

Formation of platinum and palladium clusters with carbonyl phosphine ligands

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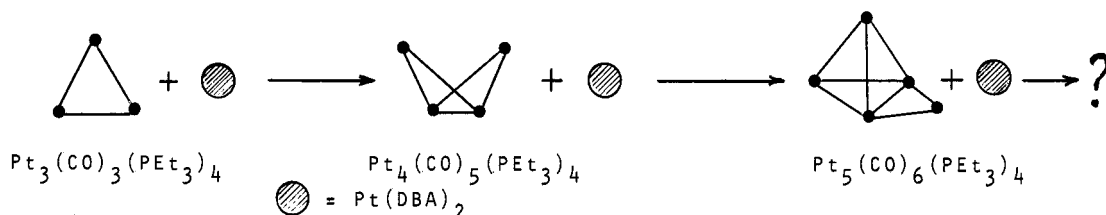
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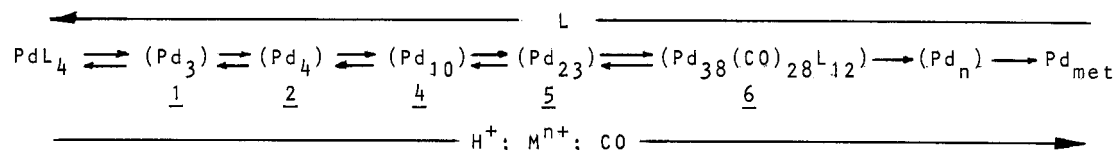
Abstract - a general method available for the synthesis of carbonyl phosphine clusters of Palladium and Platinum has been found. Structural principles of cluster framework formation are discussed. The most simple building blocks for metal polyhedra are triangle and butterfly and their combination "Tiare". This construction principle can be applied for results interpretation and for the directional synthesis of new clusters.

Metal clusters in the size range up to a hundred atoms are at present one of the most interesting frontiers of the coordination chemistry. The large clusters are of greater interest in view of both the structure and bonding in their metal core and the fact that they may model ligand coordination on metal surfaces. There is a general method available for the synthesis of large and giant clusters: the reduction of noble metal salts by various reduction agents in the presence of ligands which can block the surface of growing particles and prevent their aggregation. The problem of interest is also the mechanism of cluster enlargement in solutions. The most simple concept states that enlargement of clusters proceeds through atom by atom addition. This process can be modeled as follows:



The synthesis proceeds under mild conditions and gives products in good yields (60-80%). However this method fails at present to give much opportunities: the route doesn't lead to large cluster molecules.

We have found that under mild conditions zero-valent Palladium derivatives are able to form Pd_n clusters with carbonyl phosphine ligand shell and of N nuclearity varying between 3 and 38. (ref. 1). The step by step growth, which is possible by using some building blocks condensation processes, is clearly illustrated by transformations:



The excess of ligands would lead to the shift of equilibrium to the right up to the complete transformation of Pd to PdL_4 , on the contrary, the coordination of phosphine ligands by introduction of acceptors (H , M^{n+} ...) in the presence of CO leads to the step by step cluster enlargement (ref. 2).

This is a typical cluster series $\text{M}_n(\text{CO})_m(\text{PR}_3)_q$, where $n=3,4,10,23,38$. The whole number of clusters has been prepared in good yield and their structure determined by X-Ray analysis. The most interesting feature of this

cluster series is strictly discrete character of nuclearity. The study of fragmentation of some large Pd clusters illustrates the role of triangle and butterfly species as building blocks of such clusters. In a number of cases it has been shown, for example, by preparation of adducts of these clusters with mercury halides (ref.3). Some known carbonyl-phosphine clusters have been suggested to be formed by a certain combination of simple building blocks: triangles, butterflies and in some cases mononuclear particles. It is well known that carbonyl phosphine Pd-triangle ability to have 42 or 44 CVE depends from steric effects of phosphine ligands; the effect of bulky phosphines prevents regular prismatic stacking of carbonyl phosphine triangles as it is seen in case of $[\text{Pt}_3(\text{CO})_6]_2$ triangle (ref.4). Two terminal atoms of Pd in butterfly have square electronic configuration and two others - distorted tetrahedral environment.

We supposed that conjunction of butterfly with triangle gives the more complicated building block - a "crown" or better "tiare", which can be clearly seen in the structure of 10-(4) and 23-(5) nuclear clusters (Scheme 1).

The metal polyhedron in 5 includes the closed packed metal atom fragment, i.e. the body- and edge centered octahedron Pd_6 (ref. 5). This "large octahedron" is complemented by four non-closed $\text{Pd}(\mu\text{-CO})_2(\text{PEt}_3)$ capping moieties. Thus, the latter atoms form the open caps on the faces of the large octahedron, resembling asymmetric caps of a Pd_6 -octahedron in the structures of the $\text{Pd}_{10}(\text{CO})_{12}\text{L}_6$ and $\text{Pd}_{10}(\text{CO})_{14}\text{L}_4$ clusters (ref. 1,2), the distances from the capping atoms to atoms of the large octahedron are 2,730 Å (av), similarly to that in Pd_{10} (2,710 Å) (av).

