1390 *Inorg. Chem.* **1989**, *28*, 1390–1394

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Oxidative Addition of Phenols to $Pd(PCy_3)_2$. Synthesis and Structural Characterization of *trans*-$[Pd(PCy_3)_2(H)(OC_6H_5)]\cdot C_6H_5OH$ (1) and *trans*-$[Pd(PCy_3)_2(H)(OC_6F_5)]\cdot C_6F_5OH$ (2)

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Received July 12, 1988

The reaction of $Pd(PCy_3)_2$ (Cy = cyclohexyl) with C_6H_5OH and C_6F_5OH in toluene gives the phenoxopalladium(II) hydride derivatives *trans*-$[Pd(PCy_3)_2(H)(OAr)]\cdot ArOH$ (Ar = C_6H_5 (**1**), C_6F_5 (**2**), respectively). No reaction was observed if alcohols instead of phenols were employed. **1** and **2** react in toluene solution with CO, giving the polynuclear species $[Pd(PCy_3)(CO)]_n$ together with reductive elimination of ArOH. The structures of **1** and **2** were established by single-crystal X-ray diffraction. The structural models were refined to $R = 0.033$ ($R_w = 0.037$) for 6568 independent reflections (**1**) and to $R = 0.040$ ($R_w = 0.041$) for 6618 independent reflections (**2**). Crystal data: triclinic, space group $P\bar{1}$ for both **1** and **2**; $a = 13.535$ (6) Å, $b = 16.131$ (4) Å, $c = 11.759$ (5) Å, $\alpha = 109.24$ (3)°, $\beta = 106.34$ (3)°, and $\gamma = 84.21$ (3)° for **1**; $a = 10.423$ (6) Å, $b = 14.047$ (5) Å, $c = 17.335$ (4) Å, $\alpha = 94.38$ (2)°, $\beta = 95.16$ (3)°, and $\gamma = 103.66$ (4)° for **2**. In both compounds the oxygen of the phenoxo and pentafluorophenoxo ligands forms a hydrogen bridge with an uncoordinated phenol and pentafluorophenol molecule, respectively. The structural determination has allowed direct location of the hydride atoms in both compounds.

Introduction

The transition-metal alkoxo–hydride derivatives, which have been formulated as probable intermediates in some catalytic hydrogen-transfer reactions,[1] can formally be obtained through oxidative addition of alcohols to the proper metal fragments. There are, however, few examples of isolated alkoxo–hydrides obtained by this route.[2]

The O–H bond activation toward oxidative addition demands the metal to fulfill contrasting requirements: the metal fragment has to be (a) sufficiently oxophilic to form strong M–O bonds and (b) sufficiently basic to accept the hydrogen transfer from the alcohol as a proton.[3] These two features do not easily coexist, and only in a few cases[2–4] can the nature of the ligands impart to the metal the required electronic characteristics. Such remarks explain the scarcity of alkoxo–hydride complexes obtained through oxidative addition of alcohols to transition metals.

In this paper we report the reactivity of $Pd(PCy_3)_2$ (Cy = cyclohexyl) toward alcohols and phenols and an interpretation of the results obtained in the light of the remarks a and b. We also report the structural characterization of the phenoxo–hydride derivatives obtained through oxidative addition of phenol and pentafluorophenol to $Pd(PCy_3)_2$ together with the study of the reactivity of such phenoxo–hydrides with carbon monoxide.

This is, to the best of our knowledge, the first report of structural determinations of palladium–hydride derivatives and a rare example of the isolation of complexes containing the Pd–OR unit.[5]

Part of this work has been briefly communicated.[6]

Results and Discussion

By addition of C_6H_5OH to a toluene solution of $Pd(PCy_3)_2$ (2:1 ratio) at room temperature, the complex $[Pd(PCy_3)_2(H)(OC_6H_5)]\cdot C_6H_5OH$ (**1**) was obtained as a yellow, thermally stable, crystalline solid (60% yield). The nature of **1** was clarified through elemental analysis, the IR spectrum (ν_{O-H} 3180 (m, br), ν_{Pd-H} 2060 (w), $\nu_{C=C}$ 1605 (m), 1585 (s) cm^{-1}), and the ^1H NMR spectrum (Pd—H, δ −17.5 (s); OH, δ 8.4 (s) (−40 °C) and 5.6 (s) (30 °C)) and established by the X-ray structural determination.

By a similar procedure the complex *trans*-$[Pd(PCy_3)_2(H)(OC_6F_5)]\cdot C_6F_5OH$ (**2**) was obtained as a yellow, thermally stable, crystalline solid (ν_{O-H} 3180 (m, br), ν_{Pd-H} 2100 (w) cm^{-1}; Pd—H δ −19.0 (s), OH δ 6.06 (s) (30 °C) and 5.53 (s) (50 °C)).

No reaction occurs when aliphatic alcohols (CH_3OH, *i*-PrOH) are employed; both $Pd(PCy_3)_2$ and the aliphatic alcohol are recovered unchanged after 3 days even upon heating the toluene solution at 70 °C. The greater acidity of the phenols used, with respect to that of the aliphatic alcohols, allows the hydrogen transfer to the late transition metal as a proton; moreover, the coordination of one molecule of ArOH to the metal-bonded ArO^- residue through a hydrogen bond (see Structural Characterization) decreases the basicity of the ArO^- groups, making the phenoxide ligand more compatible with the soft metal center. To this purpose it has to be stated that **1** and **2** are the only reaction products also carrying out the reaction with a 1:1 $Pd(PCy_3)_2$:phenol ratio.

