

Synthesis and X-ray structure of a novel 12-nuclear cluster $\text{Pd}_{12}(\text{CO})_{12}(\text{PBU}_3^n)_6$ ¹

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Abstract

A novel dodecanuclear cluster compound $\text{Pd}_{12}(\text{CO})_{12}(\text{PBU}_3^n)_6$ (**I**) was obtained by a mild oxidation of the known $\text{Pd}_{10}(\text{CO})_{12}(\text{PBU}_3^n)_6$ and $\text{Pd}_4(\text{CO})_5(\text{PBU}_3^n)_4$ clusters with Me_3NO and by a reaction of $\text{Pd}_{10}(\text{CO})_{12}(\text{PBU}_3^n)_6$ with binuclear $\text{Pd}_2(\text{DBA})_3$ (where DBA = dibenzylideneacetone) under Ar. A single crystal X-ray diffraction study of (**I**) ($P\bar{1}$, $Z = 2$, $R = 0.065$ on 4452 reflections) revealed two independent hexacapped distorted octahedra of Pd atoms positioned on the crystallographic inversion centres, with six μ_2 - and six μ_3 -CO ligands as well as six PBU_3^n ligands bonded to the capping palladium atoms. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

Notable achievements in the synthesis of novel compounds containing large metal clusters M_n of late transition metals (with $n > 10$), have been made during the last decade (see, for example, [1–3]). The central element of this group of metals, palladium, shows a distinct tendency to form polyhedral molecules with a combination of CO and phosphine ligands. The relative ratios of both components in the ligand shell and the relative stability of the core polyhedral structure, are primarily influenced by the nature of the phosphine ligand.

Earlier we found that cluster growth of tetra- and decanuclear species in the $\text{Pd}_4(\text{CO})_5(\text{PEt}_3)_4/\text{Me}_3\text{NO}/\text{HOAc}$ and $\text{Pd}_{10}(\text{CO})_{12}(\text{PEt}_3)_6/\text{Me}_3\text{NO}/\text{Me}_3\text{N}$ systems leads to hexadecanuclear $\text{Pd}_{16}(\text{CO})_{13}(\text{PEt}_3)_9$ as well as to 23-nuclear $\text{Pd}_{23}(\text{CO})_{22}(\text{PR}_3)_6$ ($R = \text{Et}, \text{Bu}^n$) [4,5]. Here we report the synthesis of the novel dodecanuclear cluster $\text{Pd}_{12}(\text{CO})_{12}(\text{PBU}_3^n)_6$ (**I**) via a similar route with PBU_3^n as phosphine ligand, as well as by the reaction of $\text{Pd}_{10}(\text{CO})_{12}(\text{PBU}_3^n)_6$ with $\text{Pd}_2(\text{DBA})_3$ (DBA = dibenzylideneacetone). The substitution of PEt_3 by PBU_3^n therefore leads to a dramatic change in the outcome of the reaction, notwithstanding the close similarity in electronic and steric requirements of the ligands [6].

2. Discussion

Black hexagonal prismatic crystals of (**I**) were obtained from the reaction mixture of $\text{Pd}_4(\text{CO})_5(\text{PBU}_3^n)_4$ and $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$ (see Section 3). Similar crystals, though less suitable for an X-ray diffractometry, may be grown from the dark brown toluene solution of (**I**) by a slow evaporation of the solvent.

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¹ Professor Yuri T.Struchkov participated in this paper, both in discussions on the possible transformations of Pd clusters and in preparation of the text. The structural study was performed at his laboratory in 1990. We wish to publish this paper as a tribute to Professor Struchkov's contribution to modern structural chemistry, especially to cluster chemistry.

Eugeniy G. Mednikov, Yuri L. Slovokhotov

Table 1
Atom coordinates (Pd, P $\times 10^4$, O, C $\times 10^3$) and isotropic temperature factors^a ($\times 10^3$) in (I)