We consider that the discrete nuclearity of clusters in the system Pd-CO- PR_3 is the result of building blocks (triangles and butterflies) combination according to the formulae: $N=4n + 3q$, where n and q - whole numbers. Application of this formulae to obtained clusters is demonstrated in Table 1.

TABLE 1. Structural and electronic characteristics of carbonyl-phosphine clusters of Pd

Compound	N	CVE	CSE	n*	q*	** τ
<u>1</u> $\text{Pd}_3(\text{CO})_3(\text{PR}_3)_4$	3	44	8	0	1	2,3
<u>2</u> $\text{Pd}_4(\text{CO})_5(\text{PR}_3)_4$	4	58	10	1	0	2,25
<u>3</u> $\text{Pd}_7(\text{CO})_7(\text{PR}_3)_7$	7	98	14	1	1	2,0
<u>4</u> $\text{Pd}_{10}(\text{CO})_{12}(\text{PR}_3)_6$	10	136	16	1 (1)	2 (1)	1,8
<u>5</u> $\text{Pd}_{23}(\text{CO})_{22}(\text{PR}_3)_{10}$	23	294	20	2 (2)	5 (3)	1,39 (1,45)
<u>6</u> $\text{Pd}_{38}(\text{CO})_{28}(\text{PR}_3)_{12}$	38	460	-	2 (2)	10 (8)	1,05 (1,18)

*) $N=4n + 3q$; values in brackets of n and q correspond to formulae $N=7n + 3q$;

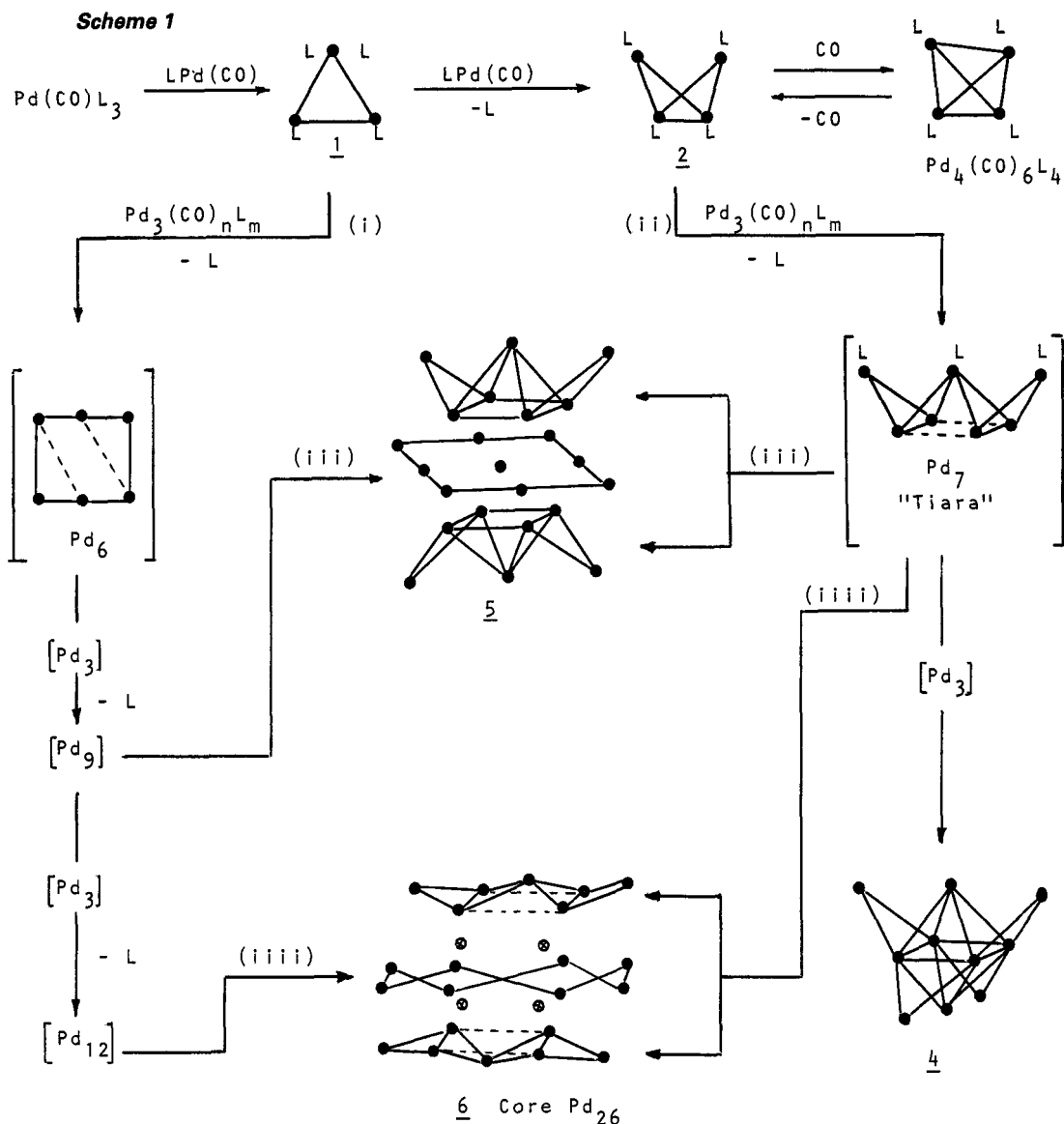
***) Number of ligands

$$\tau = \frac{\text{Number of ligands}}{\text{Cluster nuclearity}}; \quad \tau \text{ in brackets} - N=N-n_{\text{ints.}}$$

