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SYNTHESIS AND X-RAY STRUCTURE OF 10-VERTEX PALLADIUM CARBONYLPHOSPHINE CLUSTER WITH MINIMAL PBu^n_3 CONTENT

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Summary

Synthesis of the carbonylphosphine cluster $Pd_{10}(CO)_{14}(PBu^n_3)_4$ (I), a product of substitution of two PBu^n_3 ligands by terminal CO groups in the $Pd_{10}(CO)_{12}(PBu^n_3)_6$ cluster II, was carried out, and the structure of I (λ Mo, 3200 reflections, $R = 0.098$) was established by X-ray analysis. The Pd_{10} polyhedron is a four-capped octahedron with unsymmetrical caps. The average Pd–Pd distances in the inner octahedron are 2.824 Å, and Pd_{oct}–Pd_{cap} are 2.706 Å, 3.149, 3.172 Å (two independent molecules). The steric effects in molecules I and II, and their influence on the stability of the cluster are discussed.

Introduction

Clusters of transition metals with carbonyl ligands are now well known [1–4]. A large number of such compounds have been synthesized and their structures studied, both homo-ligand ($[M_n(CO)_m]^x$, where x is a possible charge on the cluster) and hetero-ligand ($[M_n(CO)_pL_q]^x$, containing other ligands L besides CO in the coordination environment of the metal polyhedron). The mixed ligand clusters of the second type can be prepared by treating the neutral clusters of the first group with L (generally, the phosphine ligand). In this case, the metal framework of the original compound (of the Fe, Co subgroup) usually retains its structure. Unique structures are typical for metals of the Ni subgroup, where the neutral homo-carbonyl clusters

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are either unknown (Pd), or have not been characterized structurally (Pt). The factors, which determine the geometry of the metal polyhedron and the configuration of the ligand environment in purely carbonyl and carbonyl-hydride clusters, have been discussed in some detail [1,3,4]. The influence of a mixed ligand environment on the structure of polynuclear molecules has been far less studied, although some interesting contributions to the field have been reported (see, e.g., [5]). Studies of palladium carbonyl-phosphine clusters [6–8] have established the formation and interconversions of various polyhedral molecules under mild conditions, similar to those investigated by the Italian authors in the case of hetero-metal cluster systems [9], and have produced novel experimental data which need interpretation.

Experimental data

Unlike the Ni and Pt carbonyl complexes, the corresponding homo-ligand derivatives of Pd are unstable and were detected through specific procedures at temperatures below 30 K [10]. All known carbonyl-containing complexes of Pd^0 are stabilized by alkyl- and arylphosphine ligands, the Pd to phosphine ratio being close to, or less than 1 [11–13]. We have obtained the ten-vertex clusters $Pd_{10}(CO)_{14}(PBu^n{}_3)_4$ (I) and $Pd_{10}(CO)_{12}(PBu^n{}_3)_6$ (II), with a low relative content of phosphine ligand in the molecule [6,7]. Cluster I seems to be the ultimate case of stabilization of the carbonyl polynuclear Pd^0 complex by the minimal number of phosphine ligands. In an attempt to obtain compounds with a lower $PBu^n{}_3$ content by treatment of I with trifluoroacetic acid, the formation of metallic palladium and a mixture of highly unstable (unidentified) brown-black products occured. It is noteworthy that in all cases the preparation of single crystals of I was accompanied by metal precipitation.

Unlike II, cluster I partially decomposes during recrystallization from Et_2O/EtOH mixtures. The decomposition is accompanied by change of colour to a deeper black, an increase in palladium content and broadening of bands in the carbonyl region of the IR. The triethylphosphine analogue of I, $Pd_{10}(CO)_{14}(PEt_3)_4$ (III), is still more unstable: it cannot be isolated in the pure form at all; the complex III, obtained as a mixture with $Pd_{10}(CO)_{14}(PEt_3)_6$ (IV) at a $Pd(OAc)_2$ to PEt_3 ratio of 1/1.5 [6] decomposes even on desiccation in vacuo for a short time.

