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Non-trivial behavior of palladium(II) acetate†

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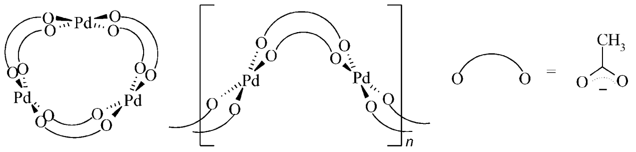
Reaction of activated palladium metal with a HNO_3/acetic acid mixture produces both orange $Pd_3(OAc)_6$, **1**, and purple $Pd_3(OAc)_5(NO_2)$, **2**. Compound **2** has a trinuclear structure derived from that of the well-known triangular complex **1** in which one acetate group has been replaced by a nitrite group which is bonded to one palladium atom by the nitrogen atom and to another Pd atom using one of the oxygen atoms. Highly pure **1** can be made by continuous removal of the nitric oxides from the reaction mixture using a flow of N_2. ^{1}H NMR spectra of solutions of **1** in $CDCl_3$ and C_6D_6 show several signals of various intensities when a small amount of water is present in the deuterated solvents but only one signal when the solvents are thoroughly dried. These results are consistent with the occurrence of one or more hydrolysis processes when the solvents contain water and suggest that hypotheses about various $[Pd(OAc)_2]_n$ aggregates that have previously been brought forward in the literature to explain the complexity of the spectrum of **1** are unnecessary, especially for nonpolar solvents. Compound **2** does not hydrolyze, and in wet or dried solvents shows a ^{1}H NMR spectrum that consists of five equal-intensity signals due to the five nonequivalent acetate groups.

Introduction

Palladium(II) acetate (**1**) is an important substance with many significant uses. It catalyses many organic reactions,[1] is easily reduced by light[2] or heat[3] to form thin films of Pd and can produce colloids[4] and nanowires.[5] The primary use of **1**, however, is as a starting material for the syntheses of other Pd(II) compounds as well as for the preparation of palladium catalysts and their precursors.[6] It is usually prepared by reaction of a slight excess of activated palladium metal, usually made by reduction of palladium dichloride with formic acid,[7] and a deficiency of nitric acid in acetic acid to assure the entire consumption of nitric acid.[8] In the solid state, the structure is generally trinuclear with nearly idealized D_{3h} symmetry, in which each of the three palladium atoms is in a square planar environment and there are six bridging acetate groups,[9] as shown in Chart 1. The structures of four crystalline forms having five independent molecules show that the D_{3h} structure is persistent and there are only small variations in the non-bonded Pd···Pd distances in the $Pd_3(OAc)_6$ molecules. This unusual structure is known in only one other case,[10] *viz.* $Cu_3[O_2C(2,4,6\text{-}(Me_2CH)_3C_6H_3]_6$. Recently, a structure was reported of a polymeric, water-insoluble form (**1′**).[11] The chain structure was determined from X-ray powder diffraction data of a pink substance formed upon prolonged heating of a mixture prepared by adding acetic acid to a solution of palladium dissolved in nitric acid.



1 1′

Chart 1

In solution, the structure of palladium acetate has remained somewhat controversial. Claims have been made supporting the persistence of the trinuclear molecules in solution,[12] while other evidence is said[13] to support the formation of various aggregates of $[Pd(OAc)_2]_n$ ($n = 1, 2, 3,$ *etc.*). The ^{1}H NMR spectrum of palladium acetate in methanol has been reported[14] to show a large number of signals in the range where a single acetate signal would be expected for the symmetrical triangular structure. This was said to be indicative of a variety of aggregates and possibly even the occurrence of ionic species. More recently in a paper describing the use of palladium acetate for the preparation of a catalyst and entitled "Too many precautions in making a catalyst is never a loss of time: A lesson we learned at our own expense", a discussion was provided for the importance of the nature of the palladium acetate in solution and the solvent used for the preparation of catalysts.[15]