It is clear that up to $N=10$, there is only one pair of n and q values that correspond to experimentally obtained cluster structures.

Alternative route of condensation is interaction of triangles with the formation of planar or nearly planar structures (Scheme 1 (i)), which have been called "raft" structures. Such structures are coordinatively unsaturated and only external atoms of metals have ligands. Finally, cluster 5 is formed by condensation of 2 tiaras and 3 triangles in the form of 9-atoms raft situated between two tiaras.

The metal core in Pd_{38} has a less regular structure compared to the large octahedron Pd_{23} (ref. 6). The flattened interstitial tetrahedron Pd_4 is enveloped by 20 atoms of Pd arranged in four approximately planar layers, and two interlayer Pd atoms, thus forming 4:8:2:8:4 configuration. The resulting 26-atomic cluster nucleus is further completed by 12 capping Pd atoms,



each cap being coordinated by one PEt_3 ligand. An interesting structural feature of the largest clusters is that they tend to minimize their molecular surface and, therefore, to form spheroidal metal polyhedra with a certain distortion of interstitial planar layers. Comparison of cores of Pd_{23} and Pd_{38} clusters demonstrates, however, a certain similarity of their structures. It can be seen that Pd_{38} -cluster contains two distorted tiaras with a highly distorted raft, consisting of nine Pd atoms and additional triangle, which is almost perpendicular to this plane.

It should be noted that clusters with $N \geq 10$ satisfy formulae version $N = 7n + 3q$, where 7 - is the number of metal atoms in the tiara, build from triangle and butterfly. When $N = 10$, n and q have the only possible value equal to 1. In particular cases when $N > 10$, cluster cores can be build from various combinations of triangles and tiaras. Thus, n value in the clusters with $N > 10$ is always equal to 2.

Finally, the absence in the reaction mixture of clusters with the cores of intermediate nuclearity is explained according to the structural characteristics of investigated clusters and ways of their origination. Cluster cores are supposed to be formed from different combinations of building blocks, while atom by atom growth leads only to capping of the cores.

Electronic structures of large carbonyl-phosphine clusters have not been under special investigation; only in (ref.7) the authors examined two limiting bonding situations in large close-packed metal clusters, in which metal atoms

lie on concentric spheres. In one situation the radial bonding effects predominate, in the other - both the radial and tangential bonding effects are equally important. Among a considerable number of investigated clusters, only two, Pd_{23} (5) and Pd_{38} (6) couldn't be described by this approximation and represent intermediate situations. It is clear, that structure of such clusters can't be described by simple addition of concentric spheres around central atom or atoms. This is in accord with construction principle discussed in the present paper.

In continuation of our investigation of large cluster molecules the first high-nuclear carbonyl-phosphine cluster of platinum has been synthesized and structurally characterized. The most common synthetic route to carbonyl-phosphine clusters of platinum is the addition of phosphines to an oligomeric "platinum dicarbonyl" $[Pt(CO)_2]_n$ in solution. However, this method allows to prepare clusters with nuclearity not more than 5 atoms only.

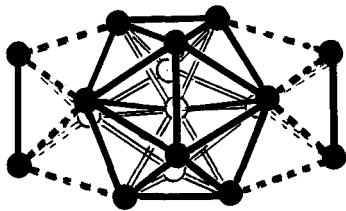


Fig. 1. Core of $Pt_{17}(CO)_{12}(PEt_3)_8$ cluster.

Thermolysis of the cluster $Pt_5(CO)_6(PEt_3)_4$ in decane under inert atmosphere leads to $Pt_{17}(\mu-CO)_4(CO)_8$ with the yield 14%. Fig. 1 demonstrates the core structures of this cluster, which consists of a distorted centered icosahedron with four caps, linked pairwise by Pt-Pt bonds. Thus this structure is the first step in the enveloping of the Pt_{13} icosahedron by second atomic shell of metal atoms.

It can be assumed that further investigations in this area will bring us closer to an understanding of the mechanism of described reactions.

Acknowledgements

The authors are grateful to Dr. E.G. Mednikov and Dr. S.S. Kurasov for their skilled synthetic work. The structural studies are collaborative with Prof. Yu.T. Struchkov and Dr. Yu.L. Slovokhotov. We would like to acknowledge and express our appreciation to them. We would like to express special thanks to Dr. I.P. Podolskaya for the help in the preparation of this manuscript.

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