Synthesis of palladium-tin carbonylphosphine clusters and X-ray study of the $Pd_3Sn_2(acac)_4(CO)_2(PPh_3)_3$ cluster

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(Received January 20th, 1987)

Abstract

It has been shown for the first time that the reaction of bi-valent tin acetylacetonate with palladium carbonylphosphine clusters, $Pd_4(CO)_5(PPh_3)_4$ (I), $Pd_4(CO)_5(PEt_3)_4$ (II) and $Pd_3(CO)_3(PPh_3)_4$ (III), results in the formation of heterometal pentanuclear clusters of general formula $Pd_3Sn_2(acac)_4(CO)_2(PR_3)_3$; R = Ph (IV), Et (V). X-ray analysis of $Pd_3Sn_2(acac)_4(CO)_2(PPh_3)_3$ at 20°C (λ(Mo), 4396 reflections, space group $P2_1/n$, $Z = 4$, $R = 0.037$) shows that IV in the form of the crystalline hydrate, $Pd_3Sn_2(acac)_4(CO)_2(PPh_3)_3 \cdot xH_2O$ ($x \sim 1$), contains a distorted "propeller"-shaped Pd_3Sn_2 metal frame with Pd–Sn distances of 2.679–2.721(1) Å; two short Pd–Pd bonds, 2.708 and 2.720(1) Å, bridged by μ_2-CO ligands, and an elongated central Pd(1)–Pd(2) bond of 2.798 Å. Sn atoms have distorted octahedral coordination, the dihedral angles formed by Pd_3 moieties and two Pd_2Sn triangles are 127.6 and 106.5°; and the angle between Pd_2Sn moieties is 126.0°.

Results and discussion

Heteronuclear clusters can be obtained from palladium carbonylphosphine clusters under mild conditions in two ways. The first is by replacing the $Pd(CO)_nL$ group with low-valent moieties and the second, is by addition of post-transition metal atoms to the metal frame. These methods have been used previously to obtain mercury clusters as in the polyhedra: $Pd_6Hg(CO)_6(PEt_3)_6$ [1] and $Pd_4Hg_2Br_2(\mu_2\text{-}CO)_4(PEt_3)_4$ [2]. The first compound probably has a sandwich structure similar to that of $Pt_6Hg_2(\mu_2\text{-}CO)_6(PPhPr^i_2)_6$ [3]. Addition of HgBr moieties to the "butterfly"-shaped $Pd_4(\mu_2\text{-}CO)_5(PEt_3)_4$ cluster, results in the formation of a second cluster, by formal iso-electron substitution of a carbonyl ligand [2]. We applied this

method to the synthesis of mixed tin-containing clusters by reaction of $Sn(acac)_2$ with tetranuclear carbonylphosphine clusters $Pd_4(\mu_2\text{-}CO)_4(PPh_3)_4$ (I), $Pd_4(\mu_2\text{-}CO)_5(PEt_3)_4$ (II) and trinuclear $Pd_3(\mu_2\text{-}CO)_3(PPh_3)_4$ (III). For X-ray studies of clusters I and III, see ref. 4.

The reaction of $Sn(acac)_2$ with tetranuclear clusters I and II in Pd/Sn molar ratios of 1/4 and 1/2.7, leads to the heteronuclear palladium-tin clusters IV and V, under mild conditions. Cluster IV was also obtained by treating suspension III with a three-fold excess of $Sn(acac)_2$.

Compounds IV and V are sensitive to moisture and are unstable in solution. Their IR spectra show only the absorption bands of the CO bridges at 1890–1770 cm^{-1}. The $^{31}P\{^1H\}$ NMR spectrum of cluster IV indicates the presence of two kinds of PPh_3 ligands in the molecule, with an intensity ratio of 2/1 (29.4 and 37.5 ppm corresponding to H_3PO_4).

Spectral and analytical data confirm the structure of cluster IV as revealed by X-ray analysis.