We previously suggested a method for preparing both I and II. On the basis of the X-ray diffraction study of II, and IR and ^{31}P NMR spectra, it was suggested that I was a product with two phosphine ligands in cluster II substituted by terminal CO ligands, and the interconversion $I \rightleftarrows II$ was studied [7]. To establish unequivocally the molecular structure of I and to study the influence of the ligand substitution on the geometric parameters of the cluster, an X-ray diffraction investigation of I has been carried out.

Crystal structure of I

Cluster I forms tetragonal crystals with two independent $Pd_{10}(CO)_{14}(PBu^n{}_3)_4$ molecules in the unit cell. The first molecule (A) occupies the special position $\bar{4}$, while the second (B), the special position 222. The geometrical parameters of the cluster nucleus, shown in Table 1, practically coincide for the independent molecules. Due to the low scattering ability of the crystal, the coordinates of the light atoms (CO ligands and butyl groups of the phosphine ligands) were established with

TABLE 1

PRINCIPAL BOND LENGTHS AND VALENCE ANGLES IN I WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Lengths (Å)			
Pd(1)–Pd(2)	2.869(5)	Pd(2)–C(4)	2.09(6)
Pd(1)–Pd(3)	3.172(3)	Pd(3)–C(4)	1.98(5)
Pd(2)–Pd(2′)	2.828(4)	Pd(5)–C(5)	1.74(3)
Pd(2)–Pd(3)	2.720(5)	Pd(4)–C(6)	2.14(4)
Pd(2)–Pd(3′)	2.719(5)	Pd(5)–C(6)	2.12(4)
Pd(4)–Pd(5)	2.807(4)	Pd(6)–C(6)	2.30(4)
Pd(4)–Pd(6)	2.800(4)	Pd(4)–C(7)	2.6(2)
Pd(4)–Pd(7)	2.689(4)	Pd(7)–C(7)	2.8(2)
Pd(5)–Pd(6)	2.808(4)	Pd(6)–C(8)	1.9(2)
Pd(5)–Pd(7)	3.149(6)	Pd(7)–C(8)	2.0(2)
Pd(6)–Pd(7)	2.724(6)	C(1)–O(1)	0.9(1)
Pd(3)–P(1)	2.29(1)	C(2)–O(2)	1.15(5)
Pd(7)–P(2)	2.24(2)	C(3)–O(3)	1.25(6)
Pd(1)–C(1)	2.01(8)	C(4)–O(4)	1.30(6)
Pd(1)–C(2)	2.12(4)	C(5)–O(5)	1.26(5)
Pd(2)–C(2)	2.30(4)	C(6)–O(6)	1.20(6)
Pd(2)–C(3)	2.12(5)	C(7)–O(7)	0.8(2)
Pd(3)–C(3)	1.92(5)	C(8)–O(8)	1.4(2)
Angles (°)			
Pd(2)Pd(1)Pd(2′)	60.0(1)	Pd(5)Pd(4)Pd(6)	60.70(7)
Pd(2)Pd(1)Pd(2″)	88.3(1)	Pd(5)Pd(4)Pd(5′)	90.30(9)
Pd(1)Pd(2)Pd(2′)	61.5(1)	Pd(6)Pd(4)Pd(6′)	90.06(9)
Pd(1)Pd(2)Pd(1′)	90.0(1)	Pd(5)Pd(4)Pd(7)	69.9(1)
Pd(1)Pd(2)Pd(3)	70.4(1)	Pd(4)Pd(5)Pd(6)	59.84(7)
Pd(2′)Pd(2)Pd(2″)	89.9(1)	Pd(4)Pd(5)Pd(4′)	89.70(9)
Pd(2)Pd(3)Pd(2′)	62.7(1)	Pd(6)Pd(5)Pd(6′)	59.84(7)
Pd(4)Pd(6)Pd(4′)	89.9(9)	Pd(2)Pd(3)P(1)	145.7(7)
Pd(4)Pd(6)Pd(5)	60.06(7)	Pd(2′)Pd(3)P(1)	151.5(7)
Pd(5)Pd(6)Pd(5′)	90.25(8)	Pd(4)Pd(7)P(2)	153.2(9)
Pd(5)Pd(6)Pd(7)	69.37(9)	Pd(6)Pd(7)P(2)	144.3(9)
Pd(4)Pd(7)Pd(6)	62.3(1)		

rather large errors and will not be discussed further.

