Synthesis of large palladium clusters. The preparation of $Pd_{38}(CO)_{28}(PR_3)_{12}$ (R = Et, Bu^n) and $Pd_{34}(CO)_{24}(PEt_3)_{12}$

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Several methods for the synthesis of the $Pd_{38}(CO)_{28}L_{12}$ cluster (L = PEt_3) by treatment of $Pd_{10}(CO)_{12}L_6$ with CF_3COOH—Me_3NO, CF_3COOH—H_2O_2, $Pd(OAc)_2$—Me_3NO, and $Pd_2(dba)_3$ mixtures (dba is dibenzylideneacetone) were proposed. The tri-*n*-butylphosphine analog, $Pd_{38}(CO)_{28}(PBu_3)_{12}$, was synthesized by the reaction of $Pd_{10}(CO)_{14}(PBu_3)_4$ with Me_3NO. The reaction of $Pd_4(CO)_5L_4$ with $Pd_2(dba)_3$ yields clusters with an icosahedral packing of the metal atoms, $Pd_{34}(CO)_{24}L_{12}$ and $Pd_{16}(CO)_{13}L_9$.

Key words: palladium, carbonylphosphine clusters, synthesis.

The methods for the synthesis of a series of individual palladium clusters containing an intrapolyhedral metal atom, *viz.*, $Pd_{16}(CO)_{13}L_9$ (**1**), $Pd_{23}(CO)_{22}(PR_3)_{10}$ (where R = Et (**2**) and Bu), and $Pd_{23}(CO)_{20}L_8$ (**3**), have been described earlier.[1]

The purpose of the present work is to develop procedures for the synthesis of two other large clusters, $Pd_{38}(CO)_{28}L_{12}$ (**4**) and $Pd_{34}(CO)_{24}L_{12}$ (**5**), which contain several intrapolyhedral atoms. Earlier, complex **4** was obtained in a low yield[2] by the reaction of $Pd_{10}(CO)_{12}L_6$ (**6**) with $Pd(OAc)_2$. This reaction usually yields a mixture of two, three, or four clusters, sometimes containing **5**. The structures of complexes **4** and **5** were established by X-ray analysis* (the structure of **4** is described in Ref. 2).

We have investigated the reactions of the clusters **6**, $Pd_4(CO)_5L_4$ (**7**), and $Pd_{10}(CO)_{12}L'_6$ (L' = PBu_3) (**8**) with CF_3COOH, H_2O_2, air, $Pd_2(dba)_3$, and CF_3COOH—Me_3NO, CF_3COOH—H_2O_2, and $Pd(OAc)_2$—Me_3NO mixtures in an inert atmosphere.

The above-mentioned reagents are capable of binding ligands through oxidation (Me_3NO, H_2O_2, O_2), protonation (CF_3COOH), or complexation ($Pd(OAc)_2$ and $Pd_2(dba)_3$). Since the elimination of even one molecule from the ligand environment of a cluster results in enlargement of this cluster, all of these ways are effective. The main difficulty is finding the conditions, which cannot be predicted, for obtaining the individual compounds. This problem is complicated by the formation of a rather great number of reaction products that have ligand environments of the same type, although their metal polyhedra have different structures. Up to now, six such "islands of stability" with nuclearity $n > 10$ have been found only by X-ray analysis.

These reactions show a clear dependence on kinetic factors. This fact made it possible to find the conditions for obtaining compounds in the individual state using a significant number of deliganding agents.

The results of deliganding *via* treatment with CF_3COOH and a CF_3COOH—Me_3NO mixture are given in Table 1. The reaction with CF_3COOH usually yields no solid crystalline products, and the addition of Me_3NO is necessary to form crystals of the carbonylphosphine clusters.

$$\underset{\mathbf{6}}{Pd_{10}(CO)_{12}L_6} + Me_3NO + CF_3COOH \longrightarrow \underset{\mathbf{4}}{Pd_{38}(CO)_{28}L_{12}} + CO + CO_2 + [HL]^+[CF_3COO]^- + [Me_3HN]^+[CF_3COO]^-$$

To obtain cluster **4** in the individual state, the following conditions must be fulfilled: the ratio **6** : Me_3NO must be (1 : 4)−(1 : 16) and Me_3NO : CF_3COOH must be (1 : 2)−(1 : 4). Low (see Table 1, entry *4*) and high concentrations of Me_3NO and CF_3COOH (entries *17*, *20—23*), as well as concentrations of Me_3NO higher than those of CF_3COOH (entries *18* and *19*) are unsuitable. In addition, the reaction is sensitive to the actual concentration of CO. Thus, even a single elimination of the CO generated results in a mixture of clusters (see Table 1, entries *5—7*, *9*, *12*, *13*).

