Kurzmitteilung / Short Communication

P – C Bond Activation and η^4-Coordination of Arene: X-ray Crystal Structure of a Dinuclear μ-Phosphido μ-η^2:η^2-Phenoxo Zwitterionic Complex of Palladium Trapping an Aggregate of Three Hydrogen-Bonded Phenol Molecules

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$Pd[P(tBu)_3]_2$ reacts photochemically with an excess of phenol in *n*-hexane to give the dinuclear complex $[\{P(tBu)_2H\}_2Pd_2\{\mu\text{-}P(tBu)_2\}(\mu\text{-}\eta^2:\eta^2\text{-}C_6H_5O)] \cdot 3\ C_6H_5OH$ (**1**); X-ray crystallography shows a linear chain of three phenol molecules hydrogen-bonded to the phenoxide ligand which is η^4-coordinated to the Pd_2 framework. The π coordination of the phenoxide ring is retained in solution, as evidenced by ^1H-NMR spectroscopy.

Recently, we have reported on the oxidative addition reaction of phenols to $Pd(PCy_3)_2$ (Cy = cyclohexyl) which affords the phenoxopalladium(II) hydride derivatives *trans*-$[(PCy_3)_2Pd(H)(OAr)] \cdot ArOH$ (Ar = C_6H_5, C_6F_5)[1]. These results, together with those obtained by the reactions of $Pd(PCy_3)_2$ with some alcohols and water[2], suggest that the basicity of the palladium fragment plays an important role in promoting the oxidative addition of the O – H bond to Pd(0). Having this hypothesis in mind, we have started investigating the effect of the phosphine by treating phenol with $Pd[P(tBu)_3]_2$[3]: an *n*-hexane solution slowly turns from colorless to orange, and orange crystals of **1** start precipitating after two weeks. No reaction is observed if the solution is kept in the dark. An X-ray structure analysis of **1** reveals that it is a dinuclear zwitterionic derivative exhibiting as the most remarkable feature a coordination of a phenoxide unit to the two Pd atoms by C=C bonds (Figure 1)[4a]. The Pd – Pd axis is parallel and slightly offset by the long diagonal of the C_6 hexagon, so that only four C atoms of the ligand are at bond distances from the Pd centers. These bonds are classified into two distinct sets of "short" (mean value 2.31 Å) and "long" (mean value 2.51 Å) lengths. The phenoxide ligand clearly establishes a μ-η^2:η^2 interaction with the Pd_2 system, thus recalling the situation observed in complexes containing V_2, Re_2, Ru_2, Os_2, and Pd_2 fragments with a similarly bound benzene molecule[5,6]; the low-temperature NMR spectra (see Experimental), showing a high-field shift of the phenoxide proton signals, confirm that the metal – ring π interaction is retained in solution[5,6]. The Pd – Pd distance [2.662(1) Å] indicates the formation of a metal – metal bond[7]. Another remarkable feature of the crystal structure of **1** is the extended network of hydrogen-bonded phenol molecules trapped in the crystal upon crystallization. A similar situation has been previously observed in the crystal structures of *trans*-$[(PCy_3)_2Pd(H)(OAr)] \cdot ArOH$[1], $[(PMe_3)_3Rh(OAr)] \cdot ArOH$[8a], and *trans*-$[(PMe_3)_2MMe(OPh)] \cdot PhOH$ (M = Ni, Pd)[8b], each molecule crystallizing with a single hydrogen-bonded phenol molecule. No appreciable differences in C – O (phenols and phenoxide ligand) bond distances can be detected in the case of **1**, the hydrogen-bonding atom can be located only in the phenol-phenoxide pair, while for the two outermost phenol moieties the existence of hydrogen-bonding is supported on the basis of the nonbonding O ··· O distances. The three O ··· O separations, ranging from 2.44 to 2.64 Å, fall in the range of O ··· O distances observed for moderately strong hydrogen bonds in $HA_2^{\ominus}$ (A = acid anion) couples[8,9].

$$[\{P(tBu)_2H\}_2Pd_2\{\mu\text{-}P(tBu)_2\}(\mu\text{-}\eta^2:\eta^2\text{-}C_6H_5O)] \cdot 3\ C_6H_5OH$$