Bond lengths in molecule IV are listed in Table 1, relevant valence angles are listed in Table 2, and the mean square planes of the most important planar moieties are summarized in Table 3. Molecule IV is depicted in Fig. 1 (phenyl substituents omitted). The heteronuclear metal frame of cluster IV is composed of three triangles $(Pd_3, Pd_2Sn(1)$ and $Pd_2Sn(2))$ with a mutual Pd(1)–Pd(2) edge. There are two short Pd–Pd bonds in IV viz. Pd(1)–Pd(3) 2.720(1) and Pd(2)–Pd(3) 2.708(1) Å, the Pd atoms are linked by slightly asymmetrical CO bridges, and resemble Pd–Pd bonds in $Pd_4Hg_2Br_2(\mu_2\text{-}CO)_4(PEt_3)_4$ of 2.687 and 2.702(1) Å [2]. A comparatively longer, central Pd(1)–Pd(2) bond, bridged by two $Sn(acac)_2$ moieties, is 2.798 Å in length. Pd–P bond of lengths between 2.291 and 2.299(3), and Pd–C bonds of lengths between 2.02 and 2.11(1) Å are common to polynuclear palladium carbonylphosphine derivatives. Elongation of the bond between the two transition metal atoms, which together with the post-transition (non-transition) metal atom form the triangle, has been observed in the trinuclear tin-cobalt complex $(acac)_2SnCo_2(CO)_6(\mu_2\text{-}CO)$, where the Co–Co distance is 2.626 compared with the more typical range of 2.4–2.5 Å [6] and in the mercury-palladium cluster $Pd_4Hg_2Br_2(\mu_2\text{-}CO)_4(PEt_3)_4$, where the central Pd–Pd edge is elongated to 3.015 Å [2]. The triangular Pd_3 moiety contains 44 valence electrons (on the assumption that the Pd–Sn bonds are two-centered bi-electronic), and is therefore isoelectronic to trinuclear cluster III, where the Pd–Pd distances vary from 2.668 to 2.777 Å [4]. Synthesis of IV from I occurs as formal substitution of the $Pd(CO)_2L$ group and one CO ligand by two $Sn(acac)_2$ molecules. On the other hand, synthesis of IV from III corresponds to formal isoelectronic substitution of a CO ligand and a PPh_3 ligand for two $\mu_2\text{-}Sn(acac)_2$ groups; this proposal is confirmed by the presence of an anomalous weakly-bonded PPh_3 ligand with a Pd–P distance 2.485 Å in III, determined from X-ray analysis.

Pd–Sn bond lengths in IV 2.679–2.721 and 2.697 (av.), Å are somewhat shorter than the sum of Pd and Sn atomic radii, which should be 2.74 Å [7], although they are fairly consistent with changes in these radii in tin-containing complexes of other metals; Co–Sn separations of 2.564 and 2.591 Å (2.578 av.) in $(acac)_2SnCo_2(CO)_7$ [6] (Co radius is 0.12 Å shorter than that of Pd), and the Os–Sn bond of 2.645 Å, which has no μ_3-H ligand, in $Os_3(CO)_{10}H_2Sn[CH(SiMe_3)_2]_2$ (Os radius is 0.03 Å smaller than that of Pd) [8]. Sn(1) and Sn(2) atoms in IV have a distorted octahedral coordination and comprises Pd(1), Pd(2) and four O atoms from corresponding

Table 1

Bond lengths in I d (Å)