Tetramer **7** may also be used as a starting compound for synthesizing cluster **4** (entry *25*).

* X-ray structure analysis was performed by Yu. L. Slovokhotov and Yu. T. Struchkov (A. N. Nesmeyanov Institute of Organoelement Compounds of the RAS).

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Table 1. Synthesis conditions, yields and compositions of the products of the reaction of cluster **6** with CF_3COOH and Me_3NO

Entry	**6** : CF_3COOH	**6** : Me_3NO	τ_r/day	Composition of the crystalline products (%) [yield (%)]					
				1	**2**	**3**	**4**	**5**	Unidentified compounds
1	1 : 5	—	—	—	—	—	—	—	—
2	1 : 30	—	—	—	—	—	100 [58]	—	—
3	1 : 40	—	1	—	—	—	—	—	—
4	1 : 5	1 : 0.5	—	—	—	—	—	—	—
5	1 : 5	1 : 0.5	7	—	23 [15]	—	70 [51]	7 [5]	—
6	1 : 40	1 : 3	0.2**	—	—	30 [18]	10 [6]	—	60 [37]
7	1 : 5	1 : 4	5	—	—	—	79 [49]	—	21 [16]***
8	1 : 10	1 : 4	—	—	—	—	100 [45]	—	—
9	1 : 10	1 : 4	0.04	—	24 [10]	—	76 [35]	—	—
10	1 : 30	1 : 4	—	—	—	—	100 [61]	—	—
11	1 : 10	1 : 8	—	—	—	—	100 [38]	—	—
12	1 : 10	1 : 8	0.04	20 [14]	71 [54]	—	6 [5]	3 [2.5]	—
13	1 : 10	1 : 8	1	—	—	—	25 [7]	25 [7]	50***
14	1 : 30	1 : 8	—	—	—	—	100 [50]	—	—
15	1 : 70	1 : 8	—	—	—	—	100 [34]	—	—
16	1 : 30	1 : 16	—	—	—	—	100 [50]	—	—
17	1 : 120	1 : 16	—	—	—	—	—	—	100 [42]
18	1 : 10	1 : 20	—	—	—	—	—	—	100[88]***
19	1 : 10	1 : 20	—	27 [9]	—	—	—	—	73***
20	1 : 60	1 : 30	—	—	—	—	81 [46]	—	19
21	1 : 120	1 : 30	—	—	—	—	—	—	100 [32]
22	1 : 120	1 : 60	—	—	—	—	15 [6]	—	85
23	1 : 240	1 : 60	—	—	—	—	—	—	100 [44]
*24**	1 : 12	—	—	—	—	—	—	—	—
*25**	1 : 40	1 : 10	—	—	—	—	100 [22]	—	—

Note. For 0.095 mmol of **6**; Me_2CO (7 mL) + Et_2O (2 mL) as the solvent; τ_r is time from the beginning of the reaction to the renewal of the atmosphere; volume of the gas phase was 120 mL; duration of the experiments was 7—17 days. Compounds were isolated as crystals, separated mechanically and identified by the IR spectra.
* Starting cluster **7** (0.2 mmol). ** With subsequent crystallization in the presence of water vapor. *** Amorphous.

$$\underset{\mathbf{7}}{Pd_4(CO)_5L_4} + Me_3NO + CF_3COOH \longrightarrow \mathbf{4} + CO + CO_2 + [HL]^+[CF_3COO]^- + [Me_3HN]^+[CF_3COO]^-$$

However, the replacement of PEt_3 with PBu_3 does not yield $Pd_{38}(CO)_{28}L'_{12}$ (**9**) as a separate compound even under the conditions that were found to be optimal. In the case of the ratio **8** : Me_3NO : CF_3COOH = 1 : 8 : 30, a mixture of clusters **9** and $Pd_{23}(CO)_{22}L'_{10}$ containing starting **8** formed. The ratio between the components of the mixture depends on many factors and is not easily controlled.

$$\underset{\mathbf{8}}{Pd_{10}(CO)_{12}L'_6} + Me_3NO + CF_3COOH \longrightarrow \underset{\mathbf{9}}{Pd_{38}(CO)_{28}L'_{12}} + Pd_{23}(CO)_{22}L'_{10} + CO + CO_2 + [HL']^+[CF_3COO]^- + [Me_3HN]^+[CF_3COO]^-$$

It was possible to obtain cluster **9** from another decanuclear isomer, $Pd_{10}(CO)_{14}L'_4$, by the treatment with 2 equiv. of Me_3NO in the absence of CF_3COOH.

$$Pd_{10}(CO)_{14}L'_4 + Me_3NO \longrightarrow \mathbf{9} + CO + CO_2 + OPBu_3 + Me_3N$$

The IR spectrum of cluster **9** exhibits the same set of absorption bands as the spectrum of **4**.