1

Some important features of the photochemical reaction giving **1** have to be outlined, namely the cleavage of a P – C bond of $P(tBu)_3$ resulting in the formation of the secondary phosphine $P(tBu)_2H$ and the μ-η^2:η^2 coordination of a phenoxide unit to the Pd – Pd framework, leading to the formation of a zwitterionic compound. Reactions that result in the cleavage of the P – C bond of tertiary phosphines are currently of interest because of their role in the deactivation of homogeneous transition-metal catalysts[10]. Recent publications are concerned with the P – C bond cleavage in Mo complexes through protolysis[11] or photolysis under H_2[12] and in Ru[6], Ir[13], or Pt[14] compounds through thermal reactions. As far as the μ-η^2:η^2-phenol coordination to the Pd – Pd unit is concerned, it is worth mentioning that η^2- and η^4-arene complexes have received much attention because of their role as intermediates in C – H bond activation and hydrogenation of arenes[15].

Moreover, the coordination mode of the phenoxide unit in **1** is novel since, to the best of our knowledge, only η^5 and η^6 coordination of $ArO^{\ominus}$ in zwitterionic derivatives have been reported[16].

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Finally, the selectivity of the coordination of phenol to palladium−phosphine compounds has to be outlined. Depending on the nature of the coordinated phosphine and the nuclearity of the complex, Pd−O (ref.[1,8]) or Pd−C (this paper) bonds are formed.

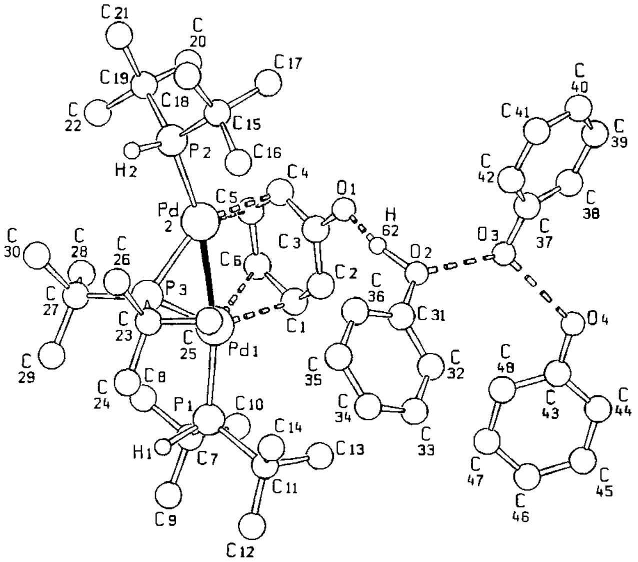

Figure 1. Molecular structure of 1; methyl and phenyl hydrogen atoms are omitted for clarity

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Experimental

1 was prepared under dry nitrogen, and all solvents were dried and distilled prior to use. Pd[P(tBu)$_3$]$_2$ was prepared according to published methods[3]. For further details of experimental techniques see previous publications of this series[1,2].

Preparation of **1**: Pd[P(tBu)$_3$]$_2$ (0.517 g, 1 mmol) was treated with phenol (0.282 g, 3 mmol) in n-hexane (50 ml). The resulting solution was allowed to stand for four weeks exposed to light; during this period 0.040 g (8% yield based on Pd) of **1** precipitated. The low yield of **1** is due to a parallel reaction which gave a red diamagnetic Pd complex not containing phenol. (This product, which is now under investigation, is conveniently prepared by irradiating an n-hexane solution of Pd[P(tBu)$_3$]$_2$ with a mercury vapor arc lamp.). − IR (nujol): $\tilde{\nu}$ = 2320 cm^{-1} (m, ν_{PH}), 1590 (ν_{CC}). − ^{1}H NMR ([D$_8$]toluene, 20°C): δ = 1.10−1.50 (m, 54H, C_4H_9), 4.71 (d, $^1J_{PH}$ = 306 Hz, 2H, PH), 6.50 (br. s, 3H, OH), 6.70−7.10 (m, 20H, C_6H_5O); (−50°C, only phenoxide and OH signals given): δ = 4.76 (br. t, J_{HH} = 6 Hz, 1H, p-H), 6.39 (br. s, 2H, o-H), 6.68 (t, J_{HH} = 6 Hz, 2H, m-H), 10.5 (br. s, 3H, OH).