Sn(1)–Pd(1)	2.679(1)	P(3)–C(321)	1.85(1)	C(112)–C(113)	1.41(2)
Sn(1)–Pd(2)	2.687(1)	P(3)–C(331)	1.80(1)	C(113)–C(114)	1.36(2)
Sn(1)–O(3)	2.213(8)	O(1)–C(1)	1.19(2)	C(114)–C(15)	1.37(2)
Sn(1)–O(4)	2.098(8)	O(2)–C(2)	1.15(1)	C(115)–C(16)	1.41(2)
Sn(1)–O(5)	2.111(9)	O(3)–C(3)	1.26(1)	C(121)–C(122)	1.38(2)
Sn(1)–O(6)	2.278(9)	O(4)–C(5)	1.28(2)	C(121)–C(126)	1.38(2)
Sn(2)–Pd(1)	2.721(1)	O(5)–C(8)	1.27(2)	C(122)–C(123)	1.40(2)
Sn(2)–Pd(2)	2.699(1)	O(6)–C(10)	1.32(2)	C(123)–C(124)	1.33(2)
Sn(2)–Pd(3)	3.722(1)	O(7)–C(13)	1.22(1)	C(124)–C(125)	1.37(2)
Sn(2)–O(7)	2.095(7)	O(8)–C(15)	1.24(1)	C(125)–C(126)	1.38(2)
Sn(2)–O(8)	2.271(8)	O(9)–C(18)	1.20(1)	C(131)–C(132)	1.40(2)
Sn(2)–O(9)	2.126(8)	O(10)–C(20)	1.25(1)	C(131)–C(136)	1.39(2)
Sn(2)–O(10)	2.241(8)	C(3)–C(4)	1.40(2)	C(132)–C(133)	1.38(2)
Pd(1)–Pd(2)	2.798(1)	C(3)–C(6)	1.49(2)	C(133)–C(134)	1.36(2)
Pd(1)–Pd(3)	2.720(1)	C(4)–C(5)	1.36(2)	C(134)–C(135)	1.35(2)
Pd(1)–P(1)	2.295(3)	C(5)–C(7)	1.55(2)	C(135)–C(136)	1.36(2)
Pd(1)–C(1)	2.08(1)	C(8)–C(9)	1.36(2)	C(211)–C(212)	1.38(2)
Pd(2)–Pd(3)	2.708(1)	C(8)–C(11)	1.45(2)	C(211)–C(216)	1.42(2)
Pd(2)–P(2)	2.291(3)	C(9)–C(10)	1.29(2)	C(212)–C(213)	1.39(2)
Pd(2)–C(2)	2.11(1)	C(10)–C(12)	1.52(2)	C(213)–C(214)	1.37(2)
Pd(3)–P(3)	2.299(3)	C(13)–C(14)	1.42(2)	C(214)–C(215)	1.37(2)
Pd(3)–C(1)	2.02(1)	C(13)–C(16)	1.52(2)	C(215)–C(216)	1.38(2)
Pd(3)–C(2)	2.05(1)	C(14)–C(15)	1.42(2)	C(221)–C(222)	1.38(2)
P(1)–C(111)	1.82(1)	C(15)–C(17)	1.50(2)	C(221)–C(226)	1.39(2)
P(1)–C(121)	1.84(1)	C(18)–C(19)	1.35(2)	C(222)–C(223)	1.41(2)
P(1)–C(131)	1.83(1)	C(18)–C(21)	1.49(2)	C(223)–C(224)	1.36(2)
P(2)–C(211)	1.85(1)	C(19)–C(20)	1.40(2)	C(224)–C(225)	1.36(2)
P(2)–C(221)	1.82(1)	C(20)–C(22)	1.53(2)	C(225)–C(226)	1.39(2)
P(2)–C(231)	1.83(1)	C(111)–C(112)	1.41(2)	C(231)–C(232)	1.37(2)
P(3)–C(311)	1.85(1)	C(111)–C(116)	1.39(2)	C(231)–C(236)	1.37(2)
C(232)–C(233)	1.39(2)	C(314)–C(315)	1.34(2)	C(325)–C(326)	1.39(2)
C(233)–C(234)	1.34(2)	C(315)–C(316)	1.37(2)	C(331)–C(332)	1.40(2)
C(234)–C(235)	1.38(2)	C(321)–C(322)	1.38(2)	C(331)–C(336)	1.40(2)
C(235)–C(236)	1.38(2)	C(321)–C(326)	1.41(2)	C(332)–C(333)	1.36(2)
C(311)–C(312)	1.36(2)	C(322)–C(323)	1.38(2)	C(333)–C(334)	1.36(3)
C(311)–C(316)	1.35(2)	C(323)–C(324)	1.39(2)	C(334)–C(335)	1.41(2)
C(312)–C(313)	1.36(2)	C(324)–C(325)	1.32(2)	C(335)–C(336)	1.39(2)
C(313)–C(314)	1.36(2)				

acetylacetonate ligands. The range of bond lengths in IV is somewhat broader for Sn–O bonds 2.095–2.278 Å, than that observed in other bis-acetylacetonate tin derivatives: *trans*-(acac)$_2$SnMe$_2$ (2.18 and 2.20 Å [9]); (acac)$_2$SnCl$_2$ (2.10–2.14 Å [10]) and (acac)$_2$SnCo$_2$(CO)$_7$ (2.09–2.15 Å [6]). The configuration of acac ligands in IV closely resembles that found in the latter complex, the Sn–O bonds, which are *trans* to each other, are elongated in IV (2.213–2.278 Å), analogously to the Sn and Co derivatives, as compared to the other bonds (2.095–2.126 Å), although in IV this elongation is much more obvious. Three chelating fragments of acetylacetonate ligands in IV are planar within 0.04 Å (fragments **A**, **C**, **D** in Fig. 1), Sn atoms deviate from their respective mean square planes by 0.30–0.42 Å. The fourth acac-ligand (fragment **B** at the Sn(1) atom in Fig. 1) is more distorted: deviation of

Table 2

Bond angles in IV ($^\circ$)