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{eq}
Pd(1)	4342(2)	893(2)	4245(1)	54
Pd(2)	5452(2)	−710(2)	4254(1)	53
Pd(3)	6197(2)	262(2)	5108(1)	54
Pd(4)	6280(2)	436(2)	3907(1)	55
Pd(5)	7127(2)	−1360(2)	4931(1)	58
Pd(6)	5141(2)	−1847(2)	5107(1)	59
Pd(7)	9843(2)	686(2)	758(1)	51
Pd(8)	10149(2)	−911(2)	734(1)	49
Pd(9)	11433(2)	−285(2)	−108(1)	51
Pd(10)	11685(2)	−491(2)	1096(1)	54
Pd(11)	11496(2)	−1865(2)	63(1)	57
Pd(12)	10967(2)	1311(2)	85(1)	54
P(1)	7023(8)	672(8)	3037(4)	62
P(2)	8701(9)	−2251(9)	5121(6)	90
P(3)	5060(12)	−3075(9)	5021(7)	109
P(4)	12633(8)	−735(8)	1974(4)	70
P(5)	12715(9)	−3093(7)	−32(5)	73
P(6)	11682(9)	2239(8)	−146(5)	80
O(1)	478(2)	300(2)	306(1)	74
O(2)	703(2)	−201(2)	377(1)	98
O(3)	759(2)	−77(2)	605(1)	74
O(4)	626(2)	−258(2)	631(1)	96
O(5)	777(2)	80(2)	463(1)	116
O(6)	610(2)	131(2)	606(1)	81
O(7)	1350(2)	−90(2)	36(1)	82
O(8)	1006(2)	−31(2)	193(1)	83
O(9)	1221(2)	−129(2)	−110(1)	76
O(10)	1096(2)	−264(2)	123(1)	88
O(11)	1196(2)	72(1)	−105(1)	60
O(12)	1040(2)	188(2)	130(1)	97
C(1)	519(3)	25(2)	351(2)	74
C(2)	681(3)	−159(2)	414(2)	57
C(3)	709(3)	−78(3)	563(2)	72
C(4)	593(3)	−211(3)	593(2)	76
C(5)	709(3)	68(3)	451(2)	105
C(6)	562(3)	120(2)	566(2)	56
C(7)	1268(3)	−82(2)	47(2)	73
C(8)	1042(3)	−22(2)	145(2)	75
C(9)	1165(3)	−120(2)	−68(2)	82
C(10)	1097(3)	−216(3)	86(2)	64
C(11)	1148(3)	64(3)	−61(2)	77
C(12)	1046(3)	154(2)	87(2)	58
C(111)	749(3)	−14(3)	259(2)	78
C(112)	836(3)	−86(3)	295(2)	74
C(113)	871(3)	−156(3)	256(2)	83
C(114)	965(4)	−222(4)	280(2)	130
C(121)	620(3)	149(2)	248(2)	57
C(122)	580(4)	227(3)	273(2)	111
C(123)	504(4)	299(3)	225(2)	113
C(124)	463(5)	371(5)	250(3)	178
C(131)	796(3)	110(3)	317(2)	64
C(132)	846(3)	131(2)	260(2)	90
C(133)	947(5)	140(3)	275(3)	150
C(134)	982(5)	149(4)	320(3)	162
C(211)	960(4)	−183(4)	517(2)	124
C(212)	971(4)	−147(3)	456(2)	108
C(213)	1058(6)	−118(5)	458(3)	174
C(214)	1098(6)	−101(5)	410(4)	222
C(221)	874(8)	−294(6)	601(4)	212
C(222)	941(10)	−314(9)	607(7)	355
C(223)	934(5)	−368(4)	687(3)	173

Table 1 (Continued)

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{eq}
C(224)	871(6)	−414(5)	698(3)	196
C(231)	924(4)	−307(3)	460(2)	108
C(232)	868(4)	−365(4)	464(3)	126
C(233)	907(6)	−405(5)	397(4)	193
C(234)	867(9)	−455(8)	407(6)	326
C(311)	372(6)	−301(5)	518(4)	211
C(312)	360(5)	−294(4)	573(3)	166
C(313)	243(7)	−294(7)	599(4)	237
C(314)	255(7)	−370(7)	601(5)	267
C(321)	604(7)	−400(6)	545(4)	183
C(322)	666(11)	−453(10)	541(8)	389
C(323)	709(9)	−528(8)	580(5)	285
C(324)	797(7)	−552(5)	579(4)	187
C(331)	504(6)	−336(5)	431(4)	221
C(332)	544(8)	−373(7)	391(6)	426
C(333)	541(8)	−408(7)	328(6)	250
C(334)	606(9)	−380(7)	312(5)	247
C(411)	1242(3)	8(2)	240(2)	59
C(412)	1275(3)	78(3)	205(2)	96
C(413)	1240(3)	147(3)	241(2)	86
C(414)	1281(4)	213(3)	217(2)	126
C(421)	1398(3)	−116(2)	184(2)	59
C(422)	1461(3)	−134(3)	242(2)	74
C(423)	1569(6)	−166(3)	227(4)	179
C(424)	1606(6)	−142(5)	185(4)	203
C(431)	1249(3)	−151(2)	254(2)	60
C(432)	1270(4)	−231(3)	229(2)	109
C(433)	1249(4)	−293(4)	276(2)	122
C(434)	1275(5)	−375(4)	249(3)	167
C(511)	1397(4)	−321(4)	28(3)	130
C(512)	1389(4)	−307(4)	88(3)	140
C(513)	1502(6)	−310(5)	108(3)	190
C(514)	1564(8)	−400(8)	115(4)	307
C(521)	1240(3)	−392(3)	37(2)	79
C(522)	1326(4)	−479(3)	38(2)	120
C(523)	1281(6)	−541(5)	72(3)	177
C(524)	1356(8)	−609(7)	72(4)	252
C(531)	1307(4)	−335(3)	−78(2)	90
C(532)	1220(4)	−336(4)	−112(3)	132
C(533)	1272(6)	−363(5)	−182(4)	190
C(534)	1200(8)	−376(6)	−202(5)	257
C(611)	1126(3)	280(3)	−95(2)	95
C(612)	1174(4)	338(4)	−119(3)	136
C(613)	1116(5)	372(5)	−187(3)	160
C(614)	1175(7)	426(6)	−206(4)	361
C(621)	1143(3)	305(3)	34(2)	89
C(622)	1030(4)	359(3)	28(2)	109
C(623)	1002(5)	424(4)	71(3)	148
C(624)	1040(5)	395(5)	131(4)	188
C(631)	1301(3)	185(3)	−17(2)	94
C(632)	1347(3)	143(3)	43(2)	93
C(633)	1464(4)	109(3)	40(2)	135
C(634)	1510(5)	90(4)	94(3)	158

^a For Pd, P and CO ligands equivalent isotropic *U*_{eq} defined as one third of the trace of the orthogonalised *U*_{ij} tensor.