The reaction of rhodium aryloxo complexes with various phenols to form the organometallic hydrogen-bonded species $L_3Rh(OAr)(HOAr)$ (L = PMe_3) has recently been reported by Bergman.[7] The association heats for hydrogen-bond formation have been measured in a number of cases, and their values have been found to be much greater than those reported for intermolecular hydrogen bonding between phenols and uncharged electron-pair donors.

Such data could suggest that, in the reaction of $Pd(PCy_3)_2$ with ArOH, the thermodynamic balance of the oxidative addition becomes favorable because of the formation of a very efficient hydrogen bond between the metal-bonded ArO^- groups and the free ArOH molecules. Reaction of **1** even with an excess of diazomethane in thf or toluene solution fails to yield anisole, corroborating the hypothesis of the engagement of phenol in robust hydrogen bonding.

Both **1** and **2** react readily in toluene solution with CO, giving a red crystalline solid (**3**), which can be isolated in high yields

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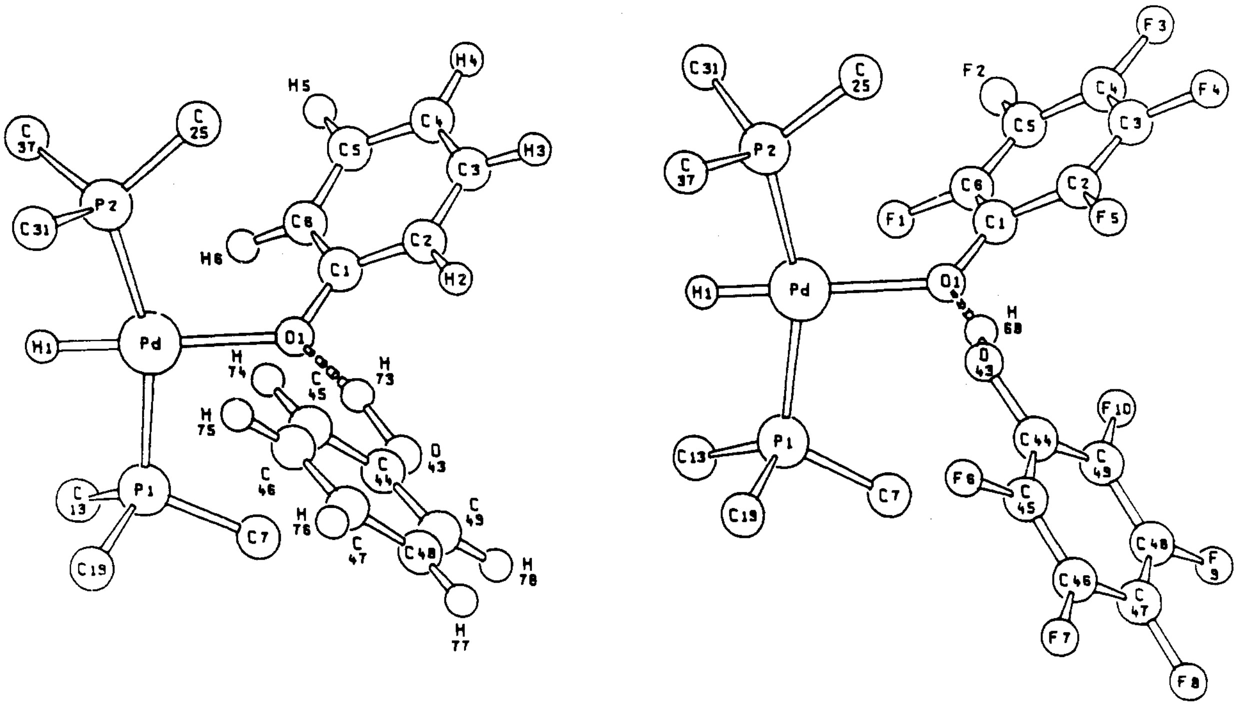

Figure 1. Molecular structures of **1** (left) and **2** (right) showing the atom labeling (only the first atoms of the cyclohexyl rings have been included for clarity).

(70%). The IR spectrum of **3** shows stretchings at 1850, 1840, and 1825 cm^{-1} (Nujol mull) and 1820 cm^{-1} (toluene solution). Free phenol can be detected by gas chromatography of the solution (2:1 PhOH:Pd), and **3** can be obtained in high yield also by reacting $Pd(PCy_3)_2$ with CO (1:1 ratio as determined by gas-volumetric absorption). The reaction of **1** and **2** with CO can therefore be described as reductive elimination of ArOH and formation of the insoluble polynuclear species $[Pd(PCy_3)(CO)]_n$ (see analytical data in the Experimental Section) containing bridging CO molecules.[8]

When the reactions of **1** and **2** with CO are carried out at −60 °C, the solution IR spectra show, in addition to the 1820-cm^{-1} absorption, a peak at 1950 cm^{-1} whose intensity increases if 1 equiv of PCy_3 is added; raising the temperature causes the disappearance of the 1950-cm^{-1} peak. The same pattern can be observed if CO reacts with $Pd(PCy_3)_2$; a possible explanation is that an equilibrium is set up between a monomeric terminal palladium carbonyl and the polynuclear bridging carbonyl **3** and that such an equilibrium is completely shifted to the right at room temperature. The IR data agree with such a hypothesis since the mononuclear $Pd(PPh_3)_3(CO)$ shows a strong band at 1957 cm^{-1}[9] and trinuclear derivatives of the formula $[Pd(PR_3)(CO)]_3$ show absorptions in the CO region very similar to those of **3**.[8]

