

## SYNTHESIS AND STRUCTURE OF POLYNUCLEAR CARBONYLPHOSPHINE CLUSTERS OF PALLADIUM

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### Summary

Reductive condensation of  $\text{Pd}(\text{OAc})_2$  in dioxane in the presence of CO and  $\text{PR}_3$  ( $\text{R} = \text{Et}, \text{Bu}^n$ ) with addition of  $\text{CF}_3\text{COOH}$  leads to the formation of decanuclear  $\text{Pd}_{10}(\mu_3\text{-CO})_4(\mu_2\text{-CO})_8(\text{PBu}^n_3)_6$  (I) and  $\text{Pd}_{10}(\text{CO})_{14}(\text{PBu}^n_3)$  (II) at  $\text{Pd}(\text{OAc})_2:\text{PR}_3$  molar ratios of 1:4–1:10 and 1:1.5–1:2.5, respectively. The use of  $\text{CH}_3\text{COOH}$  instead of  $\text{CF}_3\text{COOH}$  results in tetranuclear clusters  $\text{Pd}_4(\text{CO})_5(\text{PR}_3)_4$  (III) and  $\text{Pd}_4(\mu_2\text{-CO})_6(\text{PBu}^n_3)$  (IV).  $\text{I} \rightleftharpoons \text{III}$  and  $\text{III} \rightarrow \text{IV}$  transformations occur in organic media. The structures of I (space group  $P2_1/n$ ,  $Z = 4$ ;  $\lambda\text{Mo}$ , 12125 independent reflections,  $R = 0.047$ ) and IV ( $P\bar{3}$ ,  $Z = 3$ ;  $\lambda\text{Mo}$ , 3254 reflections,  $R = 0.098$ ) were established by X-ray diffraction analysis. Cluster I is a 10-vertex  $\text{Pd}_{10}$  polyhedron, an octahedron with four unsymmetrically centered non-adjacent faces. The average Pd–Pd distances in the octahedron are 2.825 Å, in the eight short  $\text{Pd}_{\text{oct.}}\text{--Pd}_{\text{cap.}}$  bonds with the “equatorial” Pd atoms of the inner octahedron, bridged by the  $\mu_2\text{-CO}$  ligands, are 2.709 Å, and in the four elongated (without bridging CO groups) bonds with the apical Pd atoms of the octahedron are 3.300–3.422 Å. The  $\text{PBu}^n_3$  ligands are coordinated to the apical Pd atoms and the capping atoms (Pd–P 2.291–2.324 Å). Cluster IV is tetrahedral, with the CO ligands symmetrically bridged; Pd–Pd 2.778–2.817; Pd–P 2.232–2.291; Pd–C 2.06 Å (average).

### Introduction

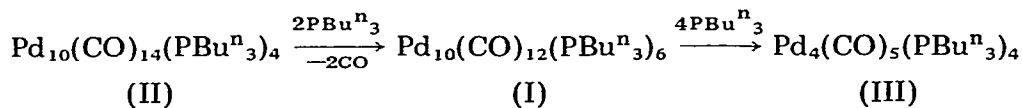
The recently discovered ability of  $\text{Pd}^{\text{II}}$  diacetate to condense during mild reduction with carbon monoxide in the presence of trialkylphosphines made it

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possible to synthesize the polynuclear cluster complexes  $\text{Pd}_n(\text{CO})_x(\text{PR}_3)_y$  [1]. Two 10-nuclear clusters were obtained in dioxane in the presence of  $\text{CF}_3\text{COOH}$ ; namely  $\text{Pd}_{10}(\text{CO})_{12}(\text{PR}_3)_6$  (I;  $\text{R} = \text{Et}, \text{Bu}^n$ ), in the range of  $\text{Pd}(\text{OAc})_2:\text{PR}_3$  molar ratios of 1:4—1:10, and  $\text{Pd}_{10}(\text{CO})_{14}(\text{PR}_3)_4$  (II,  $\text{R} = \text{Bu}^n$ ) at molar ratios of 1:1.5—1:2.5. Preliminary results of an X-ray diffraction investigation of I ( $\text{R} = \text{Bu}^n$ ) were reported earlier in a short communication [2]. Substitution of trifluoroacetic acid by acetic acid with the addition of  $\text{NaOAc}$  leads to the formation of new palladium clusters such as  $\text{Pd}_4(\text{CO})_5(\text{PR}_3)_4$  (III,  $\text{R} = \text{Et}, \text{Bu}^n$ ) [3] and  $\text{Pd}_4(\text{CO})_6(\text{PR}_3)_4$  (IV); the latter is formed from III during crystallization in CO atmosphere. Complex III can also be obtained by treatment of decanuclear cluster I by a stoichiometric amount of  $\text{PBu}^n_3$ , while I, in turn, is formed from II as two terminal CO groups are substituted by  $\text{PBu}^n_3$  ligands.



The stability of tetra- and deca-nuclear palladium clusters is characterized by the  $\text{I} \rightleftharpoons \text{III}$  interconversion observed by the authors. Both the forward and the back pathways of this reaction can be carried out with high selectivity.

In order to establish unambiguously the structure of the clusters synthesized, and, in the long run, to elucidate the mechanism of the formation of the  $\text{Pd}_n$  associates in solution, we carried out an X-ray diffraction investigation of I and IV\*.

## Results and discussion

At present, several ways of obtaining transition metal clusters are known: oxidative coupling, oxidative-reductive condensation and thermal condensation [4]. In our research the redox condensation under mild conditions (organic media, eq. 1) was employed, and a method was proposed for the preparation of the polynuclear clusters by condensation of clusters with smaller numbers of metal atoms as a result of a change in the ligand concentration (eq. 2); the formal oxidation state of the metal in this method is unchanged, because both clusters are derivatives of  $\text{Pd}^0$ :



Earlier, a series of carbonylphosphine  $\text{Pd}_n$ -clusters was obtained for  $n = 3$ :  $\text{Pd}_3(\text{CO})_3(\text{PPh}_3)_3$ ,  $\text{Pd}_3(\text{CO})_3(\text{PPh}_3)_4$  [5] and  $\text{Pd}_3(\text{CO})_3\text{L}_3$ ,  $\text{L} = \text{PBu}^t_3$  [6]; tetranuclear  $\text{Pd}_4(\text{CO})_3(\text{PPhMe}_2)_4$  (V) was also isolated and its structure was studied; its  $\text{Pd}_4$  fragment has a "butterfly" configuration [7]. The known carbonylphosphine clusters of platinum are characterized by the values of  $n = 3-5$ .

The structures of I and IV were determined by X-ray diffraction analysis. The atomic coordinates of structure I are listed in Table 1, the most important

\* The structure of III was also confirmed by X-ray data to be published separately.