Pd(1)Sn(1)Pd(2)	62.87(3)	O(7)Sn(2)O(8)	81.2(3)	Pd(1)Pd(2)Pd(3)	59.17(3)
Pd(1)Sn(1)O(3)	110.3(2)	O(7)Sn(2)O(9)	89.5(3)	Pd(1)Pd(2)P(2)	155.20(9)
Pd(1)Sn(1)O(4)	163.8(2)	O(7)Sn(2)O(10)	78.2(3)	Pd(1)Pd(2)C(2)	106.8(3)
Pd(1)Sn(1)O(5)	105.7(2)	O(8)Sn(2)O(9)	75.1(3)	Pd(3)Pd(2)P(2)	145.48(9)
Pd(1)Sn(1)O(6)	93.9(2)	O(8)Sn(2)O(10)	148.2(3)	Pd(3)Pd(2)C(2)	43.4(3)
Pd(2)Sn(1)O(3)	113.2(2)	O(9)Sn(2)O(10)	80.7(3)	P(2)Pd(2)C(2)	97.9(3)
Pd(2)Sn(1)O(4)	102.6(2)	Sn(1)Pd(1)Sn(2)	99.03(4)		
Pd(2)Sn(1)O(5)	166.2(3)	Sn(1)Pd(1)Pd(2)	58.69(3)		
Pd(2)Sn(1)O(6)	92.3(2)	Sn(1)Pd(1)Pd(3)	100.12(4)		
O(3)Sn(1)O(4)	81.2(3)	Sn(1)Pd(1)P(1)	113.30(9)		
O(3)Sn(1)O(5)	77.3(3)	Sn(1)Pd(1)C(1)	120.4(3)		
O(3)Sn(1)O(6)	150.6(3)	Sn(2)Pd(1)Pd(2)	58.53(3)	Pd(1)Pd(3)Pd(2)	62.07(3)
O(4)Sn(1)O(5)	87.6(3)	Sn(2)Pd(1)Pd(3)	86.32(4)	Pd(1)Pd(3)P(3)	145.93(9)
O(4)Sn(1)O(6)	79.0(3)	Sn(2)Pd(1)P(1)	103.90(8)	Pd(1)Pd(3)C(1)	49.3(3)
O(5)sn(1)O(6)	80.4(3)	Sn(2)Pd(1)C(1)	120.9(3)	Pd(1)Pd(3)C(2)	111.6(3)
Pd(1)Sn(2)Pd(2)	61.16(3)	Pd(2)Pd(1)Pd(3)	58.76(3)	Pd(2)Pd(3)P(3)	147.86(9)
		Pd(2)Pd(1)P(1)	155.46(9)	Pd(2)Pd(3)C(1)	110.1(3)
Pd(1)Sn(2)O(7)	164.4(2)	Pd(2)Pd(1)C(1)	105.1(3)	Pd(2)Pd(3)C(2)	50.3(3)
Pd(1)Sn(2)O(8)	93.8(2)	Pd(3)Pd(1)P(1)	142.52(9)	P(3)Pd(3)C(1)	101.4(3)
Pd(1)Sn(2)O(9)	103.6(2)	Pd(3)Pd(1)C(1)	47.5(3)	P(3)Pd(3)C(2)	101.7(4)
Pd(1)Sn(2)O(10)	111.9(2)	P(1)Pd(1)C(1)	98.8(3)	C(1)Pd(3)C(2)	152.5(5)
		Sn(1)Pd(2)Sn(2)	99.40(4)	Pd(1)P(1)C(111)	119.3(4)
Pd(2)Sn(2)O(7)	104.2(2)	Sn(1)Pd(2)Pd(1)	58.44(3)	Pd(1)P(1)C(121)	119.2(4)
Pd(2)Sn(2)O(8)	102.0(2)	Sn(1)Pd(2)Pd(3)	100.23(4)	Pd(1)P(1)C(131)	115.6(4)
Pd(2)Sn(2)O(9)	165.5(2)	Sn(1)Pd(2)P(2)	106.51(9)	C(111)P(1)C(121)	101.6(5)
Pd(2)Sn(2)O(10)	106.5(2)	Sn(1)Pd(2)C(2)	123.1(3)	C(111)P(1)C(131)	102.7(5)
		Sn(2)Pd(2)Pd(1)	59.30(3)	C(121)P(1)C(131)	99.7(5)
		Sn(2)Pd(2)Pd(3)	86.99(4)	Pd(2)P(2)C(211)	112.7(4)
		Sn(2)Pd(2)P(2)	109.27(9)	Pd(2)P(2)C(221)	114.5(4)
		Sn(2)Pd(2)C(2)	119.8(3)	Pd(2)P(2)C(231)	121.2(4)
C(211)P(2)C(221)	102.6(5)	Pd(1)C(1)Pd(3)	83.2(4)	O(6)C(10)C(9)	125(1)
C(211)P(2)C(231)	101.7(5)	Pd(1)C(1)O(1)	134.8(9)	O(6)C(10)C(12)	110(1)
C(221)P(2)C(231)	101.7(5)	Pd(3)C(1)O(1)	140.7(9)	C(9)C(10)C(12)	124(2)
Pd(3)P(3)C(311)	116.0(4)	Pd(2)C(2)Pd(3)	81.3(4)	C(7)C(13)C(14)	127(1)
Pd(3)P(3)C(321)	114.6(4)	Pd(2)C(2)O(2)	136(1)	O(7)C(13)C(16)	117(1)
Pd(3)P(3)C(331)	115.7(4)	Pd(3)C(2)O(2)	142(1)	C(14)C(13)C(16)	116(1)
C(311)P(3)C(321)	103.7(5)	O(3)C(3)C(4)	124(1)	C(13)C(14)C(15)	125(1)
C(311)P(3)C(331)	103.4(6)	O(3)C(3)C(6)	115(1)	O(8)C(15)C(14)	122(1)
C(321)P(3)C(331)	101.5(6)	C(4)C(3)C(6)	121(1)	O(8)C(15)C(17)	119(1)
Sn(1)O(3)C(3)	129.7(8)	C(3)C(4)C(5)	126(1)	C(14)C(15)C(17)	118(1)
Sn(1)O(4)C(5)	131.1(9)	O(4)C(5)C(4)	126(1)	O(9)C(18)C(19)	124(1)
Sn(1)O(5)C(8)	131.5(9)	O(4)C(5)C(7)	114(1)	O(9)C(18)C(21)	115(1)
Sn(1)O(6)C(10)	123.3(9)	C(4)C(5)C(7)	120(1)	C(19)C(18)C(21)	122(1)
Sn(2)O(7)C(13)	131.0(8)	O(5)C(8)C(9)	123(1)	C(18)C(19)C(20)	127(1)
Sn(2)O(8)C(15)	128.6(8)	O(5)C(8)C(11)	115(1)	O(10)C(20)C(19)	126(1)
Sn(2)O(9)C(18)	132.9(8)	C(9)C(8)C(11)	122(1)	O(10)C(20)C(22)	116(1)
Sn(2)O(10)C(20)	128.2(8)	C(8)C(9)C(10)	130(2)	C(19)C(20)C(22)	119(1)

