ESR spectra [2,24].

There are no known symmetrical tin(II)-oxygen polyhedra [2].

Thus it is possible that the title compounds could undergo a phase transition below their melting points, e.g., at $\leqslant 160\,^\circ\mathrm{C}$ for $M = Sn$ [6], to yield more symmetrical forms than those studied here [2].

Supplementary material available. Tables S1 and S2 containing the structure factors for **1** (46 pages) and **2** (67 pages) may be obtained from the authors.

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