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A simple synthesis and crystal structure of the dinuclear diphosphido-bridged palladium(I) complex $[Pd(P^tBu_2H)(\mu\text{-}P^tBu_2)]_2$

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Abstract

UV irradiation of $Pd(P^tBu_3)_2$ in n-hexane or THF gives the diamagnetic dinuclear complex $[Pd(P^tBu_2H)(\mu\text{-}P^tBu_2)]_2$, 2-methylpropene, and hydrogen. The complex was also obtained from the reaction of $Pd(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)$ with P^tBu_2H in toluene. Its crystal and molecular structure were determined by an X-ray diffraction study. Each Pd bears a terminal P^tBu_2H ligand and the two metal centers are bridged by two phosphido ligands.

Introduction

We became recently interested in the reactivity of bis-phosphine palladium(0) complexes towards the O–H bonds of water, alcohols and phenols. The reactions of phenols with $Pd(PR_3)_2$ (**1a**: R = Cy; **1b**: R = ^{t}Bu) were investigated and a considerable dissimilarity was observed between the behavior of **1a** and **1b**, despite the fact that PCy_3 and P^tBu_3 have similar basicities and cone angles [1].

Reactions of phenols with **1a** gave high yields of the phenoxo-hydrides [2] *trans*-$[(Cy_3P)_2Pd(H)(OAr)] \cdot ArOH$ ($Ar = C_6H_5$, C_6F_5), whereas in the reaction with **1b** the corresponding derivatives were not detected, and two dimeric complexes, **2** and **3**, were isolated in low yield [3]. Both dimers contained P^tBu_2H rather than P^tBu_3, and in only one of them, $[Pd(P^tBu_2H)]_2(\mu\text{-}P^tBu_2)(\mu:\eta^2:\eta^2\text{-}C_6H_5O) \cdot 3C_6H_5OH$ (**2**) [3] was there incorporation of phenol molecules. In order

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to see whether the second dimer was generated by an unrelated decomposition of **1b** an investigation on the stability of $Pd(P^tBu_3)_2$ in the absence of phenols was undertaken.

Solutions of complex **1b** were found, in fact, to be indefinitely stable in the dark, but to decompose upon irradiation to give **3**. We present below the results of this study and of the structural characterization of **3**, which was shown to be the dipalladium derivative $[Pd(P^tBu_2H)(\mu\text{-}P^tBu_2)]_2$.

Results and discussion

When a colourless n-hexane solution of $Pd(P^tBu_3)_2$ (**1b**) is irradiated with visible or UV light it becomes red and a red crystalline diamagnetic solid, **3**, separates and 2-methylpropene and hydrogen are evolved. The IR spectrum of **3** (Nujol) shows an absorption at 2280 cm^{-1} attributable to P–H stretching; the formation of the secondary phosphine P^tBu_2H and 2-methylpropene from metal coordinated P^tBu_3 is not unprecedented, and has been accounted for in terms of the intermediacy of cyclometallated species [4]. Under identical experimental conditions $Pd(PCy_3)_2$ is inert, in keeping with the recognised lower tendency of PCy_3 to undergo cyclometallation reactions [5].

Complex **3** can also be prepared, in better yields, through the following thermal reaction:

$$2\ CpPd(\eta^3\text{-}C_3H_5) + 4\ P^tBu_2H \rightarrow \mathbf{3} + 2\ C_5H_5CH_2CH{=}CH_2 + H_2$$

Any NMR spectroscopic analysis was prevented by the exceedingly low solubility of the complex and so an X-ray structural determination was undertaken.

The molecular structure of **3** is shown in Fig. 1 together with the atomic labelling. The asymmetric unit comprises only half a molecule, the second half being related by an inversion center at the midpoint of the Pd–Pd vector. Each Pd atom bears a terminal P^tBu_2H ligand, while two di-butylphosphido ligands bridge the Pd_2 system strictly symmetrically.

A reasonable route to **3** is suggested in Scheme 1; it takes account of the fact that the reaction of phosphines with $CpPd(\eta^3\text{-}C_3H_5)$ straightforwardly gives Pd^0 phosphine complexes [6]. Moreover, the oxidative addition of P–H bonds of primary or secondary phosphines to transition metals is well documented for the nickel [7] and other groups [8] and, finally, terminal phosphido derivatives are rare in late transition metal chemistry [9].

The μ-phosphido ligand has been found to stabilize both early and late transition metal dinuclear systems, and there are many examples of dinuclear di-μ-phosphido-bridged complexes of formula $[M_2(\mu\text{-}PR_2)_2L_n]$ ($n = 2$–8) [10–16]. To our knowledge only two similar examples of Pd_2 systems are known: $Pd_2(\mu\text{-}P^tBu_2)_2(PMe_3)_2$, reported by Jones [17] and $Pd_2(\mu\text{-}PPh_2)_2(Cl)_2(PPh_3)_2$, reported by Dixon [18].