The molecule I, as was initially expected, is a close structural analogue of II and contains a ten-vertex metal Pd_{10} cluster—an octahedron with four asymmetrically capped faces (Fig. 1), similar to that found in the structure of II [7]. The average geometrical parameters in clusters I and II, viz. the Pd–Pd distances in the inner octahedron Pd_6 (2.824 Å in I, 2.825 Å in II), the short Pd–Pd (bridged by the μ_2–CO ligands) bond length (2.706 Å in I, 2.709 Å in II), the Pd–P distances (2.27 Å in I, 2.304 Å in II), are in good agreement. The apical positions of the Pd atoms of the inner octahedron in $Pd_{10}(\mu_3\text{-CO})_4(\mu_2\text{-CO})_8(PBu^n{}_3)_4L_2$ clusters are occupied in I by terminal CO groups instead of the tri-n-butylphosphine ligands in II. This substitution diminishes the Pd_{cap}–Pd_{apic} distances from 3.300–3.422 Å in II down to 3.172 and 3.149 Å in the two independent molecules in I.

Though low accuracy does not allow discussion of the detailed geometry of the tri-n-butylphosphine substituents and intramolecular contacts, it is noteworthy,

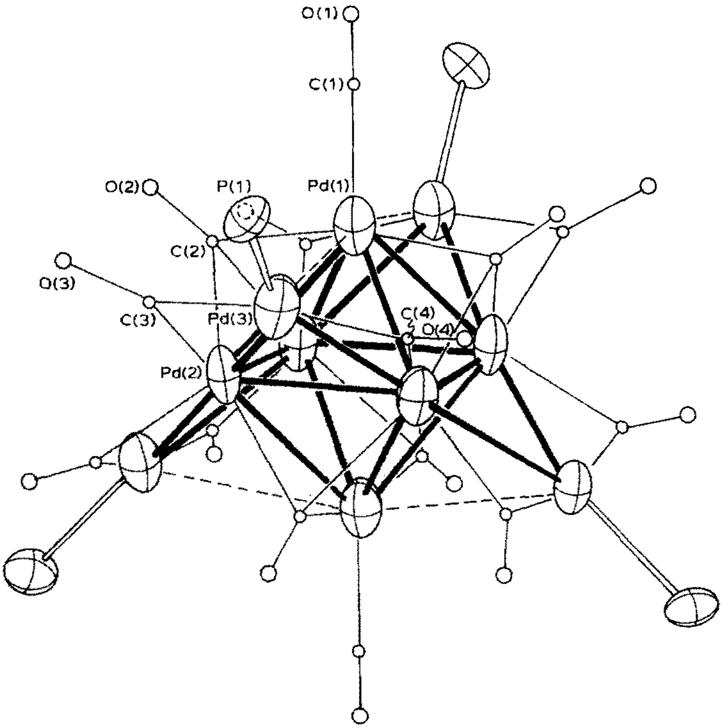

Fig. 1. Molecular structure of compound IA (n-butyl substituents omitted).

however, that the P atom of each phosphine ligand is shifted slightly from the plane of the three Pd atoms (one capping atom and two equatorial atoms of the inner octahedron) towards the apical Pd atom by 0.15 Å in the molecule (A), and by 0.11 Å in the molecule (B). The arrangement of molecules in the crystal and the intermolecular contacts correspond to the usual Van der Waals interactions.