TABLE 1

THE ATOMIC COORDINATES ( $\times 10^4$ , for Pd and P  $\times 10^5$ ) OF I

Atom	x	y	z
Pd(1)	18462(3)	73266(2)	13152(3)
Pd(2)	32069(3)	72672(2)	6669(3)
Pd(3)	24527(3)	73258(2)	-6186(3)
Pd(4)	11128(3)	73961(2)	328(3)
Pd(5)	20561(3)	66530(2)	3316(3)
Pd(6)	22507(3)	79999(2)	3835(3)
Pd(7)	29687(3)	67920(2)	18024(3)
Pd(8)	12215(3)	69166(2)	-11280(3)
Pd(9)	6607(3)	78806(2)	11009(3)
Pd(10)	38062(3)	76811(2)	-4020(3)
P(1)	19058(12)	58661(8)	2697(11)
P(2)	24771(12)	87764(8)	4113(12)
P(3)	34533(11)	64790(8)	27826(11)
P(4)	5600(12)	66418(8)	-20480(11)
P(5)	-3263(12)	82536(8)	15331(11)
P(6)	49283(12)	77818(9)	-8654(11)
O(1)	588(3)	6624(2)	1021(3)
O(2)	3478(3)	6472(2)	-386(3)
O(3)	3072(3)	8029(2)	1758(3)
O(4)	1460(3)	8179(2)	-982(3)
O(5)	1531(3)	6714(2)	2488(3)
O(6)	4457(3)	6671(2)	1197(3)
O(7)	2589(3)	6783(3)	-1900(3)
O(8)	-248(3)	6903(2)	-458(3)
O(9)	1311(3)	7830(2)	2533(3)
O(10)	4614(3)	7792(3)	937(3)
O(11)	3096(3)	7828(3)	-1793(3)
O(12)	-142(3)	8047(3)	-251(3)
C(1)	1112(5)	6798(3)	808(4)
C(2)	3031(4)	6701(3)	-134(4)
C(3)	2579(4)	7850(3)	1298(4)
C(4)	1712(5)	7940(4)	-533(4)
C(5)	1954(4)	6851(3)	2122(4)
C(6)	3869(4)	6819(3)	1263(4)
C(7)	2223(4)	6917(3)	-1481(4)
C(8)	352(4)	7008(3)	-541(4)
C(9)	1240(4)	7743(3)	1960(4)
C(10)	4163(4)	7654(3)	562(4)
C(11)	3157(4)	7701(3)	-1247(4)
C(12)	280(4)	7879(3)	129(4)
C(111)	1019(5)	5624(3)	498(5)
C(112)	377(5)	5764(3)	-5(5)
C(113)	-372(5)	5702(4)	302(5)
C(114)	-998(6)	5814(4)	-216(5)
C(121)	2024(5)	5640(3)	-585(5)
C(122)	2072(5)	5122(3)	-648(5)
C(123)	2003(6)	4964(4)	-1376(5)
C(124)	2151(7)	4430(4)	-1423(6)
C(131)	2525(5)	5511(3)	806(5)
C(132)	3350(5)	5597(4)	681(5)
C(133)	3839(6)	5270(4)	1068(6)
C(134)	4663(7)	5374(6)	962(9)
C(211)	1975(6)	9148(3)	998(5)
C(212)	2011(5)	8958(4)	1731(5)
C(213)	1671(6)	9299(4)	2227(5)
C(214)	1695(8)	9116(5)	2924(6)
C(221)	2288(5)	9097(3)	-378(5)
C(222)	2795(5)	8945(4)	-951(4)
C(223)	2470(6)	9067(4)	-1650(5)

TABLE I (continued)

THE ATOMIC COORDINATES ( $\times 10^4$ , for Pd and P  $\times 10^5$ ) OF I

Atom	x	y	z
C(224)	2378(8)	9575(5)	-1748(7)
C(231)	3447(5)	8879(3)	613(5)
C(232)	3699(5)	9384(3)	686(6)
C(233)	4549(5)	9427(4)	678(5)
C(234)	4832(6)	9370(4)	-49(6)
C(311)	4303(5)	6139(4)	2728(5)
C(312)	4681(6)	6016(4)	3408(6)
C(313)	5354(6)	5705(5)	3305(6)
C(314)	5152(8)	5229(5)	3033(7)
C(321)	2849(5)	6119(3)	3270(4)
C(322)	2581(6)	5680(4)	2903(5)
C(323)	2126(5)	5387(4)	3347(5)
C(324)	1425(7)	5610(5)	3565(7)
C(331)	3668(5)	6934(4)	3394(5)
C(332)	3101(5)	7325(4)	3366(5)
C(333)	3232(7)	7689(4)	3895(6)
C(334)	2718(9)	8098(5)	3801(8)
C(411)	-105(5)	6188(4)	-1858(4)
C(412)	-623(5)	6042(4)	-2449(5)
C(413)	-1155(6)	5661(4)	-2223(6)
C(414)	-759(7)	5217(4)	-2093(7)
C(421)	1059(5)	6408(3)	-2753(4)
C(422)	1466(5)	5968(4)	-2572(5)
C(423)	2004(6)	5818(5)	-3111(6)
C(424)	1604(7)	5689(5)	-3768(6)
C(431)	-28(6)	7095(4)	-2423(5)
C(432)	315(5)	7569(4)	-2430(5)
C(433)	1019(5)	7621(4)	-2842(5)
C(434)	1271(6)	8132(4)	-2864(6)
C(511)	5318(5)	7215(4)	-1000(4)
C(512)	5506(5)	6956(4)	-328(5)
C(513)	5805(7)	6486(4)	-456(6)
C(514)	6039(9)	6224(5)	205(7)
C(521)	4921(5)	8032(4)	-1711(5)
C(522)	4731(5)	8335(4)	-1702(5)
C(523)	4651(7)	8726(5)	-2433(6)
C(524)	4479(7)	9264(6)	-2381(9)
C(531)	5631(5)	8088(3)	-354(4)
C(532)	6416(5)	8079(4)	-625(5)
C(533)	6975(5)	8317(4)	-148(5)
C(534)	7076(6)	8075(5)	532(6)
C(611)	-802(5)	8619(3)	958(5)
C(612)	-462(7)	9024(4)	690(6)
C(613)	945(13)	710(5)	9831(8)
C(614')	688(18)	236(10)	10021(13)
C(614'')	1392(21)	410(12)	9564(19)
C(621)	-1021(5)	7837(3)	1800(5)
C(622)	-1160(6)	7465(4)	1256(5)
C(623)	-1782(6)	7146(4)	1440(5)
C(624)	-1876(9)	6771(5)	895(7)
C(631)	-148(4)	8608(3)	2272(4)
C(632)	-808(5)	8872(4)	2545(5)
C(633)	-578(6)	9145(4)	3182(5)
C(634)	-1212(6)	9431(5)	3418(6)