In general bis-phosphido bridges are not accompanied by other bridging ligands, especially when the substituents on phosphorus are as bulky as the butyl group. A few exceptions are known; for example a third bridging ligand (another phosphido, a μ-hydrido or a μ-carbonyl) was observed in Mo_2 [11] and Co_2 [13d] derivatives.

Relevant bond distances and angles for **3** are listed in Table 1. The Pd–Pd′ distance, 2.594(1) Å, is slightly longer than that in $[Pd(\mu\text{-}P^tBu_2)(PMe_3)]_2$, 2.571(1)

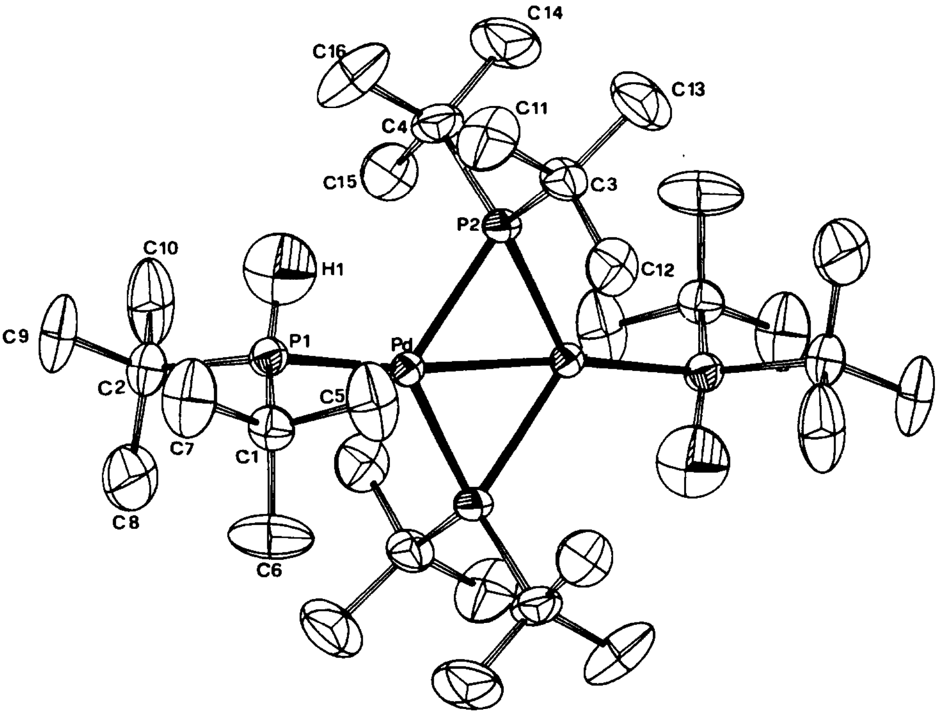
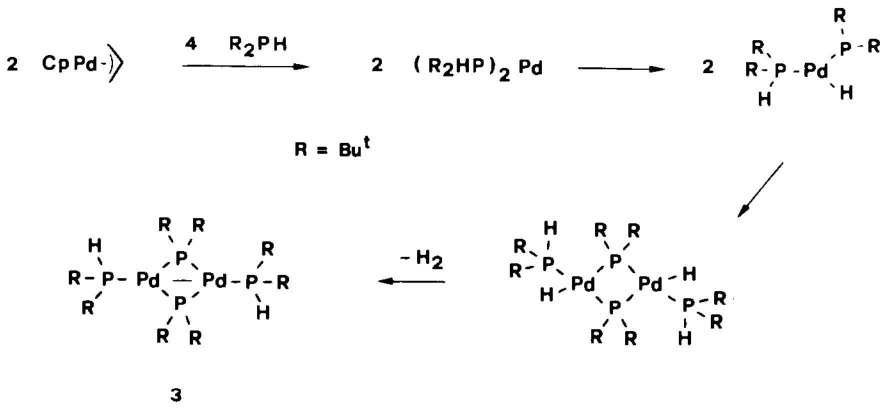


Fig. 1. ORTEP drawing of complex **3** showing the atomic labelling of the asymmetric unit. For clarity H(Me) atoms are omitted.