Discussion

The drop in the stability of purely carbonyl clusters, and on passing from homo-ligand clusters to the hetero-ligand ones, at the end of the transition metal series (the Ni subgroup, especially Pd and Pt) corresponds directly to the increase in the number of valence electrons and to the fall in the coordination capabilities of atoms in that same row. It is thus reasonable to suggest that the incorporation of bulky hetero-ligands (substituted phosphines) should raise the stability of a cluster molecule owing to the more effective shielding of its surface, given the same number of ligands in the coordination sphere of a metal polyhedron as a whole. Recently, a number of investigators have used the hypothesis of "the close packing" of ligands in the coordination sphere of a cluster [4,5], as the basis for the calculation of the ligand configuration allowing for their steric interactions [4]. The relative size of such steric interaction can be estimated without calculation by constructing a "coordination shell" around a cluster, which is contained in between the two spherical surfaces, the inner being arranged at the metal–ligand bond distance from the "surface" of the cluster, the outer being defined by the distance which leads to the vanishing of short inter-ligand contacts, and then calculating the effective volume of the coordination sphere for each CO ligand. The absolute values of such "effective volumes" (V_{eff}) of ligands are arbitrary to some extent and depend on the definition of the surfaces of the coordination sphere. However, when reasonably chosen (e.g., to include all the short inter-ligand contacts in the spherical layer), the comparison of V_{eff} for similar systems allows one to estimate the relative steric overcrowding of the ligand environment. The "close packing" of CO ligands in purely carbonyl clusters leads to V_{eff} values of about 12–15 Å^3/ligand for the majority of metal clusters of the Fe and Co subgroup, provided that the "coordination shell" thickness is chosen as equal to 1.2 Å. The proper "effective volume" of the CO group with the shell of the given thickness, calculated from Van der Waals radii for C and O, is ca. 9–10 Å^3. It can be expected that when arranging additional CO ligands in the coordination sphere it is possible in principal to come up to that limiting V_{eff} value, while with $V_{eff} < 9$ Å^3 the steric overcrowding will increase rapidly.

Such an approach can be extended to include hetero-ligand clusters, provided a method is found for estimating what part of the space in the coordination sphere is occupied by phosphine groups and thus is inaccessible to the CO ligands. The simplest method is to represent the phosphine ligand PR_3 by its Tolman's cone [14], assuming that the CO ligands occupy uniformly the rest of the space of the coordination shell. Thus for the tetrahedral cluster $Pd_4(\mu_2\text{-}CO)_6(PBu^n{}_3)_4$, studied previously by us, this method gives $V_{CO} = 4/3\pi(R_2^3 - R_1^3) - 4V_{PR_3}$ and thus, using the Tolman's cone angle of $\theta = 130°$ for $PBu^n{}_3$, $V_{CO} = 82$ Å^3 and $V_{eff} = 13.7$ Å^3. It is therefore possible to say that there is close packing of the CO ligands in the phosphine-free space in the cluster coordination shell.

Applying this qualitative approach to examine the non-bonded contacts between the CO ligands in clusters I and II, we taken a cross section of the metal polyhedron through the apical atoms of the inner octahedron and two of the four capping Pd

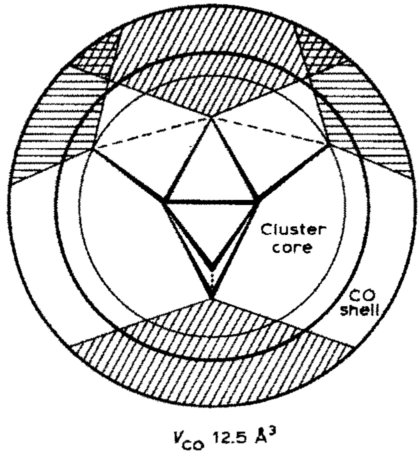

Fig. 2. Section of the coordination sphere of the Pd_{10} cluster, through the apical Pd atoms (shaded areas show Tolman's cones for the PBu_3 ligands).