C and O atoms from mean square plane can be as large as 0.07 Å, while the Sn(1) atom deviates by as much as 0.57 Å. The values of the dihedral angles formed by the planes of acac-ligands and triangular Pd_2Sn moieties (Table 3) also point to

Table 3

Mean square planes in IV

Plane [a]	Coefficients of plane equations $Ax + By + Cz + D = 0$				Atom deviation from the plane (Å)
	A	B	C	D	
I	−0.7731	−0.5324	−0.3448	−8.3667	Pd(1) (0); Pd(2) (0); Pd(3) (0); P(1) [b] (−0.40); P(2) [b] (−0.09); P(3) (−0.48)
II	0.5180	0.7058	−0.4833	−2.0036	Pd(1) (0); Pd(2) (0); Sn(1) (0); P(1) [b] (0.93), P(2) [b] (0.81); O(4) [b] (−0.27), O(5) [b] (−0.29)
III	−0.1625	0.3104	−0.9366	−10.96	Pd(1) (0); Pd(2) (0); Sn(2) (0); P(1) [b] (0.71); P(2) [b] (0.89); O(7) [b] (−0.29); O(9) [b] (−0.11)
IV	0.9851	−0.1499	−0.0847	0.3287	O(3) (0.02); O(4) (−0.03); C(3) (−0.01); C(4) (−0.02); C(5) (0.04); Sn(1) [b] (−0.33); C(6) [b] (0.01); C(7) [b] (0.13)
V	−0.2266	−0.6215	−0.7499	−9.7982	O(5) (−0.04); O(6) (0.02); C(8) (0.07); C(9) (−0.04), C(10) (0.00); Sn(1) [b] (−0.57), C(11) [b] (0.20); C(12) [b] (−0.11)
VI	−0.1287	0.9897	−0.0628	3.3029	O(7) (0.00); O(8) (−0.01), C(13) (0.01), C(14) (−0.02);C(15) (0.02), Sn(2) [b] (0.42), C(16) [b] (−0.02), C(17) [b] (0.10)
VII	−0.9285	0.3164	−0.1946	−4.7237	O(9) (−0.01); O(10) (0.00), C(18) (0.02); C(19) (−0.02) C(20) (0.01); Sn(2) [b] (−0.30); C(21) [b] (0.09), C(22) [b] (0.03)

[a] Dihedral angles (°). I/II 127.6, I/III 106.5, II/III 126.0, II/IV 63.6, II/V 101.2, III/VI 67.2, III/VII 64.6, IV/V 93.8, VI/VII 63.6. [b] Ignored in mean square plane calculations.
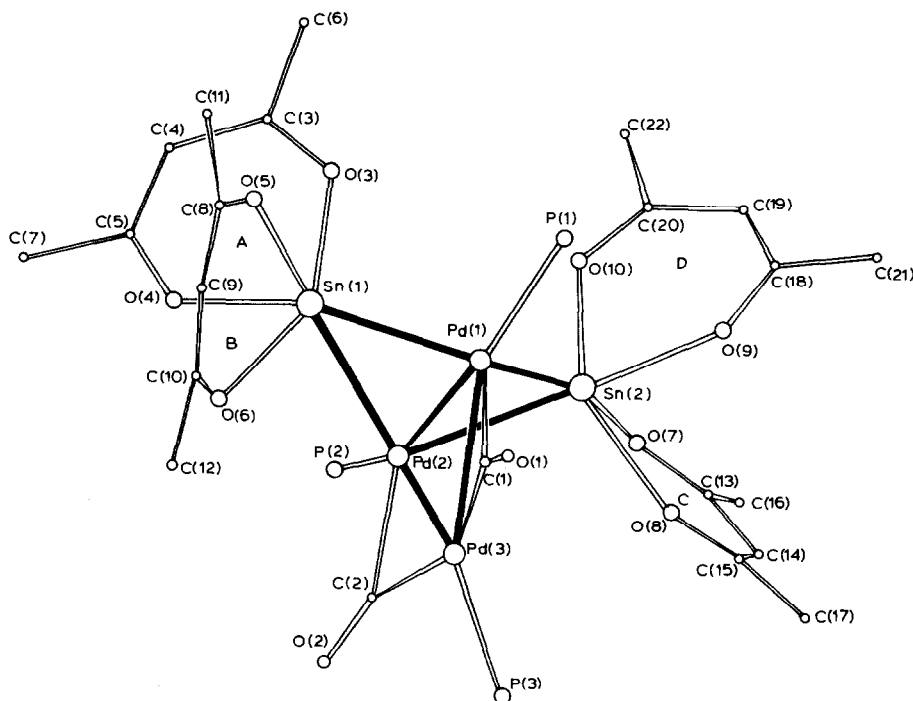