Å [17], in keeping with a metal–metal bond order of one based on a value of 1.30 Å for the covalent radius of Pd [19]. $Pd^{I}–Pd^{I}$ bond lengths are usually in a range from 2.531(1) in $[Pd_2(MeCN)_6]^{2+}$ [20] to 2.699(5) Å, $[Pd_2(m\text{-dppm})Br_2]$ [21], although longer lengths (up to 3 Å) have also been reported [22]. The Pd–P(phosphine) distance in **3**, 2.287(2) Å, is comparable to that in the related species $[Pd(\mu\text{-P}^tBu_2)(PMe_3)]_2$ [17] 2.250(5) Å. The slight lengthening can be reasonably



Scheme 1

Table 1

Relevant bond distances (Å) and angles (°) with e.s.d.'s in parentheses

Pd–P(1)	2.287(2)
Pd–P(2)	2.336(2)
Pd'–P(2)	2.336(2)
Pd–Pd'	2.594(1)
P(1)–C(1)	1.879(6)
P(1)–C(2)	1.865(6)
P(2)–C(3)	1.896(6)
P(2)–C(4)	1.890(7)
P(1)–Pd–Pd'	173.2(1)
P(1)–Pd–P(2)	116.9(1)
Pd'–Pd–P(2)	56.3(1)
Pd–P(1)–C(1)	116.3(2)
C(1)–P(1)–C(2)	112.0(3)
Pd–P(2)–Pd'	67.5(1)
Pd–P(2)–C(3)	115.3(2)
Pd–P(2)–C(4)	115.0(2)
C(3)–P(2)–C(4)	111.3(3)

attributed to the presence of the bulkier t-butyl substituents on the phosphine ligand and the lower electron-donating ability of the dialkyl than of the trialkylphosphine. The Pd–P distance is longer in the bridging ligand than in the terminally bound one (2.336(2) vs. 2.287(2) Å) as is often the case in related systems: M–P(bridging) and M–P(terminal) are 2.329(3) and 2.250(5) Å in $[Pd(\mu\text{-}P^tBu_2)(PMe_3)]_2$ [17] 2.31(1) Å in $[Pt(\mu\text{-}PPh_2)(PPh_3)]_2$ [23] 2.330(1) and 2.308(1) Å in $[Rh(\mu\text{-}P^tBu_2)(CO)(PMe_3)]_2$ [13e] 2.174(3) and 2.136(5) Å in $[Ni(\mu\text{-}P^tBu_2)(PMe_3)]_2$ [15].

The P–H hydrogen atom was directly located during the crystal structure determination from a Fourier map (see Experimental section). The P(1)–Pd–Pd'–P(1)' system is not strictly linear (P(1)–Pd–Pd' 173.2(1)°), the slight bending almost certainly arising from steric interactions between the butyl groups of the terminal and bridging ligands. The structural features make complex **3** very promising for reactivity studies: the presence of a bis-μ-phosphido bridge should allow reactions of electrophilic reagents with the Pd–Pd bond without disruption of the dinuclear structure. Moreover, the large bulk of the t-butyl groups of the phosphino and phosphido ligands could weaken the metal–phosphine bond, making substitution reactions easier.

Experimental

General procedures

All reactions were performed under purified nitrogen by standard Schlenck procedures. Solvents were refluxed under nitrogen over appropriate drying agents and distilled prior to use. Infrared spectra were recorded in the region 4000–400 cm^{-1} on a Perkin–Elmer 283-B spectrophotometer. The GLC analyses were performed with a Dani 8400 gas-chromatograph, equipped with a 10% CW-20M, 8/100 Chromo V-AW column.

P^tBu_3 [24], P^tBu_2H [25] and $CpPd(\eta^3$-$C_3H_5)$ [26] were prepared as previously described.

Preparation of $[Pd(P^tBu_2H)(\mu$-$P^tBu_2)]_2$, *(3)*

Method A. A solution of $Pd(P^tBu_3)_2$ (0.10–0.20 g) in n-hexane, benzene, or tetrahydrofuran (15 ml) was irradiated with sunlight for three weeks at room temperature, during which the colour changed from pale-yellow to red and red crystals separated. The solid was filtered off and dried *in vacuo*. Yields of **3** of 30–35% were obtained. IR (Nujol) 2280s (ν(PH)) cm^{-1}. Anal. Found: C, 47.74; H, 9.32; Pd, 26.6. $C_{32}H_{76}P_4Pd_2$ calc.: C, 48.2; H, 9.50; Pd, 26.7%.

When a solution of $Pd(P^tBu_3)_2$ in n-hexane was irradiated to light from a mercury vapor arc lamp for 30 min the colour of the solution changed from pale yellow to dark red. The solvent was removed *in vacuo* and a red oil was obtained. The IR analysis of the oil showed all the absorptions of complex **3** together with absorptions of unidentified contaminants. All efforts to crystallize the oil failed.