Because of our interest in metal–metal bonded dipalladium compounds such as those containing Pd_2^{6+} [16] and Pd_2^{5+} units,[17] we have recently initiated a broad study of these compounds. Although we had a considerable amount of palladium dichloride available, its low solubility in common organic solvents limits the utility of $PdCl_2$ as a starting material for the preparation of such complexes, and we preferred to use the soluble palladium acetate. Therefore, we sought a good method for the preparation for **1** from $PdCl_2$. What we expected to be a trivial synthetic exercise has led us to believe that not all of the so-called preparations of palladium acetate indeed lead to the desired compound in good purity. Here we report the structure of $Pd_3(OAc)_5NO_2$, **2**, which has a structure similar to that of $Pd_3(OAc)_6$ except that one acetate ion has been replaced by a bridging nitrite ion. We can now also shed some light on the solution behavior of $Pd_3(OAc)_6$ in both wet and carefully dried NMR solvents. We also provide a reliable and reproducible synthesis of $Pd_3(OAc)_6$ using $PdCl_2$ as starting material.

Results and discussion

Although palladium(II) acetate is commercially available, there are several recent reports describing its preparation.[18] We

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† *In memoriam* Mervin J. Bazile, Jr. (1977–2005).

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originally selected the reaction of activated Pd metal in nitric acid described by Zhang and coworkers,[18a] because it appeared to be a straightforward, high yield method. This method is summarized by the following pair of reactions:

$$PdCl_2 + NaHCO_2 + NaOH \rightarrow Pd + CO_2 + 2\,NaCl + H_2O \quad (1)$$

$$3Pd + 6HNO_3 + 6HOAc \rightarrow Pd_3(OAc)_6 + 6NO_2 + 6H_2O \quad (2)$$

The first reaction occurs as reported with rapid formation of finely divided palladium metal. The freshly formed powder is subsequently oxidized by a mixture of HNO_3 and acetic acid, and the product is extracted in a 1 : 2 mixture of CH_2Cl_2 : hexanes. Crystals are obtained by evaporation in a stream of N_2. However, this produced a mixture of purple and orange crystals which can be separated manually. The ^{1}H NMR spectrum of the orange crystals in $CDCl_3$ was identical to that of a commercial sample of **1** (Aldrich) and shows five resonances of various intensities at around 2 ppm as shown in Fig. 1a. This is not consistent with the D_{3h} symmetry of $Pd_3(OAc)_6$ in the solid state but is consistent with literature reports.[14] The ^{1}H NMR spectrum of the purple crystals shows five resonances of essentially equal intensities at 1.961, 2.004, 2.045, 2.073 and 2.082 ppm (Fig. 1b). The spectrum of the bulk product from the reaction mixture, shown in Fig. 1c, is a superposition of the two spectra shown in Figs. 1a and 1b which indicates that these are the only soluble species produced in the reaction. The orange crystals are a new crystalline form of the well-known triangular $Pd_3(OAc)_6$ molecule, crystallized with one CH_2Cl_2 molecule per formula unit as interstitial solvent (Fig. 2). The purple crystals, which have the composition $Pd_3(OAc)_5NO_2$, have the structure shown in Fig. 3. In this compound, the trinuclear motif is preserved but one of the acetate groups is replaced by a nitrite group (NO_2^-) which is bound to the palladium atom by the N atom and one O atom. The substitution of an acetate group breaks the D_{3h} symmetry of **1** causing the remaining acetate groups to be nonequivalent, thus accounting for the five peaks of equal intensity in the ^{1}H NMR spectrum. The formation of **2** can be attributed to the attack of nitrogen oxides on the $Pd_3(OAc)_6$ molecule. These oxides are generated during the oxidation of Pd powder with HNO_3. To avoid the formation of $Pd_3(OAc)_5NO_2$, the brown nitrogen oxide gases must be eliminated promptly by bubbling N_2 gas through the reaction mixture. In this way, pure $Pd_3(OAc)_6$ forms as the sole product.