TABLE 2  
MAIN BOND LENGTHS (Å) IN MOLECULE I

Bond	<i>d</i>	Bond	<i>d</i>
Pd(1)—Pd(2)	2.846(1)	Pd(2)—C(6)	2.112(9)
Pd(1)—Pd(4)	2.831(1)	Pd(7)—C(6)	1.999(8)
Pd(1)—Pd(5)	2.813(1)	Pd(3)—C(7)	2.116(9)
Pd(1)—Pd(6)	2.823(1)	Pd(8)—C(7)	1.983(7)
Pd(2)—Pd(3)	2.851(1)	Pd(4)—C(8)	2.093(8)
Pd(2)—Pd(5)	2.821(1)	Pd(8)—C(8)	2.023(8)
Pd(2)—Pd(6)	2.807(1)	Pd(1)—C(9)	2.112(8)
Pd(3)—Pd(4)	2.818(1)	Pd(9)—C(9)	2.007(8)
Pd(3)—Pd(5)	2.842(1)	Pd(8)—C(10)	2.095(9)
Pd(3)—Pd(6)	2.838(1)	Pd(10)—C(10)	1.996(8)
Pd(4)—Pd(5)	2.821(1)	Pd(3)—C(11)	2.131(8)
Pd(4)—Pd(6)	2.791(1)	Pd(10)—C(11)	2.011(8)
Pd(1)—Pd(7)	2.721(1)	Pd(4)—C(12)	2.090(8)
Pd(1)—Pd(9)	2.721(1)	Pd(9)—C(12)	2.021(8)
Pd(2)—Pd(7)	2.700(1)	C(1)—O(1)	1.175(10)
Pd(2)—Pd(10)	2.713(1)	C(2)—O(2)	1.181(10)
Pd(3)—Pd(8)	2.702(1)	C(3)—O(3)	1.179(10)
Pd(3)—Pd(10)	2.694(1)	C(4)—O(4)	1.210(11)
Pd(4)—Pd(8)	2.713(1)	C(5)—O(5)	1.153(10)
Pd(4)—Pd(9)	2.708(1)	C(6)—O(6)	1.168(10)
Pd(5)—Pd(7)	3.323(1)	C(7)—O(7)	1.155(10)
Pd(5)—Pd(8)	3.305(1)	C(8)—O(8)	1.154(10)
Pd(6)—Pd(9)	3.300(1)	C(9)—O(9)	1.168(10)
Pd(6)—Pd(10)	3.422(1)	C(10)—O(10)	1.152(10)
Pd(5)—P(1)	2.324(2)	C(11)—O(11)	1.147(10)
Pd(6)—P(2)	2.321(3)	C(12)—O(12)	1.162(10)
Pd(7)—P(3)	2.293(2)	P(1)—C(111)	1.838(9)
Pd(8)—P(4)	2.291(2)	P(1)—C(121)	1.842(9)
Pd(9)—P(5)	2.301(2)	P(1)—C(131)	1.840(10)
Pd(10)—P(6)	2.296(2)	P(2)—C(211)	1.862(10)
Pd(1)—C(1)	2.255(9)	P(2)—C(221)	1.847(10)
Pd(4)—C(1)	2.332(9)	P(2)—C(231)	1.820(10)
Pd(5)—C(1)	2.043(8)	P(3)—C(311)	1.849(10)
Pd(2)—C(2)	2.310(9)	P(3)—C(321)	1.831(9)
Pd(3)—C(2)	2.301(9)	P(3)—C(331)	1.832(11)
Pd(5)—C(2)	2.042(8)	P(4)—C(411)	1.848(10)
Pd(1)—C(3)	2.263(8)	P(4)—C(421)	1.833(9)
Pd(2)—C(3)	2.288(8)	P(4)—C(431)	1.845(11)
Pd(6)—C(3)	2.050(8)	P(5)—C(511)	1.839(10)
Pd(3)—C(4)	2.259(10)	P(5)—C(521)	1.852(10)
Pd(4)—C(4)	2.256(10)	P(5)—C(531)	1.815(9)
Pd(6)—C(4)	2.037(8)	P(6)—C(611)	1.831(11)
Pd(1)—C(5)	2.125(9)	P(6)—C(621)	1.830(10)
Pd(7)—C(5)	1.988(8)	P(6)—C(631)	1.836(9)

bond lengths in Table 2 and the bond angles in Table 3. Figure 1 shows cluster I. The coordinates of atoms in structure IV are given in Table 4, and Fig. 2 presents cluster IV with its main bond lengths. \*

\* Complete data on the structural amplitudes and tables of temperature parameters of atoms of structures I and IV can be obtained from the authors.

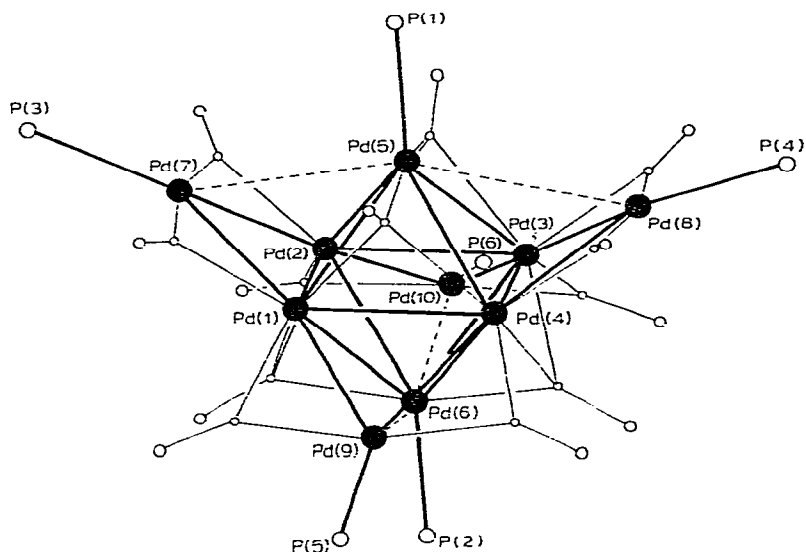


Fig. 1. Molecule I (n-butyl substituents are not shown)

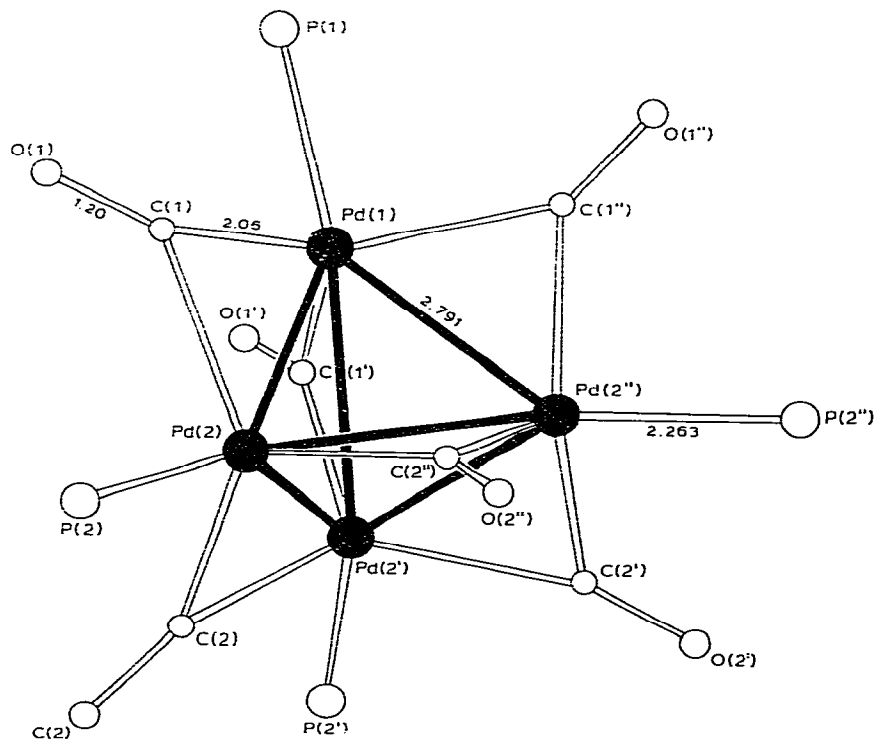


Fig. 2. Molecule IVA (n-butyl substituents not shown) with several bond lengths averaged over two crystallographically independent molecules A and B.