$C_{48}H_{79}O_4P_3Pd_2$ (1025.9)
Calcd. C 56.20 H 7.76 P 9.06 Pd 20.74
Found C 56.40 H 8.09 P 9.20 Pd 20.50

X-ray Structure Determination of **1**[17]: Diffraction intensities were collected at room temperature with an Enraf-Nonius CAD-4 diffractometer and reduced to F_o values. The structure was solved by direct methods[18] and refined by blocked full-matrix least squares; the three phenyl rings of the phenol molecules not directly coordinated to the metal atoms were treated as rigid groups with C−H = 1.08 Å. Di-*tert*-butylphosphine hydrogen atoms were directly located and refined with a common isotropic displacement parameter. Crystal data for **1**: $C_{48}H_{79}O_4P_3Pd_2$; M = 1025.8; crystal

Table 1. Selected bond distances [Å] of **1** with estimated standard deviations

Bond Distances			
Pd(1)-Pd(2)	2.662(1)	Pd(2)-C(5)	2.516(6)
Pd(1)-P(1)	2.321(1)	O(1)-C(3)	1.329(8)
Pd(1)-P(3)	2.255(1)	O(2)-H(62)	1.19
Pd(2)-P(3)	2.260(1)	P(1)-H(1)	1.41
Pd(1)-C(1)	2.300(6)	P(2)-H(2)	1.30
Pd(1)-C(6)	2.514(6)	O(1)···O(2)	2.50
Pd(2)-P(2)	2.326(1)	O(2)···O(3)	2.44
Pd(2)-C(4)	2.311(5)	O(3)···O(4)	2.64
		O(1)···H(62)	1.33
Bond Angles			
P(1)-Pd(1)-Pd(2)	167.4(1)	Pd(1)-P(3)-Pd(2)	72.3(1)
P(2)-Pd(2)-Pd(1)	166.8(1)	O(1)-H(62)-O(2)	165

Table 2. Fractional atomic coordinats and equivalent isotropic thermal parameters [Å^2] of **1** with estimated standard deviations in parentheses