The salient feature of the synthesis of cluster **4** by the oxidation of complex **6** with hydrogen peroxide and a $CF_3COOH—H_2O_2$ mixture is the narrower range of suitable concentrations, *i.e.*, the ratio **6** : H_2O_2 : CF_3COOH = 1 : 1 : (5—10) (Table 2). The oxidation of cluster **6** by air results in a similar set of products.

$$\mathbf{6} + H_2O_2 + CF_3COOH \longrightarrow \mathbf{4} + CO + CO_2 + H_2O + OPEt_3 + [HL]^+[CF_3COO]^-$$

Still more stringent requirements for the ratio of the reagent concentrations are necessary for the synthesis of cluster **4** by treatment with $Pd(OAc)_2$ and Me_3NO, *viz.*, **6** : $Pd(OAc)_2$: Me_3NO = 1 : 3 : 1.

$$\mathbf{6} + Pd(OAc)_2 + Me_3NO \longrightarrow \mathbf{4} + CO + CO_2 + L_2Pd(OAc)_2 + Me_3N$$

The most convenient procedure for the synthesis of cluster **4** is the reaction of **6** with a $CF_3COOH—Me_3NO$ mixture.

An investigation of the products of the reaction of complex **6** with $Pd_2(dba)_3$ revealed the preferential for-

Table 2. Synthesis conditions, yields and compositions of the products of the reaction of cluster **6** with H_2O_2, CF_3COOH, and air

Entry	**6** : H_2O_2	**6** : CF_3COOH	Composition of the crystalline products (%) [yield (%)]		
			2	**4**	Unidentified compounds
1	1 : 0.1	—	100 [13]	—	—
2	1 : 0.3	—	100 [15]	—	—
3	1 : 2.5	—	11 [4]	89 [36]	—
4	1 : 6.0	—	—	93 [43]	7**
5	1 : 0.5	1 : 5	34 [14]	53 [26]	13
6	1 : 1	1 : 2.5	35 [17]	65 [35]	—
7	1 : 1	1 : 5	—	100 [49]	—
8	1 : 1	1 : 10	—	100 [49]	—
9	1 : 2	1 : 20	—	30 [16]	70**
*10**	—	—	—	95 [42]	5**

Note. Duration of the reactions was 5—10 days, volume of the gas phase was 40—100 mL. For the other conditions, see the note in Table 1.
* Oxidizing agent is air. ** Amorphous.

mation of cluster **5** when the **6** : $Pd_2(dba)_3$ ratio was (1 : 2.5)−(1 : 3) (Table 3, entries *4—7*). The polyhedron of this compound consists of reciprocally penetrating icosaheda. Additions of Me_3NO and HOAc or the removal of CO decrease the selectivity of the reaction. If the reaction is carried out in the absence of Et_2O, a single product, **4**, is formed (see Table 3, entries *9—13*). The yields obtained indicate that $Pd_2(dba)_3$ not only acts as a ligand acceptor, but to a lesser degree in a series of cases the metal atoms of the dibenzylidene complex are included in the formed compounds.

Cluster **5** was synthesized by the reaction of complex **7** with 3 equiv. of $Pd_2(dba)_3$. Using half this amount of $Pd_2(dba)_3$ gives $Pd_{16}(CO)_{13}L_9$. It is of interest to note that in both cases compounds with icosahedral packing are obtained.