TABLE 3  
MAIN BOND ANGLES (degrees) IN MOLECULE I

Angle	$\omega$	Angle	$\omega$
Pd(1)Pd(5)P(1)	135.50(6)	Pd(6)C(4)O(4)	139.6(7)
Pd(2)Pd(5)P(1)	136.88(6)	Pd(1)C(5)Pd(7)	82.8(3)
Pd(3)Pd(5)P(1)	133.28(6)	Pd(1)C(5)O(5)	131.4(7)
Pd(4)Pd(5)P(1)	133.24(6)	Pd(7)C(5)O(5)	145.6(7)
Pd(1)Pd(6)P(2)	136.32(6)	Pd(2)C(6)Pd(7)	82.1(3)
Pd(2)Pd(6)P(2)	129.74(6)	Pd(2)C(6)O(6)	132.3(7)
Pd(3)Pd(6)P(2)	132.32(6)	Pd(7)C(6)O(6)	145.4(7)
Pd(4)Pd(6)P(2)	139.41(6)	Pd(3)C(7)Pd(8)	82.4(3)
Pd(1)Pd(7)P(3)	142.02(6)	Pd(3)C(7)O(7)	132.3(7)
Pd(2)Pd(7)P(3)	147.63(6)	Pd(8)C(7)O(7)	145.2(7)
Pd(1)Pd(7)Pd(2)	63.35(2)	Pd(4)C(8)Pd(8)	82.4(3)
Pd(3)Pd(8)P(4)	148.73(6)	Pd(4)C(8)O(8)	132.5(7)
Pd(4)Pd(8)P(4)	143.51(6)	Pd(8)C(8)O(8)	144.8(7)
Pd(3)Pd(8)Pd(4)	62.72(2)	Pd(1)C(9)Pd(9)	82.6(3)
Pd(1)Pd(9)P(5)	148.52(6)	Pd(1)C(9)O(9)	132.6(7)
Pd(4)Pd(9)P(5)	144.02(6)	Pd(9)C(9)O(9)	144.6(7)
Pd(1)Pd(9)Pd(4)	62.86(2)	Pd(2)C(10)Pd(10)	83.0(3)
Pd(2)Pd(10)P(6)	139.94(7)	Pd(2)C(10)O(10)	134.1(7)
Pd(3)Pd(10)P(6)	144.11(7)	Pd(10)C(10)O(10)	142.7(7)
Pd(2)Pd(10)Pd(3)	63.64(2)	Pd(3)C(11)Pd(10)	81.1(3)
Pd(1)C(1)Pd(4)	76.2(3)	Pd(3)C(11)O(11)	133.1(7)
Pd(1)C(1)Pd(5)	81.6(3)	Pd(10)C(11)O(11)	145.8(7)
Pd(4)C(1)Pd(5)	80.0(3)	Pd(4)C(12)Pd(9)	82.4(3)
Pd(1)C(1)O(1)	127.8(6)	Pd(4)C(12)O(12)	133.6(7)
Pd(4)C(1)O(1)	125.9(6)	Pd(9)C(12)O(12)	144.0(7)
Pd(5)C(1)O(1)	142.0(7)	Pd(5)P(1)C(111)	118.2(3)
Pd(2)C(2)Pd(3)	76.4(3)	Pd(5)P(1)C(121)	112.8(3)
Pd(2)C(2)Pd(5)	80.6(3)	Pd(5)P(1)C(131)	117.5(3)
Pd(3)C(2)Pd(5)	81.5(3)	Pd(6)P(2)C(211)	119.9(3)
Pd(2)C(2)O(2)	128.4(6)	Pd(6)P(2)C(221)	117.0(3)
Pd(3)C(2)O(2)	125.9(6)	Pd(6)P(2)C(231)	109.7(3)
Pd(5)C(2)O(2)	141.2(7)	Pd(7)P(3)C(311)	117.4(3)
Pd(1)C(3)Pd(2)	77.4(3)	Pd(7)P(3)C(321)	117.4(3)
Pd(1)C(3)Pd(6)	81.6(3)	Pd(7)P(3)C(331)	109.5(3)
Pd(2)C(3)Pd(6)	80.4(3)	Pd(8)P(4)C(411)	114.7(3)
Pd(1)C(3)O(3)	128.4(6)	Pd(8)P(4)C(421)	118.6(3)
Pd(2)C(3)O(3)	125.8(6)	Pd(8)P(4)C(431)	110.2(3)
Pd(5)C(3)O(3)	142.2(3)	Pd(9)P(5)C(511)	117.6(3)
Pd(3)C(4)Pd(4)	77.2(3)	Pd(9)P(5)C(521)	110.4(3)
Pd(3)C(4)Pd(6)	82.5(3)	Pd(9)P(5)C(531)	117.2(3)
Pd(4)C(4)Pd(6)	80.9(3)	Pd(10)P(6)C(611)	107.4(3)
Pd(3)C(4)O(4)	128.0(7)	Pd(10)P(6)C(621)	116.5(3)
Pd(4)C(4)O(4)	126.8(7)	Pd(10)P(6)C(631)	117.0(3)

### Crystal and molecular structure of I

The decanuclear cluster I is a four-capped octahedron which appears to be a distorted fragment of the three-layer tight packing of the metal atoms. Similar structural patterns were found earlier in homo- and heteronuclear clusters, for example  $[\text{Os}_{10}(\text{CO})_{24}\text{C}]^{2-}$  (VI) [8] and  $\text{Hg}_6\text{Rh}_4(\text{PMe}_3)_{12}$  [9] (four-capped octahedron), and also  $[\text{Pd}_6\text{Fe}_6(\text{CO})_{24}\text{H}]^{3-}$  (VII) (six-capped octahedron [10]). The metal polyhedron structure of the anionic carbide cluster VI is the closest to that of I. In both metal clusters an "inner"  $\text{M}_6$  octahedron can be identified, whose four non-neighbouring tetrahedrally positioned faces are capped by four

TABLE 4  
 ATOMIC COORDINATES ( $\times 10^3$ , for Pd, P  $\times 10^4$ ) OF IV

Atom	x	y	z	Atom	x	y	z
<i>Molecule A</i> <sup>a</sup>							
Pd(1)	0	0	1135(5)	C(32)	711(3)	488(3)	593(3)
Pd(2)	-290(2)	-912(2)	-479(2)	C(33)	722(15)	609(19)	630(18)
P(1)	0	0	2691(15)	C(34)	732(4)	635(4)	619(5)
P(2)	696(6)	2141(6)	977(9)	C(411)	572(2)	91(2)	97(3)
O(1)	-58(1)	-181(1)	125(2)	C(412)	616(3)	150(3)	32(3)
C(1)	-42(1)	-120(2)	94(2)	C(413)	563(4)	135(4)	-65(5)
C(11)	15(8)	109(11)	305(11)	C(414)	654(4)	194(4)	-150(5)
C(12)	37(6)	170(6)	284(6)	C(421)	540(3)	40(3)	283(3)
C(13)	73(7)	273(8)	305(10)	C(422)	476(3)	37(3)	285(4)
C(14)	72(5)	192(5)	430(7)	C(423)	367(10)	-56(9)	308(11)
C(211)	14(6)	272(6)	94(8)	C(424)	378(6)	-28(5)	398(6)
C(212)	-22(4)	263(4)	11(5)	C(431)	680(4)	90(4)	245(5)
C(213)	-116(6)	220(7)	29(7)	C(432)	724(3)	109(3)	318(4)
C(214)	-116(6)	263(6)	-101(8)	C(433)	834(9)	139(8)	298(9)
C(221)	106(5)	250(5)	233(6)	C(434)	807(8)	100(8)	427(9)
C(222)	76(8)	202(9)	286(9)	C(31')	250(5)	666(5)	355(6)
C(223)	61(6)	99(7)	301(7)	C(32')	319(5)	520(6)	376(6)
C(224)	46(10)	54(6)	367(10)	C(33')	289(19)	467(20)	280(21)
C(231)	160(5)	294(5)	84(6)	C(34')	278(8)	437(8)	343(15)
C(232)	-58(4)	217(4)	9(4)	C(411')	628(3)	107(3)	92(3)
C(233)	-75(4)	278(4)	4(5)	C(412')	657(4)	163(3)	22(4)
C(234)	-106(7)	301(7)	-52(9)	C(413')	614(3)	136(3)	-71(4)
<i>Molecule B</i>							
Pd(3)	2/3	1/3	4223(2)	C(414')	606(5)	175(5)	-135(6)
Pd(4)	6449(1)	2437(1)	2645(1)	C(421')	528(4)	43(3)	234(4)
P(3)	2/3	1/3	5798(6)	C(422')	489(5)	52(5)	343(6)
P(4)	6165(4)	1231(3)	2133(4)	C(423')	428(5)	-25(4)	384(6)
O(2)	627(1)	167(2)	458(2)	C(424')	310(8)	-44(7)	416(8)
O(3)	500(1)	206(1)	151(1)	C(431')	707(4)	107(3)	210(4)
				C(432')	760(4)	139(3)	285(5)
				C(433')	793(4)	100(3)	328(4)
				C(434')	870(9)	159(9)	377(12)

<sup>a</sup> Molecule A occupies the special position  $\bar{3}$  and is disordered by the inversion center; molecule B occupies position 3. The first digit in the number of the C atoms of n-butyl substituents corresponds to the number of the P atom bonded to the given Bu<sup>n</sup>. The primed numbers correspond to the second position of the C atoms in the disordered PBu<sup>n</sup><sub>3</sub>.