Structural Characterization of 1 and 2. The molecular structures of both **1** and **2** are shown in Figure 1 for comparison, and an ORTEP diagram of **2** is given in Figure 2 together with the atomic labeling. Considering that some details of the structure of **1** have already been discussed in the preliminary report[6] mentioned above, the following description will be devoted to a careful comparison of **1** and **2**. As a matter of fact, these two species offer a unique opportunity for studying the effect of changing the electronic nature of the coordinating ligand (pentafluorophenoxy, hereinafter PFP, in place of phenoxy) at the same metallic center within very similar structural environments in the solid state. Moreover, it should be pointed out that the X-ray data were of sufficient quality to allow direct location of both the Pd–H and O–H hydrogen atoms in both compounds (see Experimental Section), although a direct comparison of the structural parameters concerning these atoms cannot be made with great confidence without a neutron-diffraction study of the two species.

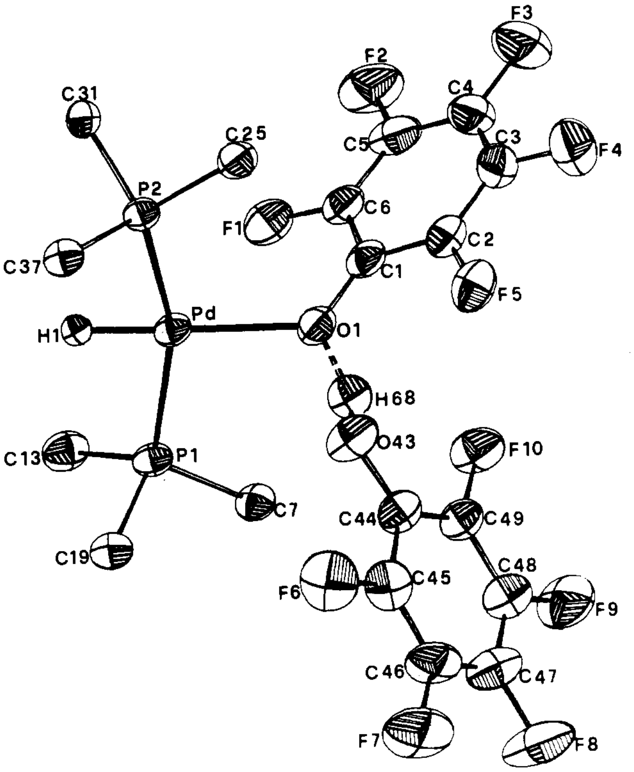

Figure 2. ORTEP diagram of **2**. For the atomic labeling, see Figure 1.

In both compounds the Pd(II) atom possesses a distorted-square-planar coordination: while the Pd atom lies in the plane of its ligands (maximum elevation from the least-squares plane 0.04 and 0.05 Å in **1** and **2**, respectively), the angles around the Pd centers show significant deviation from orthogonality [H1–Pd–P1 = 86 (1)° (**1**), 82 (1)° (**2**); H1–Pd–P2 = 76 (1)° (**1**), 78 (1)° (**2**); P1–Pd–P2 = 161.9 (1)° (**1**), 159.1 (1)° (**2**)]. On the

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(8) The low solubility and volatility of **3** has prevented the determination of its nuclearity. However, Pd carbonyls with a variety of phosphines (including phosphines of bulkiness comparable with PCy_3) were always described as trinuclear clusters (n = 3). Yoshida, T.; Otsuka, S. *J. Am. Chem. Soc.* **1977**, *99*, 2134. Uchida, Y.; Hidai, M.; Kudo, K. *J. Organomet. Chem.* **1971**, *33*, 393.

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other hand, the H1–Pd–O system is almost linear in both compounds [176 (1) and 178 (1)° in **1** and **2**]. These deformations can be ascribed to the presence of the bulky coordinating group on one side of the molecule, the expectedly larger PFP–pentafluorophenol system exerting a slightly greater effect than the phenoxy–phenol one. The main structural difference between **1** and **2** lies in the orientation of the phenoxy–phenol and PFP–pentafluorophenol system with respect to the Pd(II) coordination plane. While the P1–Pd–O1–C1 torsion angles, which describe the orientation of the C–O(phenoxy) axis with respect to the Pd center, are very similar in the two species (124.6 and 126.9° in **1** and **2**, respectively), the Pd–O1–C1–C6 angle, which is involved in the tilting of the phenoxy and PFP groups is −26.1° in **1** and −38.4° in **2**. The further "deviation from planarity" of the Pd–O–C–Ph system that accompanies the substitution of phenoxy for PFP seems again related to steric factors, as also shown by a comparison of the angular values within the Pd–O–C system (see Table IV), which are wider in **2** than in **1**.

The Pd–O distance, though falling within the range observed in other square-planar Pd(II) complexes,[10] is considerably longer in **2** [2.181 (2) Å] than in **1** [2.135 (2) Å]; the lengthening of this bond appears to be accompanied by a shortening of the Pd–H distance [1.57 (2) in **1** versus 1.46 (2) Å in **2**]. The reason for this behavior lies in the presence of the strongly electronegative F atoms in the ligand. It seems reasonable that the strong electron-withdrawing influence exerted by these atoms lowers the basicity of the O atoms, thus reducing the competition with the H atom σ-donation. Although the H(hydride) positions are known with much uncertainty, it is worth pointing out here that the IR stretchings observed for Pd–H bonds (see above) are in agreement with a somewhat stronger Pd–H interaction in **2** than in **1**.