Fig. 1. Molecule IV (phenyl substituents omitted).

considerable asymmetry of the Sn(1) atom coordination. The distribution of bond lengths in acetylacetonate frgaments of IV is typical for tin derivatives [6,9,10].

Distortion of the coordination environment of the Sn(1) atom which leads to non-equivalence of the two Sn atoms in the Pd_3Sn_2 metal frame in IV is accompanied by considerable asymmetry of the molecule as a whole. The metal frame in IV has the "propeller" configuration, analogous to that in the previously discovered mixed gold-osmium cluster $Os_3(CO)_{10}(AuPEt_3)_2$ [11]. However, as opposed to the latter compound, whose molecules have special positions on the symmetry axis 2 (which makes Os_2Au moieties structurally equivalent), the Pd_3Sn_2 metal frame in IV deviates noticeably from ideal symmetrical configuration; the dihedral angles formed by the triangular moieties Pd_3 and Pd_2Sn are essentially different viz. for Sn(1) (126.65°) and Sn(2) (106.5°, Table 3). These distortions are probably because of the overall conformational lability of the Pd_3Sn_2 moiety, whose dihedral angles can vary considerably without much loss of energy. The broad range of dihedral angles has been previously observed in structures of $Pd_4(\mu_2-CO)_5L_4$ clusters (L is phosphine ligand) with "butterfly" configuration. In related "propeller" molecules of IV the symmetrical configuration can probably also be distorted by small excitations. Such an excitation in IV can originate from van der Waals forces and hydrogen bonds of the solvate water molecule (Table 3). In crystals of IV, the X atom forms a short contact with the O(6) atom, which is incorporated into the most distorted acac ligand; the X $\cdots$ O(6) distance 2.94(4) Å corresponds to a weak hydrogen bond [12], and the sum of Sn(1)O(6)C(10) (123.3°), Sn(1)O(6)X (130.7°) and C(10)O(6)X (106.0°) angles equals 360°, i.e. corresponds to a planar trigonal (sp^2) oxygen atom.

Experimental

$Sn(acac)_2$ was prepared by a standard method [13], and the palladium cluster by published methods [14,15]. All syntheses were carried out under argon. A 0.374 M solution of $Sn(acac)_2$ was used. Analysis of CO was carried out by allowing the substances to melt in the presence of an excess of PPh_3 in an inert atmosphere. IR spectra were recorded with a Specord-75IR spectrophotometer from samples suspended in Nujol.

Syntheses of the complexes

Synthesis of IV from I. To a solution of 0.319 g (0.187 mmol) of $Pd_4(CO)_5(PPh_3)_4 \cdot C_7H_8$ (prepared under CO) in 10 ml of toluene, 2.0 ml (0.748 mmol) of $Sn(acac)_2$ in hexane solution was added, with stirring, under argon. The solution was kept at room temperature for 24 h. The yellow crystals that separated were washed with a mixture of C_6H_6/pentane (1/1), then with pentane, and dried in vacuo, to give 0.369 g (82%) of IV.

Analysis. Found: Pd, 17.48; P, 5.10; CO, 3.16; C, 50.57; H, 4.22; Sn, 13.73. $C_{76}H_{73}O_{10}P_3Pd_3Sn_2$ calc: Pd, 17.77; P, 5.17; CO, 3.12; C, 50.83; H, 4.10; Sn, 13.22%. IR spectrum: 1852s, 1829s, 1821s 1585s, 1516s cm^{-1}.

Crystals of IV suitable for X-ray analysis were obtained similarly.