The structure of (I) was determined by X-ray single crystal diffraction study. Atomic coordinates of (I) are given in Table 1. One of the two independent molecules of (I) which have almost identical geometries (both

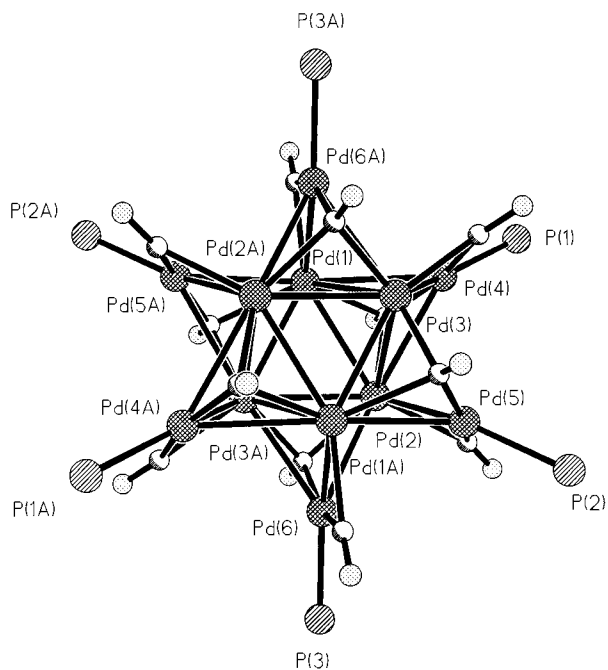


Fig. 1. Molecule (I), occupying the inversion centre in the $P1$ unit cell.

occupy symmetry centres in a triclinic cell of the $P\bar{1}$ space group) is shown in Fig. 1. Bond lengths and bond angles in (I) are presented in Table 2.

Cluster (I) has almost ideal D_{3d} molecular symmetry. It is formed from two hexanuclear $\text{Pd}_6(\mu_3\text{-CO})_3\text{L}_3$ moieties (where L is phosphine ligand), stacked in an antiparallel mode and linked together by six edge-bridging carbonyl ligands. Alternatively, the structure of (I) may be described as a hexacapped (distorted) octahedron. The closest geometric relatives of (I) are therefore the hexanuclear 'raft' clusters (for instance, $\text{Os}_6(\text{CO})_{17}[\text{P}(\text{OMe})_3]_4$ [7]), the tetracapped octahedral $\text{Pd}_{10}(\text{CO})_{12}\text{L}_6$ [8] and $\text{Pd}_{10}(\text{CO})_{14}\text{L}_4$ [9] clusters, and, especially, the dodecanuclear mixed-metal cluster $[\text{Pd}_6\text{Fe}_6(\text{CO})_{24}\text{H}]^{3-}$ with the same overall structure based on the hexacapped octahedron [10]. Among the other known examples of structurally studied 12-nuclear clusters of transition metals, one can mention a distorted icosahedral anion $[\text{Rh}_{12}\text{Sb}(\text{CO})_{27}]^{3-}$ with an interstitial antimony atom [11].

However, the Pd_{12} cluster core in (I) differs significantly in its structure even from its closest dodecanuclear Pd_6Fe_6 analogue. The inner Pd_6 octahedron in the mixed-metal Pd_6Fe_6 moiety is only slightly distorted towards a trigonal antiprism [8], but the inner Pd_6 polyhedron in (I) is actually a very distorted trigonal antiprism. The Pd–Pd edges of the basal triangles in (I) (2.740–2.767, mean value 2.749 Å) have their normal lengths for Pd clusters (see [8,9]), whereas the other six Pd...Pd side edges of the antiprism are elongated to 3.094–3.362 Å (mean 3.218 Å) and may be considered

as non-bonding distances. The elongated Pd...Pd contacts, typical for polynuclear Pd species, have been reported previously in $\text{Pd}_7(\text{CO})_7(\text{PMe}_3)_7$ [12], $\text{Pd}_8(\text{CO})_8(\text{PMe}_3)_8$ [13], $\text{Pd}_{10}(\text{CO})_{12}(\text{PBu}_3)_6$ [8], $\text{Pd}_{10}(\text{CO})_{14}(\text{PBu}_3)_4$ [9], and $\text{Pd}_{23}(\text{CO})_{22}(\text{PBu}_3)_{10}$ [14], as well as in the butterfly $\text{Pd}_4(\text{CO})_5(\text{PBu}_3)_4$ [15,16]. The other bond distances and angles in (I), given in the Table 2, are typical for the clusters of the $\text{Pd}_n(\text{CO})_x(\text{PR}_3)_y$ family.

It is interesting to note that the aforementioned non-bonding Pd...Pd side edges of the inner Pd_6 trigonal antiprism are only slightly shorter than the distances between the capping Pd atoms in (I) (3.383–3.671, mean 3.533 Å). An alternative description of (I) as a strongly distorted icosahedral cluster Pd_{12} is therefore possible, forming a link to the distorted icosahedral motif of $[\text{Rh}_{12}\text{Sb}(\text{CO})_{27}]^{3-}$ cluster anion (see [11]). Metal cluster core in (I) is therefore intermediate between the six-capped octahedron stretched along one of its three-fold symmetry axes, and the regular icosahedron compressed along the same axis (Fig. 2).

The twelve-nuclear metal core in (I) contains 156 valence electrons, which is four electrons less than in its closest structural analogue $[\text{Pd}_6\text{Fe}_6(\text{CO})_{24}\text{H}]^{3-}$ [10]. Skeletal electron count gives $N_{\text{sk}} = 12$ for (I) and $N_{\text{sk}} = 16$ for $[\text{Pd}_6\text{Fe}_6(\text{CO})_{24}\text{H}]^{3-}$ as well as for the related tetracapped octahedra $\text{Pd}_{10}(\text{CO})_{12+n}\text{L}_{6-n}$ (where N_{sk} is the number of skeletal electrons, n equals 0 [8] or 2 [9], and $\text{L} = \text{PBu}_3^{\text{t}}$). Both numbers of skeletal electrons deviate from $N_{\text{sk}} = 14$ required for an octahedron by the $2n + 2$ rule [17], and the metal cluster moieties are notably distorted in all these species. However, electron counting rules are not strictly followed in the clusters of late transition metals [18].