The oxygens of the phenoxy and fluorophenoxy moieties are bridged via an H atom to an uncoordinated phenol and pentafluorophenol molecule, respectively, the O–H–O angles being similar in the two compounds (168.3° in **1** and 164.7° in **2**.

Interestingly, we can observe here the same effect due to the F substitution: the O43–C44 bond length is considerably shorter in **2** [1.369 (5) Å in **1** and 1.344 (4) Å in **2**] as is the O1–C1 distance [1.326 (3) Å in **1** and 1.314 (5) Å in **2**]. Also, the O43–H(bridging) distance shortens significantly [1.18 (1) Å in **1** vs 0.89 (1) Å in **2**], while the corresponding O1–H(bridging) distance lengthens (1.46 in **1** and 1.70 Å in **2**, if the X-ray data on H atom positions are accepted for what they are worth. Both these structural parameters, the O–C and the O–H distances, in compound **2** are in good agreement with those found in other H-coordinated pentafluorophenols.[11] Altogether the structural comparison between **1** and **2** affords a thoroughly coherent picture: the presence of the F atoms causes a detectable contraction of the O atom orbitals, yielding systematically shorter C–O and O–H σ-bonds and lowering the O atom donating ability, toward both the metal center and the H(bridge) atom, with respect to that in the unsubstituted moieties. What is more, the phenol and pentafluorophenol rings have inverted conformations, as can be shown by the torsion angles around the O43–C44 bond [H(bridging)–O43–C44–C45 = 7.2° (**1**), −165.2° (**2**)].

The two moieties also possess different orientations, confirming that this part of the molecule is rather flexible and is easily influenced by packing forces [Pd–O1–H–O43 = 63.2° (**1**), 15.8° (**2**)].

The Pd–P bond lengths are comparable in the two compounds [2.318 (1) and 2.330 (1) Å in **1** and 2.326 (1) and 2.333 (1) Å in **2**], the longer Pd–P distance involving the P atom that forms the wider P–Pd–O angle.

Experimental Section

All reactions were carried out under a nitrogen atmosphere by using

Table I. Crystallographic Data for **1** and **2**

	1	**2**
chem formula	$C_{42}H_{72}OP_2Pd{\cdot}C_6H_5OH$	$C_{42}H_{67}F_5OP_2Pd{\cdot}C_6F_5OH$
fw	855.5	1016.9
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	13.535 (6)	10.423 (6)
b, Å	16.131 (4)	14.047 (5)
c, Å	11.759 (5)	17.335 (4)
α, deg	109.24 (3)	94.38 (2)
β, deg	106.34 (3)	95.16 (3)
γ, deg	84.21 (3)	103.66 (4)
V, Å^3	2325.9	2443.7
Z	2	2
T, °C	25	25
λ, Å	0.71069	0.17069
ρ_{calcd}, g cm^{-3}	1.22	1.39
μ, cm^{-1}	4.9	5.2
$R(F_o)$	0.033	0.040
$R_w(F_o)$	0.037	0.041