Synthesis of IV from II. To a suspension of 0.543 g (0.374 mmol) of II in 20 ml of toluene/hexane (1/1) mixture, was added 3.0 ml (1.22 mmol) of $Sn(acac)_2$ solution with stirring. The suspension was shaken periodically during 24 h, and then

Table 4

Atomic coordinates and equivalent isotropic thermal parameters B_{eq} in IV

Atom	x	y	z	B_{eq}
Sn(1)	12624(6)	11866(3)	63773(5)	3.52(2)
Sn(2)	32951(5)	18107(3)	75979(5)	3.56(2)
Pd(1)	16215(6)	16309(3)	77731(5)	2.85(2)
Pd(2)	27089(6)	9462(3)	72000(5)	2.88(2)
Pd(3)	21523(6)	8929(3)	87079(5)	3.42(3)
P(1)	1019(2)	2363(1)	7830(2)	2.9(1)
P(2)	3568(2)	615(1)	6289(2)	3.3(1)
P(3)	2365(2)	612(1)	9998(2)	3.6(1)
O(1)	605(6)	1421(4)	9225(6)	6.9(4)
O(2)	2995(7)	18(3)	8076(5)	6.5(3)
O(3)	1467(5)	1661(3)	5353(5)	3.8(3)
O(4)	1187(6)	689(3)	5446(5)	5.6(3)
O(5)	16(6)	1392(3)	6010(6)	5.9(3)
O(6)	521(6)	601(3)	6955(6)	6.5(3)
O(7)	4613(5)	1753(3)	7533(5)	4.5(3)
O(8)	3653(4)	1726(3)	8930(5)	4.4(3)
O(9)	3454(5)	2507(3)	8040(5)	4.7(3)
O(10)	3509(5)	2181(3)	6439(5)	4.6(3)
C(1)	1209(8)	1360(4)	8842(7)	3.9(4)
C(2)	2780(8)	403(4)	8062(7)	4.5(4)
C(3)	1324(8)	1594(5)	4609(7)	5.0(5)
C(4)	1144(12)	1154(8)	4271(8)	7.2(6)
C(5)	1131(11)	740(5)	4679(8)	6.8(5)
C(6)	1378(12)	2022(5)	4099(9)	7.8(6)
C(7)	992(16)	274(6)	4214(10)	11.4(9)
C(8)	−696(9)	1289(5)	6280(10)	6.5(5)
C(9)	−794(10)	964(6)	6867(11)	8.2(6)
C(10)	−275(10)	645(5)	7142(9)	7.1(6)
C(11)	−1396(11)	1574(7)	5967(13)	9.9(7)
C(12)	−471(15)	295(7)	7792(10)	11.2(8)
C(13)	5188(8)	1815(4)	8042(8)	4.7(4)
C(14)	5119(8)	1828(5)	8891(8)	5.7(5)
C(15)	4347(8)	1800(5)	9293(8)	5.1(4)
C(16)	6080(9)	1858(6)	7747(10)	7.4(6)
C(17)	4381(10)	1859(6)	10191(8)	6.7(5)
C(18)	3722(8)	2887(4)	7726(9)	4.7(4)
C(19)	3897(9)	2929(4)	6944(9)	5.9(5)
C(20)	3774(9)	2591(4)	6340(9)	5.8(5)
C(21)	3828(10)	3290(5)	8298(10)	7.0(5)
C(22)	3978(10)	2720(5)	5479(9)	6.6(5)
C(111)	1402(7)	2831(4)	7196(7)	3.4(3)
C(112)	1555(8)	2716(4)	6395(8)	4.7(4)
C(113)	1822(8)	3076(5)	5882(8)	4.9(4)
C(114)	1955(10)	3522(5)	6147(8)	6.0(5)
C(115)	1833(9)	3636(4)	6930(9)	5.5(5)
C(116)	1554(8)	3288(4)	7457(8)	4.5(4)
C(1210	−136(7)	2423(4)	7662(7)	3.4(3)
C(122)	−500(7)	2796(4)	7241(7)	3.7(4)
C(123)	−1390(8)	2823(5)	7176(8)	5.0(4)
C(124)	−1885(7)	2510(5)	7513(9)	5.2(4)
C(125)	−1507(9)	2148(5)	7944(10)	7.3(6)
C(126)	−639(7)	2091(5)	8003(9)	5.6(5)
C(131)	1154(7)	2615(4)	8839(6)	3.2(4)
C(132)	562(7)	2903(4)	9204(7)	3.9(4)

Table 4 (continued)