Pd atoms. In contrast to VI, the arrangement of the capping Pd atoms over the faces of the Pd<sub>6</sub> octahedron in I is unsymmetrical and the octahedron contains no encapsulated atoms. The metal polyhedron Pd<sub>10</sub> in I is coordinated by six PBu<sup>n</sup><sub>3</sub> ligands at the apical atoms of the inner octahedron and the capping atoms, four  $\mu_3$ -CO ligands at the free faces of the Pd<sub>6</sub> octahedron and eight  $\mu_2$ -CO ligands, each shortening two bonds with "equatorial" atoms of the octahedron Pd<sub>cap.</sub>-Pd<sub>oct.</sub> in each capping fragment (in contrast, all the 24 CO ligands in structure VI are terminal).

According to the structure of I, the metal-metal distances in this cluster can be divided into three groups: edges of the inner Pd<sub>6</sub> octahedron (2.791–2.851, average 2.825(17) Å), two short Pd–Pd bonds, connecting each of the capping atoms with two equatorial atoms of the octahedron (2.694–2.721, average



2.709(10) Å) and the distances between the apical atoms of the octahedron Pd(5) and Pd(6) and the capping atoms (one for each such atom), elongated to 3.300–3.422 Å. The cluster nucleus Pd<sub>10</sub>P<sub>6</sub>(CO)<sub>12</sub> of molecule I, occupying a general position in the crystal, is close to idealized *S*<sub>4</sub> symmetry. However, Van der Waals interactions result in slight, but significant distortions (see Tables 2 and 3). The Pd–P distances are in the range of 2.291–2.324 Å (Table 2); the PBu<sup>n</sup><sub>3</sub> ligand bonds to the apical atoms Pd(5) (2.324(2) Å) and Pd(6) (2.312(3) Å) are slightly longer than those to the Pd atoms of the caps (2.291–2.301(2) Å). The coordination of the face-bridging CO ligands is also distinctly unsymmetrical: the apical Pd(5) and Pd(6) atoms form short Pd–C contacts (2.037–2.050 Å), and long (2.255–2.332 Å) bonds with the equatorial Pd atoms (Table 2). The difference between the average values 2.043(5) and 2.283(29) Å are certainly of statistical significance. A smaller but also substantial dissymmetry is observed for the μ<sub>2</sub>-CO bridges: in all cases the Pd–C distance with the capping Pd atom (average 2.004(15) Å) is shorter than that with the Pd atom of the inner octahedron (average 2.109(15) Å). Finally, the C–O bond lengths in face- and edge-bridged ligands also differ. Though these differences lie within the limits of error, the average values 1.186(16) and 1.158(7) Å, respectively, are in good agreement with the general rule found previously [4].

There are 16 “skeletal” electrons in I, i.e. 2e more than required for an octahedron by Wade’s rule [11], while cluster VI satisfies the 2*n* + 2 rule. The main difference between metal polyhedra I and VI lies in the fact, that “slightly opened” caps exist in I, which increases the corresponding Pd–Pd distances to 3.3–3.4 Å (in VI the arrangement of caps over the Os<sub>6</sub> octahedron is symmetrical). It is interesting to note, that the heteronuclear cluster VII also contains 16 skeletal electrons in violation of the 2*n* + 2 rule. In this case, the capped Fe atoms are bonded more symmetrically to the faces of the inner Pd<sub>6</sub> octahedron; however, the octahedron itself displays significant distortions from the trigonal prismatic type [10].

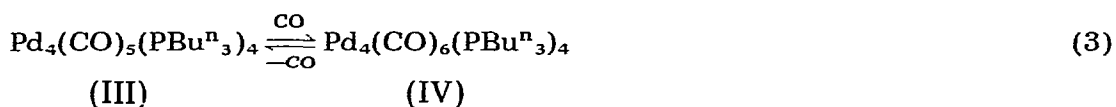
The closest coordination environment of the capping Pd(7)–Pd(10) atoms consists of two equatorial Pd atoms of the inner octahedron, two C atoms of the μ<sub>2</sub>-CO ligands and the P atom of the tri-*n*-butylphosphine ligand. Comparison of the sums of the angles C–Pd–C, C–Pd–P at the capped atoms, on the one hand, and angles Pd–Pd–Pd and Pd–Pd–P at the same atoms, on the other, suggests certain differences between their ligand and closest “cluster” environments: the ligand coordination of the capping Pd(7), Pd(8), Pd(9) and Pd(10) atoms is trigonal planar (the sums of angles being 360.0, 359.9, 359.4 and 360.0°, respectively), while the phosphine–metal coordination is slightly, but clearly nonplanar (353.0, 354.9, 355.4 and 347.7°, respectively). The P atoms are displaced from the Pd<sub>cap.</sub>–Pd<sub>eq.</sub>–Pd<sub>eq.</sub> triangle plane by 0.64, 0.53, 0.51 and 0.86 Å, respectively, in the direction away from the apical Pd(5) and Pd(6) atoms. Such a ligand environment of the Pd(7)–Pd(10) atoms testifies to the absence of strong Pd<sub>apic.</sub>...Pd<sub>cap.</sub> bonding, and the tilting of the P atoms in the direction away from the apical alkylphosphine ligands lends support to the steric origin for the “opening” of the caps. More rigorous discussion of the reasons for the polyhedron distortion in I requires an analysis of the geometry of tri-*n*-butylphosphine ligands and is presented in a special section (see below).

### Crystal and molecular structure of IV

According to the X-ray analysis, IV is a highly symmetrical tetrahedral cluster with apical  $\text{PBU}^n_3$  and edge-bridging CO ligands. In the crystal of IV there are two symmetrically independent molecules; one occupies a special position at the 3 axis, the other (disordered) at the  $\bar{3}$ -axis. However, the cluster nucleus  $\text{Pd}_4(\mu_2\text{-CO})_6\text{P}_4$  (omitting the n-butyl substituents) have a higher idealized  $T_d$  symmetry. The Pd–Pd distances in IV 2.778–2.817(2) Å (average 2.791(18) Å), are closer to the Pd–Pd distances in the inner octahedron of I (average 2.825(17) Å) than to the short Pd–Pd bonds in the same molecule (average 2.709(10) Å), though the latter are also shortened by the  $\mu_2\text{-CO}$  ligands. The Pd–P distances in IV, 2.232–2.291 (average 2.263(26)) Å, are slightly smaller than those for I (average 2.303 Å) and V (average 2.315 Å). The mean value of the Pd–C bond length (2.06(5) Å) in IV practically coincides with the value found for V (2.085 Å) [7] and for  $\mu_2\text{-CO}$  ligands of I (2.056 Å). The crystal of IV is built up of discrete cluster molecules, located at conventional Van der Waals distances from each other.

### Interconversions of I–IV

In solution the clusters obtained readily undergo interconversions and show a marked dependence of structure on the trialkylphosphine concentration. For example, treatment of I with  $\text{PBU}^n_3$  leads to evolution of CO and to a rearrangement of the metal polyhedron, the reaction products containing tetranuclear clusters III and IV. Both compounds are isolable in the solid state, and it is possible to confirm their different CO contents analytically. However, single crystals have so far been obtained only for IV. The best method for their preparation is crystallization of IV from a solution of III under an CO atmosphere, which testifies to the following equilibrium in the solution:



The transformation proceeds readily and, along with IR spectroscopic data, suggests that complex III possesses a “butterfly” structure with apical  $\text{PBU}^n_3$  and edge-bridged CO ligands, similar to that of V.

The reverse transformation III → I occurs as the phosphine is removed under the action of different reagents ( $\text{H}^+$ ,  $\text{O}_2$ , etc.). In spite of the substantial structural difference, the I ⇌ III transformations are sufficiently selective and do not result in any appreciable amounts of intermediate cluster compounds.