Table II. Fractional Atomic Coordinates and Thermal Parameters (Å^2) for **1**

atom	x	y	z	U_{iso} or U_{eq}
Pd	0.68270 (1)	0.24613 (1)	0.09373 (2)	0.0396 (1)
P1	0.60312 (5)	0.23481 (4)	0.23858 (6)	0.0409 (3)
P2	0.73970 (5)	0.30163 (4)	−0.03605 (6)	0.0420 (3)
O1	0.7714 (1)	0.1280 (1)	0.0835 (2)	0.052 (1)
C1	0.7650 (2)	0.0660 (2)	−0.0254 (3)	0.053 (1)
C2	0.8468 (2)	0.0083 (2)	−0.0447 (4)	0.070 (2)
C3	0.8436 (3)	−0.0522 (2)	−0.1587 (5)	0.091 (3)
C4	0.7600 (4)	−0.0586 (2)	−0.2588 (4)	0.094 (3)
C5	0.6753 (3)	−0.0046 (2)	−0.2421 (3)	0.073 (2)
C6	0.6771 (2)	0.0558 (2)	−0.1260 (3)	0.056 (2)
C7	0.6378 (2)	0.1315 (2)	0.2772 (2)	0.048 (1)
C8	0.6171 (3)	0.1257 (2)	0.3961 (3)	0.073 (2)
C9	0.6672 (4)	0.0409 (3)	0.4212 (4)	0.105 (3)
C10	0.6295 (3)	−0.0404 (3)	0.3110 (5)	0.104 (3)
C11	0.6434 (4)	−0.0324 (2)	0.1912 (5)	0.094 (3)
C12	0.5946 (3)	0.0515 (2)	0.1661 (3)	0.062 (2)
C13	0.4599 (2)	0.2398 (2)	0.1905 (3)	0.061 (2)
C14	0.4062 (2)	0.2700 (3)	0.2930 (3)	0.070 (2)
C15	0.2905 (3)	0.2758 (3)	0.2486 (4)	0.091 (3)
C16	0.2477 (3)	0.3086 (4)	0.1457 (5)	0.117 (4)
C17	0.2996 (3)	0.2675 (3)	0.381 (4)	0.84 (2)
C18	0.4152 (3)	0.2719 (4)	0.836 (4)	0.100 (3)
C19	0.6479 (2)	0.3235 (2)	0.3881 (2)	0.049 (1)
C20	0.7641 (2)	0.3157 (2)	0.4383 (3)	0.58 (2)
C21	0.8069 (3)	0.3883 (2)	0.5603 (3)	0.77 (2)
C22	0.7780 (3)	0.4787 (2)	0.5472 (3)	0.078 (2)
C23	0.6619 (3)	0.4873 (2)	0.5008 (4)	0.078 (2)
C24	0.6209 (3)	0.4154 (2)	0.3751 (3)	0.061 (2)
C25	0.8285 (2)	0.2311 (2)	−0.1235 (3)	0.052 (1)
C26	0.9346 (2)	0.2224 (2)	−0.0370 (3)	0.056 (2)
C27	1.0021 (3)	0.1539 (3)	−0.1069 (3)	0.075 (2)
C28	1.0128 (3)	0.1727 (3)	−0.2186 (4)	0.090 (3)
C29	0.9060 (3)	0.1803 (3)	−0.3060 (3)	0.085 (2)
C30	0.8397 (3)	0.2502 (2)	−0.2375 (3)	0.071 (2)
C31	0.7983 (2)	0.4105 (2)	0.0575 (3)	0.055 (1)
C32	0.8391 (3)	0.4608 (2)	−0.0094 (3)	0.067 (2)
C33	0.8682 (3)	0.5541 (2)	0.0752 (4)	0.086 (2)
C34	0.9408 (4)	0.5575 (3)	0.1987 (4)	0.090 (3)
C35	0.8997 (3)	0.5074 (2)	0.2661 (3)	0.74 (2)
C36	0.8724 (3)	0.4125 (2)	0.1816 (3)	0.064 (2)
C37	0.6314 (2)	0.3263 (2)	−0.1596 (2)	0.051 (1)
C38	0.5689 (2)	0.2431 (2)	−0.2387 (3)	0.057 (2)
C39	0.4813 (3)	0.2602 (3)	−0.3439 (3)	0.076 (2)
C40	0.4121 (3)	0.3345 (3)	−0.2926 (4)	0.094 (3)
C41	0.4730 (3)	0.4160 (3)	−0.2143 (4)	0.088 (3)
C42	0.5604 (3)	0.4007 (2)	−0.1076 (3)	0.070 (2)
O43	0.8967 (2)	0.0856 (2)	0.2719 (3)	0.105 (2)
C44	0.9723 (2)	0.1451 (4)	0.3465 (3)	0.083 (2)
C45	0.9780 (3)	0.2219 (3)	0.3213 (5)	0.096 (3)
C46	1.0542 (4)	0.2792 (4)	0.3996 (6)	0.112 (4)
C47	1.1217 (5)	0.2607 (7)	0.4989 (7)	0.143 (6)
C48	1.1167 (4)	0.1842 (7)	0.5250 (5)	0.141 (6)
C49	1.0394 (3)	0.1233 (5)	0.4452 (4)	0.120 (4)
H1	0.6237	0.3361	0.1030	0.075 (9)
H73	0.8485	0.1040	0.1826	0.18 (1)

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Table III. Fractional Atomic Coordinates and Thermal Parameters (Å^2) for **2**