The reasons for the formation of clusters **5** and **1** are partially associated with the stoichiometry of the reactions under conditions of a deficiency of CO.

$$\underset{\mathbf{7}}{3\,Pd_4(CO)_5L_4} + 11\,Pd_2(dba)_3 \xrightarrow{9\,CO} \underset{\mathbf{5}}{Pd_{34}(CO)_{24}L_{12}}$$

$$\underset{\mathbf{7}}{9\,Pd_4(CO)_5L_4} + 14\,Pd_2(dba)_3 \xrightarrow{7\,CO} 4\,\underset{\mathbf{1}}{Pd_{16}(CO)_{13}L_9}$$

Table 3. Synthesis conditions and compositions of the products of the reactions of clusters **6** and **7** with $Pd_2(dba)_3$

Entry	**6** : $Pd_2(dba)_3$	**7** : $Pd_2(dba)_3$	**6** : Me_3NO	HOAc /mL	τ_r/h	Composition of the crystalline products (%)				Total yield (%)
						1	**2**	**4**	**5**	
1	1 : 1	—	—	—	—	—	44	35	21	70
2	1 : 1.3	—	—	—	—	—	46	50	4	77
3	1 : 2	—	—	—	—	—	44	44	12	98
4	1 : 2.5	—	—	—	—	—	—	—	100	119
5	1 : 2.5	—	—	—	—	—	11	—	89	125
6	1 : 3	—	—	—	—	—	—	9	91	132
7	1 : 3	—	—	—	—	—	12	12	76	147
*8**	1 : 5	—	—	—	—	—	—	7***	—	59
9	1 : 2.5	—	—	—	1; 5	—	33	5	62	132
10	1 : 2.5	—	1 : 3	—	—	—	4	60	36	81
11	1 : 2.5	—	1 : 1.5	0.05	—	—	4	37	59	99
12	1 : 2.5	—	1 : 1.5	0.3	5	—	11	26	63	133
*13***	1 : 2.5	—	—	—	—	—	—	100	—	94
14	—	1 : 1.5	—	—	—	100	—	—	—	102
15	—	1 : 3	—	—	—	—	—	—	100	58

Note. For 0.062 mmol of **6** and 0.08 mmol of **7**; volume of the gas phase was 40—60 mL; duration of the experiments was 4—14 days. For the total yields are given relative to **6** or **7**, respectively. For the other conditions, see the note in Table 1.
* Dissolved with heating at 40 °C. ** In the absence of Et_2O. *** In addition to complex **4**, 50 mg (55 %) of a black amorphous precipitate was isolated. For this compound, found (%): Pd, 72.0; P, 3.0.

Of the Pd carbonylphosphine clusters containing intrapolyhedral metal atoms, clusters **5** and **1** have ligand spheres with the lowest number of CO groups.

We know only one example of the use of Pd dibenzylidene complexes for the synthesis of carbonylphosphine compounds, *viz.*, the synthesis of $Pd_8(CO)_8(PMe_3)_7$ by the reaction of $Pd(dba)_2$ with PMe_3 and CO.[3]

Experimental

The grades of the reagents and the methods for the synthesis and analysis of the compounds are described in our pervious work[1] (see also references herein). The $Pd_2(dba)_3$ complex (see Ref. 4) was recrystallized from a $CHCl_3$—heptane mixture. The concentration of H_2O_2 ("pure for analysis" grade) was monitored by permanganatometry. All of the reactions were performed in an argon atmosphere. IR spectra were recorded on a Specord M80 spectrophotometer using samples suspended in vaseline oil in an argon atmosphere.

Synthesis of cluster 4. ***A.*** The reaction of complex **6** with CF_3COOH and Me_3NO. A mixture of **6** (0.200 g, 0.095 mmol) and $Me_3NO \cdot 2H_2O$ (0.042 g, 0.378 mmol) was dissolved in a mixture of Me_2CO (7.5 mL), Et_2O (1.5 mL), and CF_3COOH (0.20 mL, 2.70 mmol) at 30 °C and stored for 17 days at room temperature. The precipitate of black crystals was washed with Me_2CO and Et_2O and dried *in vacuo*. Cluster **4** was obtained in 0.096 g (61 %) yield. Found (%): Pd, 64.37; P, 5.82. $C_{100}H_{180}O_{28}P_{12}Pd_{38}$. Calculated, (%): Pd, 64.74; P, 5.95. IR, $\nu(CO)/cm^{-1}$: 1899 s, 1885 s—m, 1849 s, 1842 s—m, 1817 m sh, 1778 w.

B. The reaction of complex **7** with CF_3COOH and Me_3NO. Compound **7** (0.217 g, 0.209 mmol) and $Me_3NO \cdot 2H_2O$ (0.232 g, 2.087 mmol) were stirred in a mixture of Me_2CO (7 mL), Et_2O (2 mL), and CF_3COOH (0.62 mL, 8.37 mmol) for 10 min at 30 °C and stored for 8 days at room temperature. The precipitate of black crystals was washed with Me_2CO and dried in a flow of Ar. The yield of cluster **4** was 0.031 g (22 %). IR, $\nu(CO)/cm^{-1}$: 1899 s, 1885 m, 1850 s, 1840 m, 1817 w.