The II → I transformation under the action of  $\text{PR}_3$  is, according to X-ray analysis data, a substitution of two terminal CO ligands at the Pd apical atoms in the  $\text{Pd}_{10}$  polyhedron of molecule II by  $\text{PR}_3$  ligands, which is accompanied by the disappearance of the  $\nu(\text{CO})$  absorption at  $2034\text{ cm}^{-1}$  in the IR spectrum, and the appearance of two signals in  $^{31}\text{P}$  NMR of complex I (the intensity ratio being 2:1) instead of one signal in II [2]. The changes in NMR spectra reflect the fact that the  $\text{PR}_3$  ligands occupy two non-equivalent positions at the apical and capping Pd atoms of cluster II.

Since no evidence on intermediates is available, the mechanism of the inter-

conversions of tetra- and deca-nuclear Pd clusters is still rather obscure. The formation of III in the reduction of Pd(OAc)<sub>2</sub> by carbon monoxide could be presented as a process of consecutive aggregation with the participation of an active intermediate PdL(CO); however, in this case the further growth of the polyhedron during interaction of III and IV should be accompanied by elimination of the ligand L. In the system we have studied the "Pd<sub>4</sub>" and "Pd<sub>10</sub>" structures are apparently the optimum ones and their stability significantly surpasses that of other possible "Pd<sub>n</sub>" complexes with 4 < n < 10. However, the intermediate clusters can probably be isolated using ligands substantially differing from trialkylphosphines, or substituting Pd for Pt, the latter forming more stable clusters.

### *Stereochemistry of the alkyl framework of the metal cluster I*

Configurational analysis of hydrocarbon substituents at the periphery of the molecule is usually thought to be somewhat beyond the main problem of structural studies of clusters, i.e. the investigation and interpretation of the cluster nucleus structure, and most papers characterize the hydrocarbon framework, if any, quite briefly. In our case, however, due to the observed Pd<sub>10</sub> polyhedron distortions, a more detailed investigation of the tri-n-butylphosphine ligands is required. The elongation of the Pd<sub>cap.</sub>...Pd<sub>apic.</sub> distances to 3.3–3.4 Å may be caused either by excess skeletal electrons in I or by intramolecular nonvalent repulsions of the PBu<sup>n</sup><sub>3</sub> ligands. The correct choice between these two possible reasons for the cluster geometry distortion can be made only with the help of a detailed analysis of the arrangement of alkyl substituents and their mutual contacts.

Crystals of I consist of discrete cluster molecules; the distances between them correspond to the usual Van der Waals interactions. In the hydrocarbon periphery formed by the n-butyl substituents of six phosphine ligands the "upper" part (P(1), P(3), P(4)) and the "lower" part (P(2), P(5), (P6)) may be distinguished; the equatorial region of the periphery is filled with bridging CO ligands. The values of bond angles at the P atoms (Table 3) point to a certain steric strain of the structure: in all phosphine ligands two angles Pd–P–C (ranging mostly from 117 to 120°) are considerably larger than the third one (107.4–112.8°).

The variety of conformations taken by the flexible n-butyl substituents is illustrated well by the values of the corresponding torsion angles (Table 5). The majority of these substituents in the PBu<sup>n</sup><sub>3</sub> ligands are in the most favourable *trans* and *gauche* conformations, though in some cases, *cis* and close to *cis* conformations are observed, which also testifies to a certain structural strain. The terminal C(614) atom in I is statistically disordered between two positions corresponding to unfavorable eclipsed conformations of the n-butyl substituent C(611)C(612)C(613)C(614). (see Experimental). Substantial conformational flexibility of the PBu<sup>n</sup><sub>3</sub> ligands provides conditions for the formation of a dense hydrocarbon periphery to efficiently shield the cluster nucleus of I.

The intra- and inter-molecular contacts in structure I were analysed, taking into account the methylene H atoms whose positions were calculated geometrically. The hydrocarbon substituents of the upper and the lower parts do not come into contact each other (the H...H and Me...Me distances are greater than

TABLE 5

TORSION ANGLES  $\tau$ (degrees) IN THE TRI(N-BUTYL)PHOSPHINE LIGANDS IN I

Fragment	$\tau$	Fragment	$\tau$
Pd(1)Pd(5)P(1)C(111)	51.5(6)	Pd(3)Pd(8)P(4)C(411)	154.8(6)
Pd(5)P(1)C(111)C(112)	66.4(7)	Pd(8)P(4)C(411)C(412)	172(1)
P(1)C(111)C(112)C(113)	-161(1)	P(4)C(411)C(412)C(413)	180(1)
C(111)C(112)C(113)C(114)	-176(1)	C(411)C(412)C(413)C(414)	-70(1)
Pd(1)Pd(5)P(1)C(121)	171.8(6)	Pd(3)Pd(8)P(4)C(421)	31.6(6)
Pd(5)P(1)C(121)C(122)	169.4(9)	Pd(8)P(4)C(421)C(422)	67.5(8)
P(1)C(121)C(122)C(123)	168(1)	P(4)C(421)C(422)C(423)	-169(1)
C(121)C(122)C(123)C(124)	173(1)	C(421)C(422)C(423)C(424)	-66(1)
Pd(1)Pd(5)P(1)C(131)	-67.6(6)	Pd(3)Pd(8)P(4)C(431)	48.4(6)
Pd(5)P(1)C(131)C(132)	-57.0(8)	Pd(8)P(4)C(431)C(432)	38.5(8)
P(1)C(131)C(132)C(133)	-174(1)	P(4)C(431)C(432)C(433)	61.8(9)
C(131)C(132)C(133)C(134)	-177(2)	C(431)C(432)C(433)C(434)	175(1)
Pd(1)Pd(6)P(2)C(211)	-31.6(6)	Pd(2)Pd(10)P(5)C(511)	55.3(6)
Pd(6)P(2)C(211)C(212)	50.3(8)	Pd(10)P(5)C(511)C(512)	-66.3(8)
P(2)C(211)C(212)C(213)	173(1)	P(5)C(511)C(512)C(513)	178(1)
C(211)C(212)C(213)C(214)	159(1)	C(511)C(512)C(513)C(514)	177(2)
Pd(1)Pd(6)P(2)C(221)	-151.0(6)	Pd(2)Pd(10)P(6)C(521)	169.6(6)
Pd(6)P(2)C(221)C(222)	-64.3(8)	Pd(10)P(5)C(521)C(522)	72.2(9)
P(2)C(221)C(222)C(223)	159(1)	P(5)C(521)C(522)C(523)	-174(1)
C(221)C(222)C(223)C(224)	62(1)	C(521)C(522)C(523)C(524)	-178(2)
Pd(1)Pd(6)P(2)C(231)	90.4(6)	Pd(2)Pd(10)P(5)C(531)	-62.3(6)
Pd(6)P(2)C(231)C(232)	-177(1)	Pd(10)P(5)C(531)C(532)	-66.3(8)
P(2)C(231)C(232)C(233)	-166(1)	P(5)C(531)C(532)C(533)	-177(1)
C(231)C(232)C(233)C(234)	76(1)	C(531)C(532)C(533)C(534)	64(1)
Pd(1)Pd(7)P(3)C(311)	-178.4(6)	Pd(1)Pd(9)P(6)C(611)	177.0(6)
Pd(7)P(3)C(311)C(312)	169(1)	Pd(9)P(6)C(611)C(612)	-63.8(9)
P(3)C(311)C(312)C(313)	176(1)	P(6)C(611)C(612)C(613)	0(1)
C(311)C(312)C(313)C(314)	-67(1)	C(611)C(612)C(613)C(614')	25(5)
Pd(1)Pd(7)P(3)C(321)	56.3(6)	C(611)C(612)C(613)C(614'')	113(4)
Pd(7)P(3)C(321)C(322)	63.5(8)	Pd(1)Pd(9)P(6)C(621)	-67.5(6)
P(3)C(321)C(322)C(323)	176(1)	Pd(9)P(6)C(621)C(622)	-45.7(8)
C(321)C(322)C(323)C(324)	62(1)	P(6)C(621)C(622)C(623)	-175(1)
Pd(1)Pd(7)P(3)C(331)	-57.6(6)	C(621)C(622)C(623)C(624)	-178(2)
Pd(7)P(3)C(331)C(332)	37.0(8)	Pd(1)Pd(9)P(6)C(631)	51.6(6)
P(3)C(331)C(332)C(333)	176(1)	Pd(9)P(6)C(631)C(632)	178(1)
C(331)C(332)C(333)C(334)	-67(1)	P(6)C(631)C(632)C(633)	178(1)
		C(631)C(632)C(633)C(634)	176(1)