atom	x	y	z	U_{iso} or U_{eq}
Pd	0.41265 (2)	0.27928 (2)	0.27829 (1)	0.0315 (1)
P1	0.48061 (8)	0.37987 (6)	0.18158 (5)	0.0335 (4)
P2	0.31694 (8)	0.22839 (6)	0.38951 (5)	0.0309 (4)
O1	0.4122 (2)	0.1383 (2)	0.2160 (1)	0.040 (1)
F1	0.6633 (2)	0.1941 (2)	0.2991 (1)	0.054 (1)
F2	0.7861 (3)	0.0590 (2)	0.3476 (2)	0.085 (2)
F3	0.6666 (4)	−0.1370 (2)	0.3208 (2)	0.106 (2)
F4	0.4218 (4)	−0.1948 (2)	0.2373 (2)	0.090 (2)
F5	0.2996 (2)	−0.0604 (2)	0.1840 (1)	0.057 (1)
F6	−0.0116 (2)	0.1498 (2)	0.0443 (2)	0.77 (2)
F7	−0.0306 (3)	0.1359 (2)	−0.1123 (2)	0.098 (2)
F8	0.1544 (3)	0.0694 (3)	−0.1898 (1)	0.107 (2)
F9	0.3591 (3)	0.0219 (2)	−0.1074 (1)	0.086 (2)
F10	0.3792 (2)	0.0372 (2)	0.0488 (1)	0.064 (1)
C1	0.4735 (3)	0.0729 (3)	0.2409 (2)	0.040 (2)
C2	0.6001 (4)	0.0982 (3)	0.2833 (2)	0.044 (2)
C3	0.6637 (4)	0.0292 (4)	0.3091 (2)	0.061 (3)
C4	0.6047 (5)	−0.0691 (3)	0.2950 (2)	0.070 (3)
C5	0.4818 (5)	−0.0979 (3)	0.2528 (2)	0.061 (3)
C6	0.4196 (4)	−0.0290 (3)	0.2259 (2)	0.045 (2)
C7	0.5323 (3)	0.3137 (2)	0.0978 (2)	0.038 (2)
C8	0.6620 (4)	0.2834 (3)	0.1199 (2)	0.060 (2)
C9	0.6880 (5)	0.2123 (4)	0.0549 (3)	0.076 (3)
C10	0.6945 (5)	0.2571 (4)	−0.0216 (3)	0.072 (3)
C11	0.5670 (4)	0.2889 (3)	−0.0433 (2)	0.058 (2)
C12	0.5403 (4)	0.3599 (3)	0.0208 (2)	0.049 (2)
C13	0.6110 (4)	0.4921 (3)	0.2182 (2)	0.046 (2)
C14	0.7177 (5)	0.4761 (4)	0.2766 (3)	0.065 (3)
C15	0.8101 (5)	0.5709 (4)	0.3143 (3)	0.077 (3)
C16	0.8619 (6)	0.6425 (4)	0.2567 (4)	0.092 (4)
C17	0.7569 (6)	0.6564 (4)	0.1982 (4)	0.080 (3)
C18	0.6652 (4)	0.5610 (3)	0.1604 (3)	0.057 (2)
C19	0.3453 (3)	0.4323 (2)	0.1400 (2)	0.039 (2)
C20	0.2927 (4)	0.4932 (3)	0.2013 (2)	0.056 (2)
C21	0.1797 (4)	0.5356 (4)	0.1662 (3)	0.073 (3)
C22	0.0695 (4)	0.4563 (4)	0.1215 (3)	0.080 (3)
C23	0.1216 (4)	0.3962 (4)	0.0598 (3)	0.069 (3)
C24	0.2304 (4)	0.3512 (3)	0.0967 (2)	0.051 (2)
C25	0.2542 (4)	0.0936 (2)	0.3923 (2)	0.041 (2)
C26	0.1484 (4)	0.0451 (3)	0.3251 (2)	0.049 (2)
C27	0.1165 (5)	−0.0673 (3)	0.3228 (2)	0.063 (3)
C28	0.0759 (5)	−0.1027 (3)	0.3969 (3)	0.062 (3)
C29	0.1788 (6)	−0.0548 (3)	0.4643 (3)	0.074 (3)
C30	0.2113 (7)	0.0591 (3)	0.4678 (2)	0.075 (3)
C31	0.4288 (3)	0.2644 (2)	0.4813 (2)	0.035 (2)
C32	0.5567 (4)	0.2300 (3)	0.4759 (2)	0.054 (2)
C33	0.6478 (4)	0.2555 (4)	0.5523 (3)	0.068 (3)
C34	0.6791 (4)	0.3643 (4)	0.5792 (3)	0.065 (3)
C35	0.5528 (4)	0.3984 (3)	0.5851 (2)	0.054 (2)
C36	0.4656 (4)	0.3762 (3)	0.5067 (2)	0.047 (2)
C37	0.1832 (3)	0.2931 (2)	0.4012 (2)	0.036 (2)
C38	0.0833 (4)	0.2793 (3)	0.3288 (2)	0.051 (2)
C39	−0.0038 (4)	0.3523 (4)	0.3352 (2)	0.065 (3)
C40	−0.0747 (4)	0.3442 (4)	0.4089 (2)	0.062 (2)
C41	0.0233 (4)	0.3556 (3)	0.4811 (2)	0.054 (2)
C42	0.1087 (3)	0.2794 (3)	0.4739 (2)	0.045 (2)
O43	0.1898 (3)	0.1064 (2)	0.1294 (1)	0.059 (2)
C44	0.1851 (3)	0.0954 (3)	0.0515 (2)	0.044 (2)
C45	0.0816 (3)	0.1175 (3)	0.0069 (2)	0.052 (2)
C46	0.0707 (4)	0.1103 (3)	−0.0728 (2)	0.061 (2)
C47	0.1642 (5)	0.0771 (3)	−0.1116 (2)	0.064 (3)
C48	0.2666 (4)	0.0529 (3)	−0.0697 (2)	0.056 (2)
C49	0.2764 (3)	0.0615 (3)	0.0101 (2)	0.044 (2)
H1	0.4173	0.3737	0.2783	0.05 (1)
H68	0.2656	0.1063	0.1571	0.10 (1)

Table IV. Relevant Bond Distances (Å) and Angles (deg) for **1** and **2**

	1	**2**
Pd–H1	1.57 (2)	1.46 (2)
Pd–P1	2.318 (1)	2.326 (1)
Pd–P2	2.330 (1)	2.333 (1)
Pd–O1	2.135 (2)	2.181 (2)
O1–C1	1.326 (3)	1.314 (5)
C1–C2	1.392 (4)	1.405 (5)
C2–C3	1.366 (6)	1.375 (7)
C3–C4	1.367 (6)	1.366 (6)
C4–C5	1.387 (6)	1.372 (7)
C5–C6	1.387 (4)	1.373 (6)
C1–C6	1.401 (4)	1.403 (5)
P–C (mean)	1.86 (1)	1.85 (1)
C–F (mean)		1.35 (1)
C–C(Cy) (mean)	1.52 (2)	1.52 (2)
O43–H(bridging)	1.18[a]	0.89[a]
O43–C44	1.369 (5)	1.344 (4)
C44–C45	1.379 (8)	1.379 (5)
C45–C46	1.365 (7)	1.369 (6)
C46–C47	1.36 (1)	1.381 (7)
C47–C48	1.38 (1)	1.361 (7)
C48–C49	1.409 (9)	1.372 (5)
C44–C49	1.380 (7)	1.389 (5)
P1–Pd–H1	86 (1)	82 (1)
P2–Pd–H1	76 (1)	78 (1)
P1–Pd–P2	161.9 (1)	159.1 (1)
H1–Pd–O1	176 (1)	178 (1)
P1–Pd–O1	96.0 (1)	98.2 (1)
P2–Pd–O1	101.8 (1)	101.3 (1)
Pd–O1–C1	120.5 (2)	126.4 (2)
O1–C1–C2	120.9 (2)	123.3 (3)
O1–C1–C6	122.1 (2)	123.0 (3)
C2–C1–C6	117.0 (3)	113.7 (4)
O43–C44–C45	120.0 (4)	119.1 (4)
O43–C44–C49	116.3 (5)	125.4 (3)
C45–C44–C49	123.7 (4)	115.6 (3)