Based on the geometry of known clusters of the $\text{Pd}_n(\text{CO})_x(\text{PR}_3)_y$ family, a route to medium-size clusters via aggregation of smaller units may be suggested (Scheme 1). The isolation of a key hypothetical step in the Scheme, viz. 6-nuclear $\text{Pd}_6(\text{CO})_x\text{L}_y$ 'raft' cluster, would be of great importance for a proving or rejecting of this proposed mechanism.

Extending the growth of the metal core, enables clusters of higher nuclearity based on the centred icosahedron, such as $\text{Pd}_{16}(\text{CO})_{13}(\text{PET}_3)_9$ (see [4]) to be obtained. The isolation of the very different products from the similar-type reaction mixtures containing PET_3 and PBu_3^{t} phosphines, may therefore result from subtle differences in the stability of the corresponding species.

3. Experimental

Initial reagents were obtained as in [4,5] and references therein. The $\text{Pd}_2(\text{DBA})_3$ complex was synthesised

Table 2
Bond lengths d (Å) and selected bond angles ω (deg.) in (I)

Bond	d , Å	Angle	ω , deg.
Pd(1)–Pd(2)	2.740(4)	Pd(4)–P(1)–C(111)	117(2)
Pd(1)–Pd(4)	2.812(4)	C(111)–P(1)–C(121)	102(2)
Pd(1)–Pd(5)a	2.813(4)	C(111)–P(1)–C(131)	110(2)
Pd(2)–Pd(3)	3.198(5)	Pd(5)–P(2)–C(211)	117(2)
Pd(2)–Pd(5)	2.702(4)	C(211)–P(2)–C(221)	106(3)
Pd(2)–Pd(6)	2.808(5)	C(211)–P(2)–C(231)	104(3)
Pd(3)–Pd(5)	2.807(5)	Pd(6)–P(3)–C(311)	108(3)
Pd(3)–Pd(2)a	2.740(4)	C(311)–P(3)–C(321)	114(4)
Pd(6)–Pd(1)a	2.691(4)	C(311)–P(3)–C(331)	94(4)
Pd(5)–Pd(1)a	2.813(3)	Pd(10)–P(4)–C(411)	118(1)
Pd(7)–Pd(9)	3.188(4)	C(411)–P(4)–C(421)	108(2)
Pd(7)–Pd(12)	2.708(5)	C(411)–P(4)–C(431)	101(2)
Pd(7)–Pd(9)a	2.741(4)	Pd(11)–P(5)–C(511)	115(2)
Pd(8)–Pd(9)	3.095(5)	C(511)–P(5)–C(521)	107(2)
Pd(8)–Pd(11)	2.700(4)	C(511)–P(5)–C(531)	97(3)
Pd(8)–Pd(11)c	2.804(4)	Pd(12)–P(6)–C(611)	111(2)
Pd(9)–Pd(11)	2.792(5)	C(611)–P(6)–C(621)	105(2)
Pd(9)–Pd(7)a	2.741(4)	C(611)–P(6)–C(631)	103(2)
Pd(11)–Pd(7)a	2.799(3)	Pd(1)–C(1)–Pd(2)	77(1)
Pd(4)–P(1)	2.32(1)	Pd(2)–C(1)–Pd(4)	85(1)
Pd(6)–P(3)	2.29(2)	Pd(2)–C(1)–O(1)	126(3)
Pd(11)–P(5)	2.32(1)	Pd(2)–C(2)–Pd(5)	81(1)
Pd(1)–C(1)	2.24(4)	Pd(3)–C(6)–Pd(6)a	84(1)
Pd(1)–C(4)a	2.07(5)	Pd(2)a–C(6)–Pd(6)a	86(1)
Pd(2)–C(2)	2.09(3)	Pd(9)–C(7)–O(7)	127(3)
Pd(3)–C(3)	2.07(4)	Pd(7)–C(8)–Pd(8)	79(3)
Pd(3)–C(6)	2.13(3)	Pd(8)–C(8)–Pd(10)	83(1)
Pd(4)–C(5)	2.00(5)	Pd(8)–C(8)–O(8)	114(3)
Pd(5)–C(3)	1.99(4)	Pd(9)–C(9)–Pd(11)	85(2)
Pd(6)–C(6)a	2.04(4)	Pd(11)–C(9)–O(9)	137(2)
Pd(7)–C(12)	2.11(4)	Pd(11)–C(9)–Pd(7)a	87(2)
Pd(8)–C(8)	2.28(4)	Pd(8)–C(10)–Pd(11)	81(1)
Pd(8)–C(11)a	2.30(4)	Pd(11)–C(10)–O(10)	149(3)
Pd(9)–C(9)	2.13(4)	Pd(9)–C(11)–O(11)	133(3)
Pd(10)–C(7)	2.01(4)	Pd(9)–C(11)–Pd(8)a	82(2)
Pd(11)–C(9)	2.01(4)	O(11)–C(11)–Pd(8)a	120(2)
Pd(12)–C(11)	2.06(4)	Pd(7)–C(12)–O(12)	125(3)
Pd(1)–C(3)a	2.23(4)	P(1)–C(111)–C(112)	111(3)
Pd(2)–C(6)a	2.09(4)	C(112)–C(113)–C(114)	113(4)
Pd(7)–C(9)a	2.06(4)	C(121)–C(122)–C(123)	111(4)
P(1)–C(111)	1.78(5)	P(1)–C(131)–C(132)	115(3)
P(1)–C(131)	1.87(5)	C(132)–C(133)–C(134)	133(7)
P(2)–C(221)	2.22(10)	C(211)–C(212)–C(213)	108(5)
P(3)–C(311)	1.98(9)	P(2)–C(221)–C(222)	95(9)
P(3)–C(331)	1.75(9)	C(222)–C(223)–C(224)	122(7)
P(4)–C(421)	1.90(4)	C(231)–C(232)–C(233)	97(5)
P(5)–C(511)	1.91(6)	P(3)–C(311)–C(312)	107(7)
P(5)–C(531)	1.82(5)	C(312)–C(313)–C(314)	102(7)
P(6)–C(621)	1.85(5)	C(321)–C(322)–C(323)	132(9)
O(1)–C(1)	1.18(5)	P(3)–C(331)–C(332)	151(8)
O(3)–C(3)	1.20(5)	C(332)–C(333)–C(334)	86(10)
O(5)–C(5)	1.14(5)	C(411)–C(412)–C(413)	106(4)
O(7)–C(7)	1.20(5)	P(4)–C(421)–C(422)	112(3)
O(9)–C(9)	1.25(5)	C(422)–C(423)–C(424)	128(6)
O(11)–C(11)	1.24(5)	C(431)–C(432)–C(433)	111(4)
C(111)–C(112)	1.59(5)	P(5)–C(511)–C(512)	109(4)
C(113)–C(114)	1.51(6)	C(512)–C(513)–C(514)	103(8)
C(122)–C(123)	1.65(7)	C(521)–C(522)–C(523)	104(4)
C(131)–C(132)	1.56(6)	P(5)–C(531)–C(532)	109(4)
C(133)–C(134)	1.20(9)	C(532)–C(533)–C(534)	94(7)
C(212)–C(213)	1.57(10)	C(611)–C(612)–C(613)	100(5)
C(221)–C(222)	0.9(2)	P(6)–C(621)–C(622)	110(4)