4.0 and 5.0 Å, respectively). In each hydrocarbon periphery region the H...H distances are usually greater than the doubled Van der Waals radius 2.4 Å [12]; in the crystal, contacts at similar distances exist between the neighboring molecules of I. The shortest intramolecular contacts (2.6–2.7 Å, Table 6) are H...O with oxygen atoms of cluster carbonyl ligands (the sum of Van der Waals radii of H and O is equal to 2.6 Å) [12]). These results might seem to contradict the steric interpretation of the elongation of the Pd<sub>cap</sub>...Pd<sub>apic</sub> distance. It should be noted, though, that all the intramolecular interactions of n-butyl substituents in I are confined to contacts of the PBu<sup>n</sup><sub>3</sub> ligands at the apical and capping Pd atoms in the respective cluster region. Taking into account the systematic underestimation of Van der Waals radii determined from the crystallographic data \*, as well as evident distortions of geometry of the PBu<sup>n</sup><sub>3</sub> ligands

\* Energetically unfavourable shortened nonvalent contacts of the nearest atoms of the neighboring molecules in the crystal are compensated by tightening due to interactions of more distant atoms, falling into the attraction region of the intermolecular potential [see 13].

TABLE 6

INTRAMOLECULAR NONVALENT CONTACTS IN STRUCTURE I<sup>a</sup>

HC(121)···HC(422)	3.00	O(4)···HC(432)	2.95
HC(121)···HC(411)	2.89	O(4)···C(434)	3.74
HC(121)···HC(422)	2.54	O(5)···HC(321)	2.58
HC(131)···HC(322)	3.01	O(5)···HC(322)	3.04
HC(131)···HC(322)	2.33	O(5)···HC(332)	2.93
HC(211)···HC(512)	3.24	O(6)···C(134)	3.85
HC(212)···HC(531)	2.85	O(6)···C(614)	3.79
HC(231)···HC(622)	3.47	O(6)···HC(132)	2.84
HC(231)···HC(631)	3.42	O(6)···HC(311)	2.67
C(114)···C(411)	3.86	O(6)···HC(612)	2.80
C(114)···C(413)	4.01	O(7)···HC(421)	2.84
C(114)···C(414)	4.12	O(7)···HC(422)	2.71
C(224)···C(624)	4.18	O(7)···HC(423)	3.29
C(234)···C(631)	4.09	O(7)···HC(433)	3.07
C(231)···C(622)	4.09	O(8)···C(114)	3.51
O(1)···HC(111)	2.64	O(8)···C(524)	4.10
O(1)···HC(112)	2.74	O(8)···HC(112)	2.68
O(1)···HC(113)	2.77	O(8)···HC(411)	2.65
O(1)···HC(522)	2.99	O(9)···HC(214)	3.90
O(2)···HC(121)	2.75	O(9)···HC(334)	3.60
O(2)···HC(132)	2.88	O(9)···HC(212)	2.94
		O(9)···HC(531)	2.82
O(2)···HC(612)	3.14	O(10)···HC(631)	2.55
O(3)···HC(212)	2.71	O(11)···C(434)	3.97
O(3)···HC(212')	3.06	O(11)···HC(222)	2.83
O(3)···HC(231)	2.59	O(11)···HC(621)	2.65
O(3)···HC(332)	2.72	O(11)···HC(622)	3.06
O(4)···HC(221)	2.76	O(12)···HC(511)	2.59
O(4)···HC(222)	2.82	O(12)···HC(512)	3.03
O(4)···HC(223)	2.74		

<sup>a</sup> The contacts between the neighboring CO ligands and in  $\text{PBu}^n_3$  ligands are not presented.

and the above-mentioned displacement of the P atoms, coordinated to the capping Pd atoms, from the  $\text{Pd}_{\text{cap.}}-\text{Pd}_{\text{eq.}}-\text{Pd}_{\text{eq.}}$  planes in the direction away from the apical  $\text{PBu}^n_3$  ligands, a certain steric interaction resulting in increased  $\text{Pd}_{\text{cap.}} \cdots \text{Pd}_{\text{apic.}}$  is present. \* The absence of shortened H···H contacts, however, indicates that these interactions are weak and suggests that the observed geometry of cluster I arises from a balance of "weak" factors involving no appreciable metal-metal bonding between the apical and the capping atoms (the trigonal planar coordination of the capping Pd atoms also supports this assumption). A more rigorous discussion should probably include a quantitative evaluation of the steric strains in the hydrocarbon periphery of I by atom-atom potential calculation. At the present stage, the X-ray diffraction data enable us to present the elongation of the  $\text{Pd}_{\text{cap.}} \cdots \text{Pd}_{\text{apic.}}$  bonds as being a result of steric repulsion of the  $\text{PBu}^n_3$  ligands. The electronic factors take part in this effect by providing two excess (over  $2n + 2$ ) skeletal electrons in an antibonding orbital with respect to the  $\text{Pd}_{10}$  polyhedron [11], which weakens the metal-metal bonding and facilitates the distortion of the cluster structure.

\* The  $\text{Pd}_{\text{cap.}} \cdots \text{Pd}_{\text{apic.}}$  distance decrease to 3.10–3.15 Å in the structure of II, where the apical cluster positions are occupied by terminal CO ligands instead of bulky  $\text{PBu}^n_3$  ligands, provides further evidence in favour of this conclusion.

## Experimental

All the preparations of Pd<sup>0</sup> carbonylphosphine clusters, all operations with them and storage were performed in an atmosphere of CO. Oxygen was removed from the solvents under Ar. IR spectra were recorded on a Specord-75 IR spectrophotometer in benzene and cyclohexane solutions.

### *Preparation of single crystals of Pd<sub>10</sub>(CO)<sub>12</sub>(PBU<sup>n</sup><sub>3</sub>)<sub>6</sub> (I)*

To a solution of 0.087 g (0.39 mmol) of Pd(OAc)<sub>2</sub> in 13 ml of dioxane 4 ml of CF<sub>3</sub>COOH, 0.44 ml (1.76 mmole) of PBU<sup>n</sup><sub>3</sub> and 2 ml of H<sub>2</sub>O were added consecutively with stirring. The solution was stirred for 75 minutes in an atmosphere of CO and 2.5 ml of acetone were added gradually; 0.030 g (29%) of crystals of I were isolated after four days.

### *Preparation of Pd<sub>4</sub>(CO)<sub>5</sub>(PBU<sup>n</sup><sub>3</sub>)<sub>4</sub> (III) from I*

To a solution of 0.200 g (0.077 mmol) of I in 10 ml of hexane 0.77 ml (0.31 mmol) of PBU<sup>n</sup><sub>3</sub> in hexane (1:10) and 10 ml of EtOH were added with stirring. After 30 minutes the solvent was removed in vacuo, and the product was washed with EtOH, 0.238 g of III was obtained (90%).

Anal. Found: Pd, 31.10; C, 46.23; H, 7.71. Calcd. for Pd<sub>4</sub>(CO)<sub>5</sub>(PBU<sup>n</sup><sub>3</sub>): Pd, 30.58; C, 46.30; H, 7.86%.