Atom	x	y	z	B_{eq}
C(133)	723(9)	3074(4)	9973(8)	5.1(4)
C(134)	1469(9)	2969(4)	10384(8)	5.0(4)
C(135)	2041(8)	2686(4)	10051(7)	4.7(4)
C(136)	1894(7)	2509(4)	9297(7)	3.6(4)
C(211)	3385(8)	−21(4)	6159(7)	4.0(4)
C(212)	2554(8)	−169(4)	6031(8)	4.8(4)
C(213)	2389(9)	−642(4)	5874(9)	5.6(5)
C(214)	3055(10)	−952(4)	5854(8)	5.6(5)
C(215)	3881(9)	−811(4)	5989(8)	5.2(4)
C(216)	4065(8)	−347(4)	6142(7)	4.4(4)
C(221)	4696(7)	643(4)	6575(7)	3.7(4)
C(222)	4953(8)	577(5)	7373(8)	5.3(5)
C(223)	5823(10)	561(6)	7615(8)	6.7(5)
C(224)	6428(9)	620(5)	7073(9)	6.3(5)
C(225)	6163(9)	694(5)	6293(9)	6.0(5)
C(226)	5316(7)	704(4)	6025(8)	4.3(4)
C(231)	3547(7)	818(4)	5242(7)	3.5(4)
C(232)	3571(9)	514(4)	4605(7)	5.3(5)
C(233)	3563(10)	690(5)	3823(8)	6.4(5)
C(234)	3527(10)	1155(5)	3681(8)	6.1(5)
C(235)	3479(9)	1464(4)	4313(8)	5.1(4)
C(236)	3495(7)	1289(4)	5087(7)	3.7(4)
C(311)	2028(7)	−3(4)	10162(7)	3.5(4)
C(312)	2473(3)	−322(5)	10621(10)	6.5(5)
C(313)	2176(10)	−766(5)	10706(10)	7.0(6)
C(314)	1420(11)	−899(5)	10353(9)	7.2(6)
C(315)	978(10)	−592(6)	9883(11)	8.5(6)
C(316)	1287(11)	−145(5)	9799(9)	7.3(6)
C(321)	1819(7)	947(4)	10766(7)	4.0(4)
C(322)	1896(8)	1430(4)	10754(8)	4.5(4)
C(323)	1495(9)	1699(5)	11307(9)	6.0(5)
C(324)	997(9)	1481(5)	11858(9)	6.2(5)
C(325)	914(11)	1018(6)	11870(9)	7.7(6)
C(326)	1292(10)	728(5)	11316(9)	6.3(5)
C(331)	3445(9)	621(4)	10404(8)	4.8(4)
C(332)	4120(9)	595(5)	8999(8)	5.9(5)
C(333)	4948(10)	588(6)	10174(11)	8.5(7)
C(334)	5155(9)	610(5)	10977(11)	7.9(6)
C(335)	4512(10)	653(6)	11527(10)	8.0(6)
C(336)	3672(9)	665(6)	11225(9)	6.8(5)
X	1009(24)	9638(13)	7372(23)	9(1) [a]

[a] B_{iso}.

kept at −5°C for an additional 24 h. The substance was washed in hexane and yielded 0.546 g (81%) of a compound identical to cluster IV by comparison of IR spectra.

Synthesis of V from III. To a solution of 0.470 g (0.453 mmol) of III in 11 ml of hexane, was added 3.3 ml (1.234 mmol) of $Sn(acac)_2$ solution. After 24 h the solution was filtered, and concentrated to 1 ml. The yellow crystals were washed in cooled pentane and yielded 0.300 g (36%) of V. Analysis. Found: Pd, 22.37; P, 6.84; CO, 3.75. $C_{40}H_{73}O_{10}P_3Pd_3Sn_2$ calc: Pd, 23.41; P, 6.81; CO, 4.11%. IR spectum: 1832s, 1802s, 1773w, 1592s, 1513s cm^{-1}.

X-ray diffraction study of IV

Crystals of IV are monoclinic, a 15.781(2), b 28.469(2), c 16.647(1) Å, β 93.09(1)°, space group $P2_1/n$, $Z = 4$. Unit cell parameters and intensities of 4617 independent reflections measured at room temperature on a Hilger-Watts Y/290 automatic fourcircle diffractometer (λ(Mo-K_α), graphite monochromator, $\theta/2\theta$-scan, $2\theta < 56°$); to avoid sample decomposition due to contact with air, the monocrystal was placed in a Pyrex capillary under argon. The calculations involved 4396 observed reflections ($I > 2\sigma$), absorption was ignored.

The structure of IV was solved by the direct method using the MULTAN program and refined by the block-diagonal least-squares method in an anisotropic approximation to $R = 0.041$. During differential Fourier synthesis, most of H atoms, and one strong electron density maximum were located; the maximum was ascribed to non-stoichiometric amounts of solvate water, molecules of which fill the cavities of crystal IV. The composition of IV, therefore, corresponds to the formula $Pd_3Sn_2(acac)_4(CO)_2(PPh_3)_3 \cdot xH_2O$, where $x \sim 1$. H atoms were included in the refinement with fixed positional and isotropical thermal parameters B_{iso} 6.0 Å^2; for the X atom, which corresponds to a solvate H_2O molecule, the type of oxygen was specified and positional parameters and B_{iso} were refined. Final R value 0.037, R_w -0.038. Atomic coordinates and their equivalent isotropic thermal parameters of IV are listed in Table 4. Calculations were carried out with the ECLIPSE S/200 computer using INEXTL programs [5].

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