Table 2 (Continued)

Bond	d , Å	Angle	ω , deg.
C(223)–C(224)	1.5(1)	C(622)–C(623)–C(624)	114(5)
C(232)–C(233)	1.77(9)	C(631)–C(632)–C(633)	111(4)
C(311)–C(312)	1.27(9)	Pd(4)–P(1)–C(121)	114(1)
C(313)–C(314)	1.3(2)	Pd(4)–P(1)–C(131)	112(1)
C(322)–C(323)	1.4(2)	C(121)–P(1)–C(131)	100(2)
C(331)–C(332)	1.2(2)	Pd(5)–P(2)–C(221)	106(3)
C(333)–C(334)	1.3(2)	Pd(5)–P(2)–C(231)	119(2)
C(412)–C(413)	1.50(7)	C(221)–P(2)–C(231)	104(3)
C(421)–C(422)	1.54(6)	Pd(6)–P(3)–C(321)	117(4)
C(423)–C(424)	1.21(9)	Pd(6)–P(3)–C(331)	119(3)
C(432)–C(433)	1.57(8)	C(321)–P(3)–C(331)	103(4)
C(511)–C(512)	1.43(9)	Pd(10)–P(4)–C(421)	112(1)
C(513)–C(514)	1.52(11)	Pd(10)–P(4)–C(431)	114(1)
C(522)–C(523)	1.63(8)	C(421)–P(4)–C(431)	103(2)
C(531)–C(532)	1.52(8)	Pd(11)–P(5)–C(521)	109(1)
C(533)–C(534)	1.3(1)	Pd(11)–P(5)–C(531)	119(1)
C(612)–C(613)	1.70(9)	C(521)–P(5)–C(531)	109(2)
C(621)–C(622)	1.59(6)	Pd(12)–P(6)–C(621)	117(2)
C(623)–C(624)	1.43(9)	Pd(12)–P(6)–C(631)	117(2)
C(632)–C(633)	1.61(8)	C(621)–P(6)–C(631)	103(2)
Pd(1)–Pd(3)	3.134(4)	Pd(1)–C(1)–Pd(4)	83(2)
Pd(1)–Pd(3)a	2.759(5)	Pd(1)–C(1)–O(1)	118(3)
Pd(1)–Pd(6)a	2.691(4)	Pd(4)–C(1)–O(1)	145(3)
Pd(2)–Pd(4)	2.807(5)	O(6)–C(6)–Pd(2)a	128(3)
Pd(2)–Pd(3)a	2.740(4)	O(6)–C(6)–Pd(6)a	137(3)
Pd(3)–Pd(4)	2.697(3)	Pd(9)–C(7)–Pd(10)	82(1)
Pd(3)–Pd(1)a	2.759(4)	Pd(10)–C(7)–O(7)	143(3)
Pd(3)–Pd(6)a	2.792(4)	Pd(7)–C(8)–Pd(10)	89(1)
Pd(5)–Pd(6)	3.382(5)	Pd(7)–C(8)–O(8)	127(2)
Pd(7)–Pd(8)	2.746(5)	Pd(10)–C(8)–O(8)	141(2)
Pd(7)–Pd(8)a	3.341(4)	Pd(9)–C(9)–O(9)	123(3)
Pd(7)–Pd(10)	2.805(4)	Pd(9)–C(9)–Pd(7)a	82(1)
Pd(7)–Pd(1)b	2.799(4)	O(9)–C(9)–Pd(7)a	126(2)
Pd(8)–Pd(10)	2.801(5)	Pd(8)–C(10)–O(10)	130(3)
Pd(8)–Pd(9)a	2.772(4)	Pd(9)–C(11)–Pd(12)	88(1)
Pd(9)–Pd(10)	2.701(4)	Pd(12)–C(11)–O(11)	134(3)
Pd(9)–Pd(12)	2.782(5)	Pd(12)–C(11)–Pd(8)a	80(1)
Pd(9)–Pd(8)a	2.772(4)	Pd(7)–C(12)–Pd(12)	83(1)
Pd(12)–Pd(8)a	2.804(4)	Pd(12)–C(12)–O(12)	151(3)
Pd(5)–P(2)	2.30(1)	C(111)–C(112)–C(113)	109(3)
Pd(10)–P(4)	2.33(1)	P(1)–C(121)–C(122)	112(3)
Pd(12)–P(6)	2.30(2)	C(122)–C(123)–C(124)	111(4)
Pd(1)–C(3)a	2.23(5)	C(131)–C(132)–C(133)	113(4)
Pd(2)–C(1)	2.17(4)	P(2)–C(211)–C(212)	108(4)
Pd(2)–C(6)a	2.09(4)	C(212)–C(213)–C(214)	121(8)
Pd(3)–C(5)	2.15(5)	C(221)–C(222)–C(223)	91(9)
Pd(4)–C(1)	1.99(5)	P(2)–C(231)–C(232)	111(3)
Pd(5)–C(2)	1.98(4)	C(232)–C(233)–C(234)	91(7)
Pd(6)–C(4)	2.10(4)	C(311)–C(312)–C(313)	115(7)
Pd(7)–C(8)	2.05(5)	P(3)–C(321)–C(322)	145(8)
Pd(7)–C(9)a	2.06(4)	C(322)–C(323)–C(324)	111(9)
Pd(8)–C(10)	2.11(4)	C(331)–C(332)–C(333)	151(9)
Pd(9)–C(7)	2.10(3)	P(4)–C(411)–C(412)	112(3)
Pd(9)–C(11)	1.93(5)	C(412)–C(413)–C(414)	110(4)
Pd(10)–C(8)	1.95(4)	C(421)–C(422)–C(423)	109(4)
Pd(11)–C(10)	2.04(4)	P(4)–C(431)–C(432)	112(3)
Pd(12)–C(12)	1.96(4)	C(432)–C(433)–C(434)	109(5)
Pd(1)–C(4)a	2.07(4)	C(511)–C(512)–C(513)	104(4)
Pd(6)–C(6)a	2.04(4)	P(5)–C(521)–C(522)	112(3)
Pd(8)–C(11)a	2.30(4)	C(522)–C(523)–C(524)	100(7)
P(1)–C(121)	1.86(3)	C(531)–C(532)–C(533)	100(4)
P(2)–C(211)	1.77(7)	P(6)–C(611)–C(612)	117(4)
P(2)–C(231)	1.92(6)	C(612)–C(613)–C(614)	94(6)