The IR spectrum is in good agreement with the IR spectrum of Pd<sub>4</sub>(CO)<sub>5</sub>(PBU<sup>n</sup><sub>3</sub>)<sub>4</sub> [3].

### *Preparation of Pd<sub>10</sub>(CO)<sub>12</sub>(PR<sub>3</sub>) from Pd<sub>4</sub>(CO)<sub>5</sub>(PR<sub>3</sub>)*

To a solution of 0.160 g (0.15 mmol) of Pd<sub>4</sub>(CO)<sub>5</sub>(PEt<sub>3</sub>) (IIIa) in a mixture of 37 ml of anhydrous ethanol and 7 ml of pentane, 5 ml of CH<sub>3</sub>COOH were added. Five days later the solvent was evaporated in vacuo so that residual volume of the mixture was 15 ml; the red crystalline precipitate formed was washed with pentane. The yield of Pd<sub>10</sub>(CO)<sub>12</sub>(PEt<sub>3</sub>)<sub>6</sub> (Ia) was 0.075 g (58%).

Anal. Found: Pd, 50.43. Calcd. for Pd<sub>10</sub>(CO)<sub>12</sub>(PEt<sub>3</sub>)<sub>6</sub>: Pd, 50.47%.

The IR spectrum is identical to that of Pd<sub>10</sub>(CO)<sub>12</sub>(PEt<sub>3</sub>)<sub>6</sub> prepared by a direct synthesis from Pd(OAc)<sub>2</sub> [2]. The reaction of Pd<sub>4</sub>(CO)<sub>5</sub>(PBU<sup>n</sup><sub>3</sub>) (III) is similar, but due to the similar solubilities of III and Pd<sub>10</sub>(CO)<sub>14</sub>(PBU<sup>n</sup><sub>3</sub>) (II), isolation of compound I is difficult. Compound I was identified from IR and <sup>31</sup>P NMR spectra\*.

### *Preparation of Pd<sub>4</sub>(CO)<sub>6</sub>(PBU<sup>n</sup><sub>3</sub>)<sub>4</sub> (IV) from III*

0.210 g (0.081 mmol) of III, obtained according a reported method [3], were dissolved in a mixture of 23% pentane, 67% anhydrous ethanol and 10% CH<sub>3</sub>COOH. Two days after the crystallization had started half of the solvent was removed in vacuo; 0.110 g of a red crystalline precipitate was filtered off, washed with EtOH and dried in vacuo. According to analytical data and the IR spectrum, a mixture of I (yield 28%) and III (31%) was obtained. 25 days later, 0.025 g (12%) of crystals (IV) were separated from the filtrate. The results of a

\* The synthesis can be performed preparatively during one hour using a strong acid (CF<sub>3</sub>COOH), with a yield of I of over 90%.

X-ray diffraction analysis give the composition of these crystals as  $\text{Pd}_4(\text{CO})_6(\text{PBU}^n)_4$ . IR spectrum,  $\nu(\text{CO})$  ( $\text{cm}^{-1}$ ): 2007w, 1880(sh), 1845s, 1997(sh).

#### *Preparation of IV by reduction of Pd(OAc)<sub>2</sub>*

To a solution of 0.112 g (0.5 mmol) of  $\text{Pd}(\text{OAc})_2$  in 13 ml of dioxane 4 ml of  $\text{CH}_3\text{COOH}$ , 0.13 ml (0.5 mmol) of  $\text{PBU}^n_3$ , 2 ml of water and 3 ml of acetone were added in succession. Upon stirring for a short time in an atmosphere of CO the solution changed its pale yellow colour to red. Five days later, 0.08 g of bright red crystals of two types were isolated from the solution: trapezoidal IV (according to structural data) and platelets, supposedly of III.

#### *X-Ray diffraction investigation of I*

Crystals of I are monoclinic,  $a = 12.218(10)$ ,  $b = 29.299(16)$ ,  $c = 19.845(9)$  Å,  $\beta = 92.43(4)^\circ$ , space group  $P2_1/n$ ,  $Z = 4$ . The cell parameters and intensities of 12 764 independent reflections were measured with a "Sintex P2<sub>1</sub>" four-circle automatic diffractometer at  $-120^\circ\text{C}$  ( $\lambda\text{Mo-K}_\alpha$ , graphite monochromator,  $\theta/2\theta$  scan,  $2\theta \leq 44^\circ$ ). The calculations were performed using 12 127 reflections with  $I \leq 2\sigma$ . Correction for absorption taking into account the actual single crystal shape [14] did not result in any substantial increase in accuracy in the structure ( $\mu = 18.6 \text{ cm}^{-1}$ ). The Pd atom positions were determined by a direct method, using the MULTAN program; the coordinates of non-hydrogen atoms were obtained by subsequent Fourier-synthesis. A block-diagonal least-square anisotropic refinement of the structure gave  $R = 0.069$ . A disorder in the C(614) atom location was detected in the process of difference electronic density synthesis. This carbon atom was then assigned two positions (C(614') and C(614''), Table 1) with half weights. Finally  $R = 0.047$ ,  $R_w = 0.075$ , using 10 251 reflections with  $I > 5\sigma$ .

#### *X-Ray diffraction investigation of IV*

Crystals of IV are hexagonal,  $a = 19.892(11)$ ,  $c = 14.333(6)$  Å, space group  $P\bar{3}$  (after refinement),  $Z = 3$ . The cell parameters and intensities of 3 643 independent reflections were measured with the Sintex P2<sub>1</sub> diffractometer at  $-120^\circ\text{C}$  using  $\text{Mo-K}_\alpha$  radiation. The calculations were performed using 3 254 reflections with  $I > 2\sigma$ . The initial structure resolution using the MULTAN program for the  $P\bar{3}$  space group revealed 3 independent  $\text{Pd}_4$  tetrahedral clusters, occupying special positions at threefold axes. It was found that two clusters, independent in this space group are related to each other by an inversion center emerging in the real space group  $P\bar{3}$ , and that the third cluster is disordered with approximately equal population factors between two positions, related by a symmetry center in (0, 0, 0), which corresponds to its localization in the special position  $\bar{3}$  of the space group  $P\bar{3}$ . Further structure refinement was performed for the space group  $P\bar{3}$ , where two independent molecules are present (Table 4), one of which (molecule A, disordered with population factors 1/2) occupies a special position  $\bar{3}$ , and the other (molecule B) a special position 3. Superposition of the  $\text{Bu}^n$  substituents for both positions of the disordered molecule A hinders structure refinement and leads to large uncertainties in configurations of the cluster hydrocarbon periphery. The coordinates of the C(1) and O(1) atoms of the  $\mu_2$ -CO ligands, bonded to the Pd(1) atom on the  $\bar{3}$ -axis in

one position of the disordered molecule, are close to those of the  $\mu_2$ -CO ligands at the base of the polyhedron in the second position. Therefore these atoms were not separated during the refinement but assigned a population factor of 1.

A full-matrix anisotropic (Pd, P)-isotropic least-square refinement gave  $R = 0.13$ . At this stage disorder of the tri-n-butylphosphine ligands in molecule B (occupying special position 3, Table 4) was found. The two positions (present with a population factor of 1/2) correspond to a slight rotation of these ligands around the Pd-P bond. Finally,  $R = 0.098$ ,  $R_w = 0.134$ . Due to the above-mentioned strong disorder of the structure of IV, the coordinates of the C atoms of the n-butyl substituents are determined with low accuracy. However, the geometry of the cluster "nucleus"  $\text{Pd}_4(\text{CO})_6\text{P}_4$ , which is of main interest, is determined quite reliably. The modified EXTL\* programs were used for all calculations for structures I and IV on an Eclipse S/200 computer.

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\* The EXTL programs were modified in our laboratory by A.I. Yanovsky and R.G. Gerr.