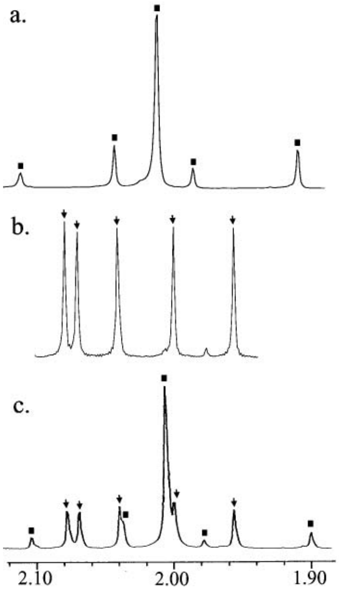


Fig. 1 ^{1}H NMR spectra taken at 300 MHz in solutions of $CDCl_3$ (as supplied by the manufacturer). (a) commercial $Pd_3(OAc)_6$, (b) $Pd_3(OAc)_5(NO)_2$, (c) "$Pd_3(OAc)_6$" prepared according to ref. 12*a*.

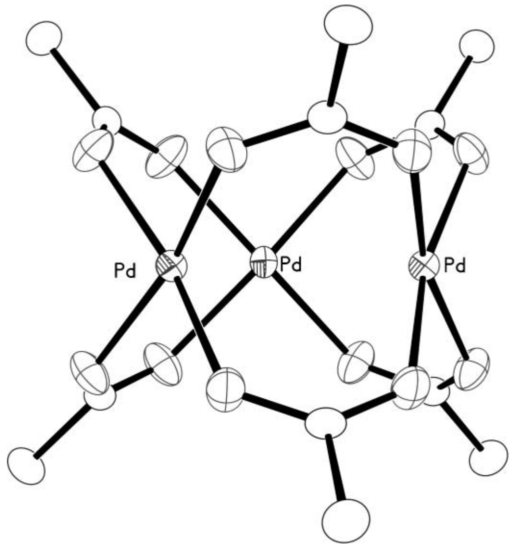


Fig. 2 Molecular structure of $Pd_3(OAc)_6$ with ellipsoids drawn at the 30% probability level and hydrogen atoms removed.

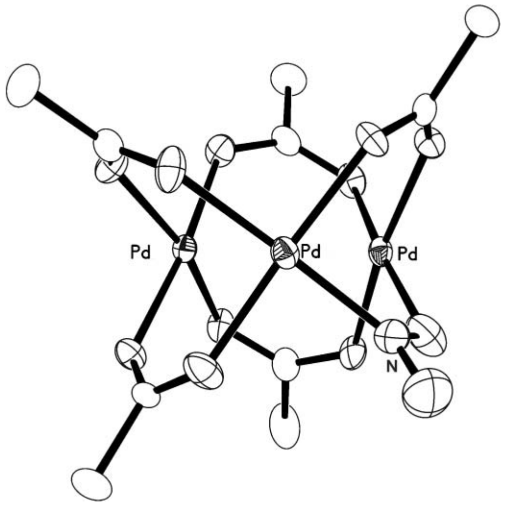
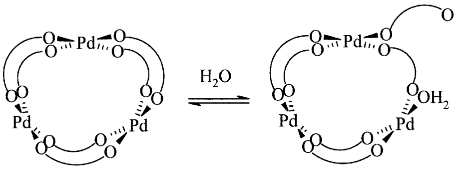


Fig. 3 Molecular structure of $Pd_3(OAc)_5(NO_2)$ with ellipsoids drawn at the 30% probability level and hydrogen atoms removed.

The appearance of various signals in the ^{1}H NMR spectrum of freshly prepared and commercial samples of **1** was puzzling. We studied this issue by examining several ^{1}H NMR spectra of $Pd_3(OAc)_6$ in commercial solvents, such as CD_3OD, $CDCl_3$ and C_6D_6. It was noted that the number and relative intensities of some peaks are extremely sensitive to the nature of the solvent but more importantly the signal for water that was always present in the solvents $CDCl_3$ and C_6D_6 was absent in solutions of **1**. Furthermore, when rigorously dry $CDCl_3$ or C_6D_6 was used to dissolve either freshly synthesized or commercial samples of **1**, each spectrum displayed only one sharp signal. In $CDCl_3$ this signal is at 2.006 ppm and corresponds to the major peak in Fig. 1c. The signal shifts to 1.622 ppm when the spectrum is obtained in C_6D_6.[19] We now believe that these observations are consistent with the occurrence of one or more hydrolysis processes when the nonpolar solvents contain a small amount of water (Scheme 1). Because molecular weight determinations



Scheme 1

in benzene and dichloromethane solutions indicate that the molecule is trinuclear,[7,12] it is likely that this trinuclear core is retained.