TABLE 2

ATOMIC COORDINATES IN I ($\times 10^3$; FOR P AND Pd $\times 10^4$)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pd(1)	0	0	1285(3)	Pd(2)	9243(1)	457(1)	−39(3)
Pd(3)	1356(2)	304(1)	998(3)	Pd(4)	0.5	0	3727(3)
Pd(5)	5223(1)	623(1)	0.5	Pd(6)	4380(1)	620(1)	0.5
Pd(7)	4804(3)	1169(2)	3567(4)	P(1)	12077(5)	396(5)	2024(8)
P(2)	4916(8)	2044(5)	2918(10)	O(1)	0	0	317(6)
O(2)	960(1)	130(1)	147(8)	O(3)	812(2)	94(2)	76(3)
O(4)	836(1)	108(1)	−130(2)	O(5)	656(2)	156(2)	0.5
O(6)	363(2)	−5(2)	357(3)	O(7)	574(2)	38(3)	220(4)
O(8)	403(2)	191(2)	462(3)	C(1)	0	0	258(5)
C(2)	975(2)	89(2)	108(3)	C(3)	846(2)	504(2)	72(3)
C(4)	888(2)	104(2)	−93(4)	C(5)	617(2)	117(2)	0.5
C(6)	407(2)	−6(2)	400(3)	C(7)	548(7)	52(7)	242(10)
C(8)	431(8)	139(8)	456(10)	C(111)	1205(4)	117(4)	249(6)
C(112)	1258(5)	121(5)	308(7)	C(113)	1259(4)	200(4)	369(6)
C(114)	1217(4)	185(4)	414(7)	C(121)	1208(4)	−17(4)	270(6)
C(122)	1171(3)	−56(3)	306(4)	C(123)	1180(5)	−115(5)	336(7)
C(124)	1246(6)	−154(5)	348(8)	C(131)	1287(3)	51(3)	172(5)
C(132)	1314(5)	74(5)	940(8)	C(133)	1369(4)	30(4)	60(5)
C(134)	1394(4)	−6(4)	9(6)	C(211)	521(4)	263(3)	374(5)
C(212)	567(9)	331(8)	385(12)	C(213)	555(8)	366(7)	404(10)
C(214)	497(5)	377(4)	452(6)	C(221)	418(5)	239(5)	259(7)
C(222)	397(3)	202(3)	181(5)	C(223)	345(3)	219(3)	120(5)
C(224)	360(4)	272(4)	66(7)	C(231)	535(5)	211(4)	225(7)
C(232)	592(4)	192(4)	206(6)	C(233)	652(4)	200(5)	136(7)
C(234)	636(6)	141(6)	102(9)				

atoms (giving a section which coincides with the idealized σ_v plane of the Pd_{10} polyhedron with S_4 symmetry), and drew two spheres of radii 3.5 Å and 4.7 Å, respectively. The "coordination shell" constructed in this way involves μ_2–CO ligands and the terminal CO ligands of the cluster I, whereas the μ_3-CO ligands are arranged nearer to the centre and thus diminish the free volume of the coordination shell insignificantly (Fig. 2). The PBu^n_3 ligands were represented in the usual manner as Tolman's cones with a θ angle of 130°. With such a model the free volume for I and II is about 180 and 100 Å^3, respectively, or, for each CO ligand the V_{eff} will amount to 18 (I) and 12.5 (II) Å^3. Thus, "close packing" is possible, at least for II. Fig. 2 shows, however, that the absence of steric overcrowding in I occurs in the "apical" regions only, where the terminal CO ligands are located, while the values of the free volume in the coordination sphere at the "equatorial belt" for I and II are close to each other. This fact provides an explanation for the shortening of the Pd_{apic}–Pd_{cap} distances when passing from II to I, and for the displacement of the P atoms in I towards the apical palladium atom. Namely, these features arise as a result of a "pressure" of equatorial CO ligands when a "hole" (the region of low steric overcrowding) appears due to the substitution of "apical" PBu^n_3 by CO ligands. The small overlap of the PBu^n_3 ligands' cones in II does not correspond to important steric hindrance, since the Tolman's angle seems to exceed the Van der Waals volume for the phosphine ligand [15] leaving out of account the different conformations of the flexible n-Bu substituents. Indeed, the fact that there were no short intramolecular contacts, $PBu^n_3 \ldots PBu^n_3$, in II [7], caused certain perplexity before the concept of the "coordination shell" was employed.

Within the framework of our approach it is rather easy to account for the different stability of I and II. Actually, the poor shielding in the region of "apical" Pd atoms in I render the cluster more exposed to ligands' attack, whereas the donating of "excessive" electrons to a polyhedron must lead to its opening and subsequent destruction. This potential of terminal CO's for substitution is of certain preparative interest, since it provides the possibility of obtaining mixed ligand clusters by substitution of "apical" CO's by other ligands—phosphine and similar ones. The lower stability of III—the triethylphosphine analogue of I—can be explained likewise, since the PEt_3 ligands must shield the cluster nucleus less efficiently than PBu^n_3. The Tolman's angles for PEt_3 and PBu^n_3 are equal; they neglect, however, the conformational flexibility of PBu^n_3, in consequence of which the solid cone angles [15] for these ligands should differ. In contrast to III, the stability of IV, which is the analogue of II, is close to that of II. The shielding of the cluster nucleus should also play an essential role in the stereochemistry of the clusters $Pd_n(CO)_x(PR_3)_y$ with other phosphine ligands PR_3; in particular in the case of the very interesting series of PPh_3 derivatives, which are currently under investigation.