Table 2 (Continued)

Bond	<i>d</i> , Å	Angle	ω , deg.
P(3)–C(321)	1.91(9)	C(621)–C(622)–C(623)	112(5)
P(4)–C(411)	1.77(4)	P(6)–C(631)–C(632)	111(5)
P(4)–C(431)	1.85(4)	C(632)–C(633)–C(634)	114(5)
P(5)–C(521)	1.86(5)		
P(6)–C(611)	1.96(5)		
P(6)–C(631)	1.83(5)		
O(2)–C(2)	1.15(5)		
O(4)–C(4)	1.10(4)		
O(6)–C(6)	1.23(5)		
O(8)–C(8)	1.24(5)		
O(10)–C(10)	1.14(5)		
O(12)–C(12)	1.18(5)		
C(112)–C(113)	1.53(6)		
C(121)–C(122)	1.49(7)		
C(123)–C(124)	1.41(9)		
C(132)–C(133)	1.59(9)		
C(211)–C(212)	1.48(7)		
C(213)–C(214)	1.30(11)		
C(222)–C(223)	2.0(2)		
C(231)–C(232)	1.54(6)		
C(233)–C(234)	1.26(9)		
C(312)–C(313)	1.8(1)		
C(321)–C(322)	1.1(2)		
C(323)–C(324)	1.2(2)		
C(332)–C(333)	1.6(2)		
C(411)–C(412)	1.63(4)		
C(413)–C(414)	1.57(2)		
C(422)–C(423)	1.54(2)		
C(431)–C(432)	1.55(2)		
C(433)–C(434)	1.56(2)		
C(512)–C(513)	1.71(3)		
C(521)–C(522)	1.61(2)		
C(523)–C(524)	1.31(3)		
C(532)–C(533)	1.80(4)		
C(611)–C(612)	1.50(2)		
C(613)–C(614)	1.6(2)		
C(622)–C(623)	1.55(8)		
C(631)–C(632)	1.50(6)		
C(633)–C(634)	1.34(8)		

by the published method [19] and isolated from CHCl_3 media as $\text{Pd}_2(\text{DBA})_3\text{CHCl}_3$ solvate. (Found: Pd 20.25%, $\text{C}_{52}\text{H}_{43}\text{O}_3\text{Cl}_3\text{Pd}_2$ calculated: Pd 20.56%.) All operations on the synthesis and isolation of the compounds studied were carried out under argon. IR spectra were recorded on Specord 75IR spectrometer in Nujol mulls. ^{31}P NMR spectra in toluene were obtained on Bruker AMX-400 spectrometer at working frequency of 161.9 MHz for protons.