Atom	x	y	z	U_{eq}
Pd(1)	0.58804(3)	0.02605(1)	-0.30894(2)	0.0235(2)
Pd(2)	0.39627(3)	0.02121(1)	-0.23501(2)	0.0222(2)
P(1)	0.77581(11)	0.02878(6)	-0.34975(7)	0.0291(7)
P(2)	0.25859(10)	0.01890(6)	-0.14896(7)	0.0307(7)
P(3)	0.58063(9)	0.02621(5)	-0.19226(6)	0.0186(6)
O(1)	0.2589(4)	0.1245(2)	-0.3436(3)	0.084(4)
C(1)	0.4822(5)	0.0273(3)	-0.4117(3)	0.055(4)
C(2)	0.4284(5)	0.0799(3)	-0.3932(3)	0.057(4)
C(3)	0.3226(4)	0.0778(3)	-0.3567(3)	0.047(3)
C(4)	0.2796(4)	0.0229(2)	-0.3343(3)	0.035(3)
C(5)	0.3413(5)	-0.0279(3)	-0.3477(3)	0.049(4)
C(6)	0.4440(5)	-0.0261(3)	-0.3869(3)	0.053(4)
C(7)	0.8298(5)	-0.0386(3)	-0.3933(3)	0.044(3)
C(8)	0.7912(8)	-0.0889(3)	-0.3486(5)	0.090(6)
C(9)	0.9609(6)	-0.0427(4)	-0.3978(5)	0.073(5)
C(10)	0.7739(8)	-0.0475(5)	-0.4650(4)	0.103(7)
C(11)	0.8208(5)	0.0978(3)	-0.3957(3)	0.043(3)
C(12)	0.9498(6)	0.1018(4)	-0.4063(5)	0.086(6)
C(13)	0.7618(9)	0.1027(5)	-0.4659(4)	0.114(7)
C(14)	0.7783(10)	0.1469(3)	-0.3503(5)	0.111(7)
C(15)	0.1653(4)	0.0852(3)	-0.1407(3)	0.053(4)
C(16)	0.2440(6)	0.1360(3)	-0.1529(5)	0.086(6)
C(17)	0.0690(5)	0.0869(4)	-0.1964(4)	0.072(5)
C(18)	0.1151(9)	0.0928(6)	-0.0682(4)	0.119(8)
C(19)	0.1753(4)	-0.0512(3)	-0.1404(3)	0.045(3)
C(20)	0.1006(6)	-0.0622(3)	-0.2043(4)	0.069(5)
C(21)	0.0977(7)	-0.0517(5)	-0.0770(4)	0.091(6)
C(22)	0.2670(6)	-0.0985(3)	-0.1318(5)	0.079(5)
C(23)	0.6242(4)	0.0948(2)	-0.1454(2)	0.031(2)
C(24)	0.7578(4)	0.1033(3)	-0.1407(4)	0.060(4)
C(25)	0.5741(5)	0.1439(2)	-0.1898(3)	0.042(3)
C(26)	0.5710(7)	0.0985(3)	-0.0733(3)	0.061(4)
C(27)	0.6379(4)	-0.0401(2)	-0.1467(2)	0.030(2)
C(28)	0.5949(5)	-0.0913(2)	-0.1898(3)	0.050(3)
C(29)	0.7717(5)	-0.0411(3)	-0.1441(4)	0.055(4)
C(30)	0.5893(6)	-0.0468(3)	-0.0734(3)	0.056(4)
O(2)	0.3254(6)	0.2143(3)	-0.4037(4)	0.179(7)
C(32)	0.4914(6)	0.2709(2)	-0.4237(2)	0.108(7)
C(33)	0.5898(6)	0.2999(2)	-0.3980(2)	0.110(7)
C(34)	0.6137(6)	0.3013(2)	-0.3267(2)	0.112(7)
C(35)	0.5394(6)	0.2737(2)	-0.2812(2)	0.137(9)
C(36)	0.4410(6)	0.2446(2)	-0.3070(2)	0.096(6)
C(31)	0.4171(6)	0.2432(2)	-0.3782(2)	0.088(5)
O(3)	0.2224(5)	0.2203(3)	-0.5157(4)	0.126(5)
C(38)	0.0347(5)	0.2255(2)	-0.5680(2)	0.079(5)
C(39)	-0.0819(5)	0.2414(2)	-0.5638(2)	0.091(6)
C(40)	-0.1228(5)	0.2658(2)	-0.5029(2)	0.119(8)
C(41)	-0.0470(5)	0.2745(2)	-0.4462(2)	0.101(7)
C(42)	0.0695(5)	0.2586(2)	-0.4504(2)	0.073(5)
C(37)	0.1104(5)	0.2342(2)	-0.5113(2)	0.063(4)
O(4)	0.3055(9)	0.2374(4)	-0.6404(7)	0.221(11)
C(44)	0.4538(7)	0.2408(3)	-0.7216(4)	0.120(9)
C(45)	0.5683(7)	0.2291(3)	-0.7390(4)	0.133(9)
C(46)	0.6432(7)	0.2019(3)	-0.6911(4)	0.121(9)
C(47)	0.6038(7)	0.1865(3)	-0.6259(4)	0.099(7)
C(48)	0.4893(7)	0.1982(3)	-0.6085(4)	0.097(6)
C(43)	0.4143(7)	0.2254(3)	-0.6563(4)	0.105(7)
H(1)	0.864	0.028	-0.298	
H(2)	0.308	0.027	-0.089	
H(62)	0.303	0.173	-0.369	

size 0.3 × 0.2 × 0.15 mm; monoclinic; space group $P2_1/n$; a = 11.514(4), b = 23.000(3), c = 19.290(4) Å; β = 91.49(2)°; V = 5106.6(8) Å^3; Z = 4; $F(000)$ = 2144; $\mu(\text{Mo-}K_\alpha)$ = 0.82 mm^{-1}, Θ range 2.5−25°; 9777 reflections collected; final R value 0.049 (R_w = 0.054) for 7217 out of 8367 unique reflections [$I \geqslant 2\sigma(I)$] collected by the $\omega/2\Theta$ scan method. Absorption correction (correction range 0.48−1.0) was applied by the Walker and Stuart method[19]. Selected bond distances and angles are listed in Table 1 and the atomic coordinates in Table 2.

CAS Registry Numbers

1: 130246-97-8 / **1** (without 3 C_6H_5OH): 130246-96-7 /$Pd[P(tBu)_3]_2$: 53199-31-8 / C_6H_5OH: 108-95-2

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