Application of Tolman's cones to the interpretation of the stability of mononuclear phosphine derivatives gave rise to a number of limitations [15–17]. Thus it was shown that for the real crystalline structures it would be more correct to define the steric requirements of the PR_3 ligand by a solid cone angle, instead of a cone of constant aperture θ; the former being defined as $\Omega = \int_0^{2\pi} (1 - \cos^{1/2}\theta)d\theta$, and bounded in all directions by the tangent to the true Van der Waals surface of the ligand [15]. The values of Ω (as well as the effective values θ_{eq}, calculated from them) vary over a wide range for different compounds [15], and they should be used with caution [16,17]. The θ_{eq} values seem to be more suitable for the realistic description, however our simple approach proves to be useful for the qualitative considerations.

Experimental

Preparation of single crystals of $Pd_{10}(CO)_{14}(PBu^n_3)_4$ (I)

To a solution of $Pd(OAc)_2$ (0.086 g, 0.38 mmol) in dioxane (14 ml) in a 100 ml flask, CF_3COOH (4.0 ml), PBu^n_3 (0.15 ml, 0.60 mmol), H_2O (1.9 ml), and acetone (2.5 ml) were added consecutively with stirring. The flask was filled with CO, and the solution was stirred for 12 min in an atmosphere of CO and left for 48 h. During this time a mirror of metal Pd was precipitated, and the black-red crystals of I separated. The product was washed with EtOH and dried in a flow of dry CO to give I (0.015 g, 17%). IR (Nujol cm^{-1}): $\nu_{CO-bridge}$ 1913s, 1898s, 1896s, 1831sh, 1818s; $\nu_{CO-term}$ 2033s; identical with that of I [6] with a $Pd(OAc)_2$ to PBu^n_3 ratio of $1/1.5 + 1/2$.

Preparation of $Pd_{10}(CO)_{14}(PBu^n_3)_4$ (I) from $Pd_{10}(CO)_{12}(PBu^n_3)_6$

To II (0.400 g, 0.15 mmol) was added a mixture of acetone (35 ml), CF_3COOH (10 ml) and H_2O (5 ml) and the reaction was stirred in an atmosphere of CO for 3.5 h. The dark-red material was isolated, washed with EtOH and dried in vacuo over a liquid nitrogen for 20 min, to yield I (0.317 g, 91%). (Found: Pd, 47.00; P, 5.18. $C_{62}H_{108}O_{14}P_4Pd_{10}$ calcd.: Pd, 46.97; P, 5.47%). The IR spectrum is identical to that of the authentic material [6,7]. To isolate I for a given concentration of acid, the reaction must be carried out for a controlled period of time.

X-ray diffraction investigation of I

Crystals of I are tetragonal, a 15.556(6), c 22.594(8) Å, $Z = 4$, space group $P\bar{4}b2$ (confirmed by structure determination), d_c 2.77 g/cm^3. The cell parameters and intensities of 3360 independent reflections were measured with the Syntex $P2_1$ four-circle automatic diffractometer (λ(Mo-K_α), graphite monochromator, $\theta/2\theta$ scan, $2\theta \leqslant 48°$). The calculations were performed using 3200 reflections with $I > 2\sigma$. The structure was resolved using the heavy atom procedure (initially for the $P\bar{4}$ space group) and further refined by the full-matrix anisotropic (Pd,P)-isotropic least squares to $R = 0.096$, $R_w = 0.124$ using 2817 reflections with $I > 3\sigma$; absorption was neglected. Atomic coordinates are listed in Table 2. All calculations were performed on an Eclipse S/200 computer using EXTL programmes modified by A.I. Yanovskii and R.G. Gerr.

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