Method B. A solution of P^tBu_2H (1.406 g, 9.56 mmol) in toluene (10 ml) was added dropwise to a solution of $CpPd(\eta^3$-$C_3H_5)$ (4.78 mmol) in toluene (15 ml).

Table 2

Crystal data and details of measurements for $C_{32}H_{74}P_4Pd_2$

Formula	$C_{32}H_{74}P_4Pd_2$
M_r	795.6
Crystal size (mm)	0.30×0.12×0.15
System	monoclinic
Space group	$C2/c$
a (Å)	20.672(6)
b (Å)	11.975(4)
c (Å)	17.848(2)
β (°)	116.34(5)
U (Å^3)	3959.5
Z	4
$F(000)$	1672
D_{calc} (g cm^{-3})	1.34
λ(Mo-K_α) (Å)	0.71069
μ(Mo-K_α) (cm^{-1})	10.7
θ-range (°)	2.5–25
ω-scan width (°)	1.3
Requested counting $\sigma(I)/I$	0.01
Prescan rate (deg min^{-1})	8
Prescan acceptance $(I)/I$	0.5
Maximum scan time (s)	100
Range of reflections measured (h_{min} h_{max}, k_{min} k_{max}, l_{min} l_{max})	−24 24, 0 14, 0 21
Measured reflections	4250
Unique observed reflections used in the refinement [$I_o > 2\sigma(I_o)$]	1998
No. of refined parameters	210
R, R_w [a]	0.042, 0.048
K, g [a]	1.0, 0.0099

[a] $R_w = \Sigma[(F_o - F_c)w^{1/2}]/\Sigma F_o w^{1/2})$, where $w = k/[\sigma(F) + g\,|F^2|]$.

Table 3

Fractional atomic coordinates

Atom	x	y	z
Pd	0.43326(2)	0.00134(3)	0.44374(2)
P(1)	0.3164(1)	0.0264(1)	0.3458(1)
P(2)	0.5004(1)	0.1621(1)	0.5033(1)
C(1)	0.2951(3)	−0.0146(5)	0.2356(4)
C(2)	0.2448(4)	−0.0194(5)	0.3758(4)
C(3)	0.5194(4)	0.2544(5)	0.4289(4)
C(4)	0.4679(4)	0.2471(6)	0.5692(5)
C(5)	0.3551(5)	0.0391(10)	0.2194(5)
C(6)	0.3004(7)	−0.1384(7)	0.2261(6)
C(7)	0.2224(5)	0.0291(9)	0.1700(5)
C(8)	0.2427(7)	−0.1480(8)	0.3789(10)
C(9)	0.1697(4)	0.0256(9)	0.3203(6)
C(10)	0.2646(5)	0.0277(11)	0.4627(5)
C(11)	0.4498(5)	0.3116(7)	0.3641(7)
C(12)	0.5456(5)	0.1765(7)	0.3820(6)
C(13)	0.5766(6)	0.3424(7)	0.4728(7)
C(14)	0.5217(7)	0.3304(8)	0.6251(7)
C(15)	0.4536(5)	0.1632(7)	0.6237(6)
C(16)	0.3952(6)	0.3068(9)	0.5148(7)

The resulting solution was stirred at 75–80 °C for 48 h and the red solid which separated was filtered off and vacuum dried (1.37 g of **3** 72% yield based on Pd). IR and analytical data were identical to those of a sample prepared by method A.

X-Ray structural determination

Crystal data for **3** are presented in Table 2 together with some experimental details. Diffraction intensities were collected at room temperature on an Enraf–Nonius CAD-4 diffractometer with Mo-K_α radiation and reduced to F_o values. Absorption correction was by the Walker and Stuart method [27] after a complete structural model had been obtained, and all atoms were refined isotropically. The relative correction factors varied from 1.0 to 0.85. The structure was solved by direct and Fourier methods and refined by full-matrix least-squares, the function minimized being $w(|F_o - F_c|)^2$. The weighting scheme employed was $w = k/[\sigma^2(F_o) + g|F_o^2|]$, where k and g were refined ($g = 0.009978$). The SHELX86 [28] and SHELX76 [29] packages of crystallographic programs were used for all the computations, with the analytical scattering factors taken from ref. 30. Thermal vibrations were treated anisotropically for all non-hydrogen atoms.

The P-bound hydrogen atom was located in a difference Fourier map but not refined, except for its thermal parameters (0.145 Å^2).

All the remaining H-atoms were placed in calculated positions (C–H 1.08 Å) and refined riding on the corresponding C atoms. The final difference Fourier map showed a residual peak of about 1 e Å^{-3} near the Pd atoms. The atomic coordinates are listed in Table 3. Tables of anisotropic thermal parameters and structure factors are available from the authors.

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