C. The reaction of complex **6** with CF_3COOH and H_2O_2. A mixture of Me_2CO (7 mL), Et_2O (2 mL), CF_3COOH (0.07 mL, 0.945 mmol), and a 2.15 % solution of H_2O_2 (0.15 mL, 0.095 mmol) was added to compound **6** (0.200 g, 0.095 mmol). The reaction mixture was stirred until dissolution and stored for 7 days at room temperature. Cluster **4** was obtained in 0.076 g yield as black crystals. The IR spectrum was identical to that of cluster **4** prepared by procedures ***A*** and ***B***.

D. The reaction of complex **6** with $Pd(OAc)_2$. A mixture of **6** (0.200 g, 0.095 mmol), $Pd(OAc)_2$ (0.064 g, 0.285 mmol), and $Me_3NO \cdot 2H_2O$ (0.011 g, 0.099 mmol) was dissolved in a mixture of Me_2CO (7.4 mL), Et_2O (1.6 mL), and EtOH (0.3 mL) and stored for 8 days at room temperature. Cluster **4** (0.085 g) was obtained as black crystals in 54 % yield. The IR spectrum was identical to that of cluster **4** prepared by the above described procedures.

Synthesis of cluster 5. ***A.*** Reaction of **6** with $Pd_2(dba)_3$. A mixture of **6** (0.130 g, 0.062 mmol) and $Pd_2(dba)_3 \cdot CHCl_3$ (0.160 g, 0.155 mmol) was dissolved in a mixture of Me_2CO (7 mL) and Et_2O (2 mL) and stored for 4 days at room temperature. The precipitate of black flakes was washed with Me_2CO and dried in a flow of Ar. The yield of cluster **5** was 0.123 g (119 %). Found (%): Pd, 62.93; P, 6.40. $C_{96}H_{180}O_{24}P_{12}Pd_{34}$. Calculated (%): Pd, 63.38; P, 6.51. IR, $\nu(CO)/cm^{-1}$: 1892 s, 1865 s, 1837 s, 1809 s—m.

Analogously, but in the absence of Et_2O, cluster **4** (0.095 g) was obtained in 94 % yield as black crystals identified by its IR spectrum.

B. Reaction of **7** with $Pd_2(dba)_3$. Cluster **7** (0.082 g, 0.079 mmol) and $Pd_2(dba)_3 \cdot CHCl_3$ (0.245 g, 0.237 mmol) were stirred in a mixture of Me_2CO (7 mL) and Et_2O (2 mL) at 30 °C until most of the solids were dissolved. The reaction mixture was stored for 5 days at room temperature. The precipitate of black flakes and finely divided crystals was washed with Me_2CO and dried in a flow of Ar. The yield of cluster **5** was 0.031 g (58 %) and the yield of $Pd(dba)_2$ was 0.041 g. The IR spectrum of **5**, $\nu(CO)/cm^{-1}$: 1893 s, 1865 s, 1836 s, 1809 s, 1756 w. The IR spectrum of $Pd(dba)_2$ (tablets with KBr), ν/cm^{-1}: 1645 (C=O); 1617 ($C=C_{aliph}$); 1578 ($C=C_{arom}$); 1545 ($C=C_{arom}$).

Synthesis of cluster 9. A mixture of $Pd_{10}(CO)_{14}L'_4$ (0.200 g, 0.088 mmol) and $Me_3NO \cdot 2H_2O$ (0.020 g, 0.180 mmol) was dissolved in a mixture of Me_2CO (6 mL) and EtOH (1 mL). After 3 h, the atmosphere was renewed by introducing another portion of Ar. After an additional 24 h, the atmosphere was repeatedly renewed, and the solution was stored under the EtOH—H_2O vapor liberated by a 1 : 6 H_2O—EtOH mixture. After an additional 3 days, the black crystals that formed were washed with EtOH and dried *in vacuo*. The yield of cluster **9** was 0.046 g (27 %). Found (%): Pd, 55.33; P, 5.06. $C_{172}H_{324}O_{28}P_{12}Pd_{38}$. Calculated (%): Pd, 55.73; P, 5.12. IR, $\nu(CO)/cm^{-1}$: 1902 m, 1889 sh, 1852 m, 1845 sh, 1816 w.

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