It is interesting to note that a similar hydrolysis process does not occur in the nitrito compound **2**, since the five expected resonances for the acetate groups all have equal intensity, and no extraneous peaks are present even in the presence of small amounts of water. A structurally analogous complex having five acetate ligands and one oxazolone ligand around the triangular Pd_3 core also shows only five acetate resonances in its ^1H NMR spectrum.[20] Thus, it appears that once one acetate ligand is replaced by a stronger bidentate ligand, the resulting $Pd_3(OAc)_5(L)$ complex is kinetically less labile than the $Pd_3(OAc)_6$ precursor. This would also explain why a more complex mixture of $Pd_3(OAc)_n(NO_2)_{6-n}$ species is not observed in the reaction mixture.

The occurrence of hydrolysis is also consistent with the known reactivity of $Pd_3(OAc)_6$ toward ligands such as amines, phosphines and arsines leading to mononuclear complexes such as *trans*-$[Pd(OAc)_2(PR_3)_2]$, in which the acetate groups are monodentate.[7,21] The results we report here would seem to provide an explanation for the previously reported "anomalous" behavior of palladium(II) acetate. We note particularly that the hypothesis about various $[Pd(OAc)_2]_n$ species in solution with n other than 3 seems unnecessary.

Experimental

General procedures

Unless otherwise stated, operations were carried out in air. Solvents were purified using a Glass Contour purification system. Deuterated solvents were used as received, except for samples that were carefully dried using freshly dried molecular sieves. $Pd_3(OAc)_6$ was purchased from Aldrich and deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc.

Physical measurements

The IR spectra were recorded on a Perkin-Elmer 16PC FTIR spectrometer using KBr pellets. Elemental analyses were carried out by Canadian Microanalytical Services in British Columbia, Canada. Samples were vacuum dried prior to elemental analyses in order to remove the interstitial solvent molecules of the crystals. ^1H and ^{13}C NMR spectra were obtained on a VXR-300 NMR spectrometer.

Synthesis of $Pd_3(OAc)_6$ (1). A mixture of sodium hydroxide (1.0 g, 25 mmol) and HCOONa (0.80 g, 11.7 mmol) was added to a solution of $PdCl_2$ (0.500 g, 2.86 mmol) in 50 ml of water. Formation of a palladium powder occurred immediately. The suspension was stirred for 30 min to allow the palladium particles to coagulate. The palladium was separated by filtration, washed with acetone and dried under vacuum. The solid was then suspended in 20 ml of glacial acetic acid, and 0.3 ml of concentrated nitric acid was slowly added with stirring. The resulting solution was heated to reflux for 30 min while N_2 was bubbled through the reaction mixture and the volume of the solution was then reduced to a third of the original volume by slow evaporation using mild heating. After cooling to room temperature, an orange powder was isolated by filtration. Yield: 0.605 g (94.4%). ^1H NMR (very dry $CDCl_3$, 300 MHz, δ, ppm): 2.006 (s); IR (KBr, cm^{-1}): 1600 vs, 1430 vs, 1350 w, 1157 vw, 1047 vw, 951 vw, 696 m, 625 vw.

Crystals of **1** were obtained by addition of 50 mg of the $Pd_3(OAc)_6$ synthesized as just described to a mixture of 10 ml of CH_2Cl_2 and 10 ml of hexanes. After filtration, slow evaporation of the solvent under a N_2 stream produced orange plates the following day.