[a] The esd's for the two distances have not been reported because they are unreliably low.

standard Schlenk techniques. All solvents were refluxed on a proper drying agent and distilled and stored under nitrogen. $Pd(PCy_3)_2$ was prepared as previously described.[12] IR spectra were recorded on a Perkin-Elmer 283-B spectrophotometer. NMR spectra were recorded on Varian XL 100 and XR 300 spectrometers; chemical shifts were referenced to $SiMe_4$. GLC analyses were performed by using a Dani instrument and a 2.5 m × 6 mm stainless steel column packed with 10% of Carbowax 20M on Chromosorb W-AW.

Synthesis of $[Pd(PCy_3)_2(H)(OC_6H_5)]\cdot C_6H_5OH$ (1). Two equivalents of PhOH was added to a solution of 1.391 g (2.088 mmol) of $Pd(PCy_3)_2$ in 40 mL of toluene. The reaction mixture was kept at room temperature for 10 h. After evaporation to small volume and addition of *n*-hexane, the complex precipitated as yellow crystals at −30 °C. It was filtered off and dried in vacuo; yield ca. 60%. Anal. Calcd for $C_{48}H_{78}O_2P_2Pd$: C, 67.41; H, 9.13. Found: C, 67.02; H, 9.39; IR (Nujol, cm^{-1}): 3180 (m, br), 2060 (w), 2040 (w), 1605 (m), 1585 (s). ^1H NMR (toluene-d_8, −40 °C, 300 MHz): δ 8.40 (1 H, s, OH), 7.10 (10 H, m, C_6H_5O), 1.80 (66 H, m, PCy_3), −17.50 (1 H, s, Pd–H).

Synthesis of $[Pd(PCy_3)_2(H)(OC_6F_5)]\cdot C_6F_5OH$ (2). A solution of 1.511 g (2.269 mmol) of $Pd(PCy_3)_2$ and 2 equiv of C_6F_5OH in 50 mL of toluene was kept at room temperature for 1 day. After evaporation to small volume, addition of *n*-hexane, and cooling at −30 °C, yellow crystals precipitated and were filtered and vacuum-dried; yield ca. 55%. Anal. Calcd for $C_{48}F_{10}H_{68}O_2P_2Pd$: C, 55.63; H, 6.64. Found: C, 55.57; H, 6.49. IR (Nujol, cm^{-1}): 3180 (m, br), 2100 (w), 1535 (m), 1520 (m), 1500 (s), 1470 (m). ^1H NMR (C_6D_6, 30 °C, 100 MHz): δ 6.06 (1 H, s, C_6F_5OH), 1.90–1.10 (66 H, m, PCy_3), −19.00 (1 H, s, Pd–H).

Synthesis of $[Pd(PCy_3)(CO)]_n$ (3). (a) From 1. A solution of 104 mg (0.122 mmol) of **1** in 5 mL of toluene was saturated with CO. The solution became red in a few minutes, and the IR spectrum of the solution showed absorptions at 1950 (vw) and 1820 (s) cm^{-1}. The red microcrystalline solid that precipitated after 8 h was filtered and vacuum-dried; yield ca. 70%. Anal. Calcd for $C_{19}H_{33}OPPd$: C, 55.02, H, 7.96. Found: C, 53.96; H, 7.96. IR (Nujol, cm^{-1}): 1850 (s), 1840 (s), 1825 (s). GLC analysis revealed the presence of PhOH in the solution.

The same reaction was carried out at −60 °C, with IR spectra of the solution being recorded. The IR spectrum initially showed two absorptions of the same intensity at 1950 and 1820 cm^{-1}. The band at 1950 cm^{-1} decreased while the band at 1820 cm^{-1} increased after a few minutes. When the temperature was raised to 25 °C, only a weak absorption at 1950 cm^{-1} and a strong absorption at 1820 cm^{-1} were observed. Addition of PCy_3 at room temperature caused the increase of the 1950-cm^{-1} absorption with a corresponding decrease of the 1820-cm^{-1} absorption.

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(b) From 2. A solution of 223 mg (0.216 mmol) of **2** in 10 mL of toluene was saturated with CO. The red microcrystalline **3**, which precipitated after 8 h, was filtered and vacuum-dried.

(c) From Pd(PCy$_3$)$_2$. The absorption of CO by a solution containing 434 mg (0.652 mmol) of Pd(PCy$_3$)$_2$ in 20 mL of toluene was measured with a gas-volumetric apparatus; 0.645 mmol of CO was absorbed. From the solution a red microcrystalline solid precipitated, which was shown to be identical with a sample prepared by method a.

X-ray Crystallography. Crystal data and details of measurements for **1** and **2** are reported in Table I.

Diffraction intensities were collected at room temperature by the $\omega/2\theta$ scan method of an Enraf-Nonius CAD-4 diffractometer with Mo Kα radiation (λ = 0.71069 Å) and reduced to F_o values.