3.1. Synthesis of $\text{Pd}_{12}(\text{CO})_{12}(\text{PBu}_3)_6$ from $\text{Pd}_4(\text{CO})_5(\text{PBu}_3)_4$ and Me_3NO

Samples of 1 ml HOAc and 1 ml of EtOH were added to a solution of 0.200g (0.145 mmol) of $\text{Pd}_4(\text{CO})_5(\text{PBu}_3)_4$ and 0.081g (0.73 mmol) of $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$, in the mixture of 5 ml of Me_2CO and 1 ml of Et_2O . The mixture was left for 24 h, and crystals were precipitated in an

atmosphere of H_2O vapour over 5 days. The obtained mixture of two types of the crystals was washed by EtOH, dried in vacuo and subdivided manually under microscope. 0.032g of red crystalline $\text{Pd}_{10}(\text{CO})_{12}(\text{PBu}_3)_6$ (21% yield), identified by the IR spectra, and 0.018 g of black hexagonal prismatic crystals of $\text{Pd}_{12}(\text{CO})_{12}(\text{PBu}_3)_6$ (**I**, 13% yield), suitable for X-ray study, were obtained. Found: C 35.47, H 5.67%. $\text{C}_{84}\text{H}_{162}\text{O}_{12}\text{P}_6\text{Pd}_{12}$ calculated: C 35.69, H 5.78%. IR data for **I** (ν_{CO} , cm^{-1}): 1882ms, 1859s, 1803s. ^{31}P NMR: -3.41 ppm.

3.2. Synthesis of $\text{Pd}_{12}(\text{CO})_{12}(\text{PBu}_3)_6$ from $\text{Pd}_{10}(\text{CO})_{12}(\text{PBu}_3)_6$ and Me_3NO

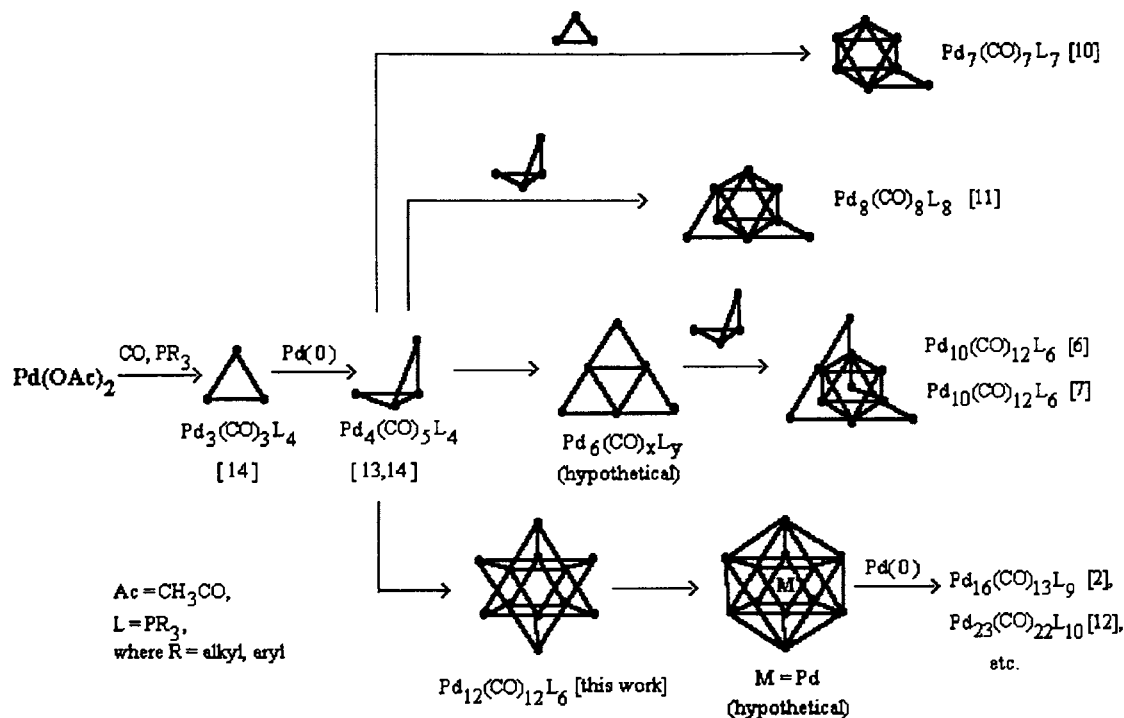
Six millilitres of Me_2CO , 1 ml of EtOH and 0.3 ml of 25% solution of Me_3N in water were added to 0.200g (0.076 mmol) of $\text{Pd}_{10}(\text{CO})_{12}(\text{PBu}_3)_6$ and 0.034g (0.31 mmol) of $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$. The mixture was stirred 10 min at 50°C (thermostated), then cooled to room temperature, and the gas atmosphere changed with fresh argon. After leaving the mixture for 24 h, 0.029 g of black tiny crystals of $\text{Pd}_{12}(\text{CO})_{12}(\text{PBu}_3)_6$ were isolated (16% yield). Found: Pd 44.53, P 6.56%. $\text{C}_{84}\text{H}_{162}\text{O}_{12}\text{P}_6\text{Pd}_{12}$ calculated: Pd 45.17, P 6.57%. IR (ν_{CO} , cm^{-1}): 1881m, 1858ms, 1803s. ^{31}P NMR: -3.39 ppm.