Synthesis of $Pd_3(OAc)_5(NO_2)$ (2). This was prepared similarly to **1** but when the palladium metal was allowed to react with a mixture of acetic acid and nitric acid, no N_2 flow was applied to eliminate the brown gases formed. Concentration of the solution by a factor of 3 was accomplished by slow evaporation under mild heating, and cooling to room temperature yielded an orange powder. To this powder was added a mixture of 10 ml of CH_2Cl_2 and 10 ml of hexanes. A small amount of solid was eliminated after filtration. Slow evaporation of the solution was performed by passing a constant N_2 flow over it. Two types of crystals were obtained. Orange plates were $Pd_3(OAc)_6$ and purple cubes were $Pd_3(OAc)_5(NO_2)$. The products were separated manually. Yield of **2**: 0.2601 g (40.0%). ^1H NMR ($CDCl_3$, 300 MHz, δ, ppm): 1.960 (s, 1H), 2.004 (s, 1H), 2.043 (s, 1H), 2.072 (s, 1H), 2.081 (s, 1H); IR (KBr, cm^{-1}): 1608 vs, 1560 s, 1541 s, 1517 s, 1420 vs, 1351 m, 1261 m, 1197 m, 1153 w, 1098 s, 1024 s, 949 w, 867 w, 800 m, 696 m, 622 w.

X-Ray quality crystals of **2** were obtained by recrystallization of 50 mg of the purple solid from the reaction in a mixture of 10 ml of CH_2Cl_2 and 20 ml of hexanes.

X-Ray diffraction analyses

A suitable crystal of $\mathbf{1}\cdot CH_2Cl_2$ was placed inside a loop using a small amount of stopcock grease, and was mounted on the goniometer of a Bruker SMART 1000 CCD area detector diffractometer. The crystal was centered in the goniometer, and cooled to −60 °C in a stream of cold nitrogen. Geometric and intensity data were collected using SMART software.[22] The data were processed using SAINT software,[23] and corrections for absorption were applied using the program SADABS.[24] Crystal data are presented in Table 1. Table 2 lists pertinent bond distances and angles for $\mathbf{1}\cdot CH_2Cl_2$ and **2**. The positions of the Pd atoms were determined using the Patterson method available in the SHELX-97 software package.[25] This was followed by least squares refinement and difference Fourier synthesis to determine the positions of the remaining heavy atoms. Hydrogen atoms were placed in calculated positions based on a riding model.

CCDC reference numbers 262707 and 262708 for **2** and $\mathbf{1}\cdot CH_2Cl_2$, respectively.

Table 1 Crystal data and structure refinement for $\mathbf{1}\cdot CH_2Cl_2$ and **2**

	$\mathbf{1}\cdot CH_2Cl_2$	**2**
Empirical formula	$Pd_3C_{13}H_{20}O_{12}Cl_2$	$Pd_3C_{10}H_{15}O_{12}N$
Formula weight	758.39	660.43
Space group	*Pbcm*	$Pna2_1$
a/Å	8.139 (2)	15.854 (4)
b/Å	15.891(4)	11.608 (3)
c/Å	17.500 (5)	10.109 (3)
V/Å^3	2263.5(11)	1860.5(8)
Z	4	4
Density (calcd.)/g cm^{-3}	2.226	2.358
μ(Mo–Kα)/mm^{-1}	2.649	2.927
$R1^a$, $wR2^b$ $[I > 2\sigma(I)]$	0.0214, 0.0563	0.0280, 0.0717
$R1^a$, $wR2^b$ (all data)	0.0244, 0.0583	0.0309, 0.0736

[a] $R1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$. [b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{\frac{1}{2}}$, $w = 1/\sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [\max(0 \text{ or } F_o^2) + 2(F_c^2)]/3$.

Table 2 Selected interatomic distances[a] for $\mathbf{1}\cdot CH_2Cl_2$ and **2**

	$\mathbf{1}\cdot CH_2Cl_2$	**2**
Pd···Pd[b]	3.1678[7]	3.103 [1]
Pd–O	1.995[2]	2.011 [5]
Pd–N	—	1.949(7)

[a] Distances given in Å. Numbers in square brackets correspond to average values. [b] In trinuclear forms the reported Pd···Pd separations are in the range of 3.081(2) to 3.203(1) Å (see ref. 9) while the unique distance in the polymeric form is 2.9192(1) Å (see ref. 11).

See http://www.rsc.org/suppdata/dt/b5/b502122g/ for crystallographic data in CIF or other electronic format.

Acknowledgements

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