The structures were solved by Patterson and direct methods and refined by full-matrix least-squares calculations. For all computations the SHELX76 and SHELX86[13,14] packages of crystallographic programs were used with the analytical scattering factors, corrected for real and imaginary parts of anomalous dispersions, taken from ref 14b. Thermal vibrations were treated anisotropically.

In both compounds the H atoms bound to Pd(II) were found in a final difference map by using a reduced reflection sphere ($(\sin\theta)/\lambda$ = 0.3) and kept at their observed distances [1.57 (2) and 1.46 (2) Å, respectively] from Pd. Also, the phenol and pentafluorophenol O-bound H atoms were directly located and kept at their found positions of 1.18 and 0.89 Å, respectively, from O43. All the remaining H atoms were added in calculated positions (C–H = 1.08 Å) and refined riding on the corresponding C atoms. Common temperature factors were refined for chemically equivalent H atoms, while the H(hydride) and H(bridging) atoms were treated independently.

Final difference Fourier maps showed residual peaks lower than 1 e Å^{-3} in both compounds. Final atomic coordinates for **1** and **2** are listed in Tables II and III, while relevant bond distances and angles are reported in Table IV.

Absorption correction was made by applying the Walker and Stuart[15] method after a complete structural model was obtained and all atoms were refined isotropically for **1**. For **2** an empirical absorption correction was applied by measuring scans at intervals of 10° around the diffraction vectors of eight selected reflections near χ = 90° (transmission range 71–100%).

Registry No. 1, 112469-70-2; **2**, 119455-96-8; **3** (n = 3), 95246-51-8; Pd(PCy$_3$)$_2$, 33309-88-5; PhOH, 108-95-2; C_6F_5OH, 771-61-9; CH_3OH, 67-56-1; *i*-PrOH, 67-63-0.

Supplementary Material Available: Hydrogen atom coordinates (Tables S-I and S-II), anisotropic thermal parameters (Tables S-III and S-IV), bond distances and angles (Tables S-V and S-VI), and crystal data and intensity collection parameters (Table S-IX) (74 pages); observed and calculated structural factors (Tables S-VII and S-VIII) (78 pages). Ordering information is given on any current masthead page.

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Crystal Structure of and Mechanism of Water Exchange on $[Mo_3O_4(OH_2)_9]^{4+}$ from X-ray and Oxygen-17 NMR Studies

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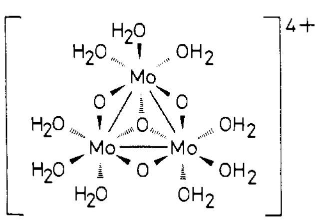
Received June 14, 1988

Acid dissociation and water exchange on $[Mo_3O_4(OH_2)_9]^{4+}$ have been studied by ^{17}O NMR and UV–visible spectrophotometry in noncomplexing acidic aqueous solution. Contrary to an earlier report, the oxygen atoms of the "core" are extremely inert with no exchange observed on either over a 2-year period. Exchange at the d-H_2O ligands, trans to the μ_2-bridging oxygen atoms of the "core", occurs readily ($k_{OH}^{298} = 1.6 \times 10^2$ s^{-1}) and much faster than that occurring at the c-H_2O, trans to the capping oxygen ($k_{OH}^{298} = 1.5 \times 10^{-3}$ s^{-1}). A mechanism of exchange for both waters involving solely the same conjugate base $[Mo_3O_4(OH_2)_8(OH)]^{3+}$ is relevant. The positive $\Delta S^\ddagger$ value (+35 J K^{-1} mol^{-1}) for the d-H_2O exchange and comparison with available data for 1:1 anation reactions of $[Mo_3O_4(OH_2)_9]^{4+}$ with NCS^- and $HC_2O_4^-$ add support for an I_d mechanism. Chemical shifts for both the c- and d-H_2O ^{17}O NMR resonances followed as a function of H^+ concentration confirmed that the relevant deprotonation occurred uniquely at a d-H_2O. Values for $K_a^{298}(Mo_3O_4^{4+})$, determined from the kinetic treatment (0.31 M) and from UV–visible spectrophotometry (0.24 M), were in satisfactory agreement and indicative of high acidity at the d positions. The compound $[Mo_3O_4(OH_2)_9](CH_3C_6H_4SO_3)_4\cdot 13H_2O$ crystallizes in the monoclinic space group *Cc*: a = 31.99 (1) Å, b = 9.886 (2) Å, c = 17.789 (5) Å, β = 99.67 (2)°. The final agreement was R = 0.059 with 5183 observed reflections. The packing is mainly characterized by the large number of crystallization water molecules and H-bond interactions. It consists of alternate layers of opposite charge.

Introduction

The aqua ion of molybdenum(IV), first isolated by Souchay in 1966,[2] is now well established as containing the cyclic trinuclear metal cluster unit $[Mo_3O_4(OH_2)_9]^{4+}$ (**1**). Thus, X-ray crystallographic characterization of Mo(IV) complexes such as $[Mo_3O_4(C_2O_4)_3(OH_2)_3]^{2-}$ [3,4] and $[Mo_3O_4(NCS)_8(OH_2)]^{4-}$ [5] together with isotopic labeling of the core μ_2- and μ_3-oxygen atoms with ^{18}O[4] and, more recently, ^{17}O[6] have demonstrated that the trinuclear unit is retained for solutions of the red aqua ion.



1

The two types of "core" oxygen atom labeled "a" and "b" and coordinated H_2O ligands "c" and "d" can be readily distinguished in the 4 atom % enriched ^{17}O NMR spectrum of the Mo(IV) ion

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