3.3. Synthesis of $\text{Pd}_{12}(\text{CO})_{12}(\text{PBu}_3)_6$ from $\text{Pd}_{10}(\text{CO})_{12}(\text{PBu}_3)_6$ and $\text{Pd}_2(\text{DBA})_3$

A sample of 0.220 g $\text{Pd}_{10}(\text{CO})_{12}(\text{PBu}_3)_6$ (0.084 mmol) was added to 0.079g of $\text{Pd}_2(\text{DBA})_3$ in a mixture of 5 ml of Me_2CO and 3 ml of EtOH. The suspension was stirred for 1.5 h at 40°C , then 3 h more with a continuous cooling to room temperature. 0.082g of $\text{Pd}_{12}(\text{CO})_{12}(\text{PBu}_3)_6$ was obtained [41% yield on $\text{Pd}_{10}(\text{CO})_{12}(\text{PBu}_3)_6$]. Found: Pd 44.75, P 6.43%. $\text{C}_{84}\text{H}_{162}\text{O}_{12}\text{P}_6\text{Pd}_{12}$ calculated: Pd 45.17, P 6.57%. IR (ν_{CO} , cm^{-1}): 1880m, 1859s, 1803s.

3.4. X-ray study of (**I**)

Crystals of (**I**) are triclinic, $a = 14.831(3)$, $b = 18.007(4)$, $c = 22.549(5)$ Å, $\alpha = 83.27(3)$, $\beta = 89.97(3)$, $\gamma = 68.25(3)^\circ$, space group $P\bar{1}$, $Z = 2$ (two molecules in two independent inversion centres). Unit cell parameters and intensities of 7410 independent reflections were measured with Siemens P3/PC diffractometer at -100°C ($\lambda\text{Mo } K_\alpha$, graphite monochromator, $\theta/2\theta$ scan, $2\theta_{\text{max}} = 44^\circ$). The structure was solved by direct methods and refined by the block-diagonal least squares technique to $R = R_w = 0.0645$ on 4452 unique nonzero reflections ($\mathbf{I} > 3\sigma_{\mathbf{I}}$). Atomic co-ordinates and full list of the geometric parameters in **I** are deposited in the Cambridge Crystal Structure Data Centre. Calculations were carried out using the SHELXTL + programmes (PC version).



Scheme 1.

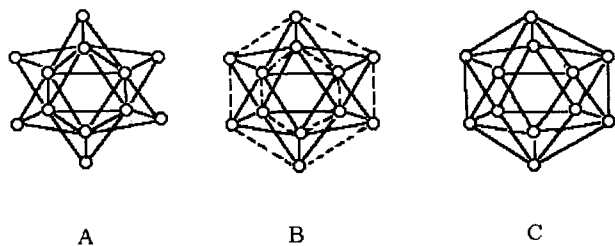


Fig. 2. Metal polyhedron in (I) (B) as an intermediate geometry type between a regular six-capped octahedron (A) and a regular icosahedron (C).

References

- [1] G. Schmid (Ed.), Clusters and Colloids. From Theory to Applications, VCH, Weinheim, 1994.
- [2] L.F. Dahl, J. Am. Chem. Soc. 119 (1997) 4545, and references therein.
- [3] G. Suss-Fink, Angew. Chem. 103 (1991) 73.
- [4] E.G. Mednikov, Yu.L. Slovokhotov, Yu.T. Struchkov, Metalloorg. Khim. (Russ.) 4 (1991) 123.
- [5] E.G. Mednikov, Metalloorg. Khim. 4 (1991) 885.

- [6] C.A. Tolman, Chem. Rev. 77 (1977) 313.
- [7] R.J. Gaudsmit, B.F.G. Johnson, J. Lewis, P.R. Raithby, K.H. Whitmire, J. Chem. Soc. Chem. Commun. (1982) 640.
- [8] E.G. Mednikov, N.K. Eremenko, S.P. Gubin, Yu.L. Slovokhotov, Yu.T. Struchkov, J. Organometal. Chem. 239 (1982) 401.
- [9] E.G. Mednikov, N.K. Eremenko, Yu.L. Slovokhotov, Yu.T. Struchkov, S.P. Gubin, J. Organometal. Chem. 252 (1983) 247.
- [10] G. Longoni, M. Manassero, M. Sansoni, J. Am. Chem. Soc. 102 (1980) 7973.
- [11] J.L. Vidal, J.M. Troup, J. Organometal. Chem. 213 (1981) 351.
- [12] R. Goddard, P. Jolly, C. Krueger, K.-P. Schick, G. Wilke, Organometallics 1 (1982) 1709.
- [13] M. Bochmann, I. Hawkins, M.B. Hursthouse, R.L. Short, Polyhedron 6 (1987) 1987.
- [14] E.G. Mednikov, N.K. Eremenko, Yu.L. Slovokhotov, Yu.T. Struchkov, J. Organometal. Chem. 301 (1986) 35.
- [15] R.D. Feltham, G. Elbaze, R. Ortega, C. Eck, J. Dubrawskii, Inorg. Chem. 24 (1985) 1503.
- [16] E.G. Mednikov, N.K. Eremenko, Yu.L. Slovokhotov, Yu.T. Struchkov, S.P. Gubin, Koord. Khim. (Russ.) 13 (1987) 979.
- [17] K. Wade, Adv. Inorg. Chem. Radiochem. 18 (1976) 1.
- [18] Yu.L. Slovokhotov, Yu.T. Struchkov, J. Organometal. Chem. 333 (1987) 217.
- [19] Y. Takahashi, Ts. Ito, S. Sakai, Y. Ishii, J. Chem. Soc. Chem. Commun. (1970) 1065.