

Note

An organometallic tetranuclear cluster with phosphine and phosphido ligands in nonclassical bonding modes: X-ray structural characterization [☆]

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Abstract

The elimination of the NCMe ligand in $[(C_6F_5)_2Pt(\mu-PPh_2)_2M(NCCH_3)_2]$ ($M = Pd, Pt$) results in the formation of the tetranuclear clusters $[Pt_2Pd_2(\mu-PPh_2)_3(C_6F_5)_3(PPh_2C_6F_5)]$ **1** and $[Pt_4(\mu-PPh_2)_4(C_6F_5)_4]$ **2**. The structure of **1** indicates that one of the palladium centres is connected to the rest of the centres through two M–M bonds and two weaker $\eta^2-C_6H_5$ and η^2-P-C interactions.

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1. Introduction

Several years ago we reported that the tetranuclear $[\{(C_6F_5)_2Pt(\mu-PPh_2)_2M(\mu-Cl)\}_2]^{2-}$ ($M = Pd, Pt$) anionic derivatives could be transformed into the tetranuclear clusters $[Pt_2Pd_2(\mu-PPh_2)_3(C_6F_5)_3(PPh_2C_6F_5)]$ (**1**) and $[Pt_4(\mu-PPh_2)_4(C_6F_5)_4]$ (**2**) when the bridging halide ligands were eliminated as silver chloride [1,2]. The structure of the homonuclear Pt complex **2** was established by X-ray diffraction and it resulted to be a tetranuclear cluster with three metal–metal bonds and one phosphido ligand bridging the three metal centres through at least two M–P bonds and a η^2 -phenyl–Pt interaction (see structure in Scheme 1) [2]. However, at that time we were not fortunate enough to obtain suitable crystals of the heterotetranuclear cluster **1** and from the ¹⁹F and ³¹P NMR data it could be construed that a PPh₂/C₆F₅ intramolecular reductive coupling had

taken place with formation of the PPh₂C₆F₅ phosphine. With all the data available a structure with one of the palladium centres connected to the rest of the centres through three M–M' bonds and two η^2 -phenyl–Pd interactions was tentatively assigned [1]. We have now been able to prepare this complex by a different reaction and suitable crystals for an X-ray study to be carried out and we reported here the molecular structure, which displays several important structural differences.

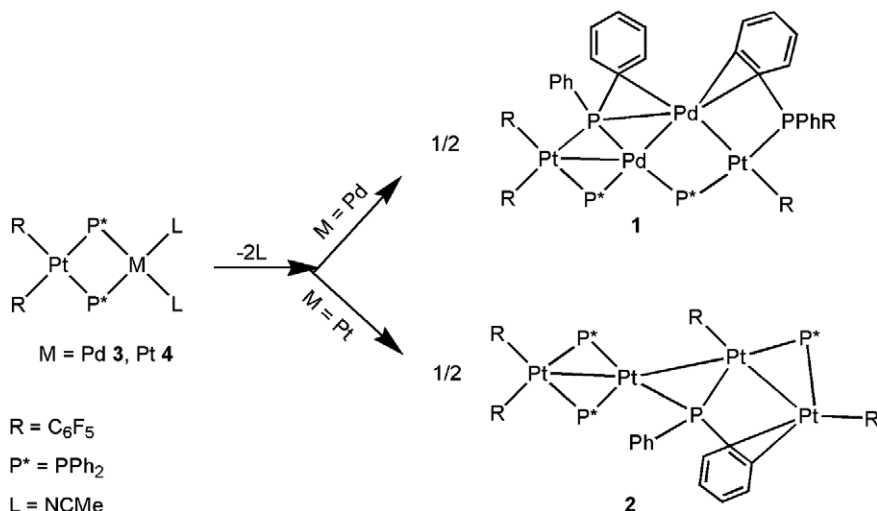
2. Results and discussion

We have recently reported a straightforward method for the synthesis of the heterodinuclear complex $[(C_6F_5)_2Pt(\mu-PPh_2)_2Pd(NCCH_3)_2]$ (**3**) [3], as a yellow solid and studied some reactions of this complex. We observed that CH₂Cl₂ solutions of **3** at room temperature became dark in colour and, after work up of the mixture, a purple solid was isolated. The IR spectrum of the solid and its ¹⁹F and ³¹P NMR spectra in solution are exactly the same that previously obtained for **1** [1] and the elementary analysis are in fully agreement with its stoichiometry. The elimination of two MeCN ligands from the dinuclear **3** gives an unsat-

[☆] Polynuclear homo- or heterometallic palladium(II)–platinum(II) pentafluorophenyl complexes containing bridging diphenylphosphido ligands. 23. For part 22 see Ref. [29].

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Scheme 1.

urated intermediate that evolves to the tetranuclear cluster [Pt₂Pd₂(μ-PPh₂)₃(C₆F₅)₃(PPh₂C₆F₅)] **1** (Scheme 1). In addition, we have now been able to obtain suitable crystals for an X-ray study to be carried out. A drawing of **1** and the atom-labelling scheme is shown in Fig. 1. Crystal data and other details of the structure analysis are presented in Table 1. Complex **1** is a tetranuclear cluster in which the “(C₆F₅)₂Pt(1)(μ-PPh₂)₂Pd(1)” fragment shows the usual arrangement with the diphenylphosphido ligands bridging the metal centres [1,2,4–7]. The core of this fragment is almost planar and the Pt(1)–Pd(1) distance is 2.745(1) Å. The “{P(1)Ph₂C₆F₅}(C₆F₅)Pt(2)P(4)Ph₂” fragment shows the P(1), C(13), Pt(2) and P(4) atoms almost in the same plane and is bonded to Pd(1) through the P(4) atom, the Pt(2)–Pd(1) distance being 3.004(1) Å.

One point of real interest in **1** lies in the environment of the Pd(2) centre. The Pt(2)–Pd(2) and Pd(1)–Pd(2) dis-

tances are 2.730(1) and 2.792(1) Å, within the range expected for metal–metal bond distances [1,2,4–10]. The phosphine P(1)Ph₂(C₆F₅) coordinates to Pd(2) atom through a η² coordination of one of the phenyl rings, which does not lose its aromaticity. The interatomic Pd(2)–C(26) and Pd(2)–C(25) distances are 2.415(5) and 2.503(5) Å, respectively, while the long P(1)–Pd(2) distance, 2.806(1) Å, excludes a P(1)–Pd(2) interaction. Thus, the P(1)Ph₂(C₆F₅) phosphine group is acting as a bridging ligand between Pt(2) and Pd(2) although using different donor atoms to each metal centre. Precedents of this coordination mode for an aryl phosphine ligand are already known [1,11–17]. The interaction between the phosphido containing P(2) and the Pd(2) centre is very noteworthy and different to the previously proposed interaction. The Pd(2)–C(37) distance (2.391(5) Å) is rather short [18–25], as is the Pd(2)–P(2) distance (2.272(1) Å), in fact it is even

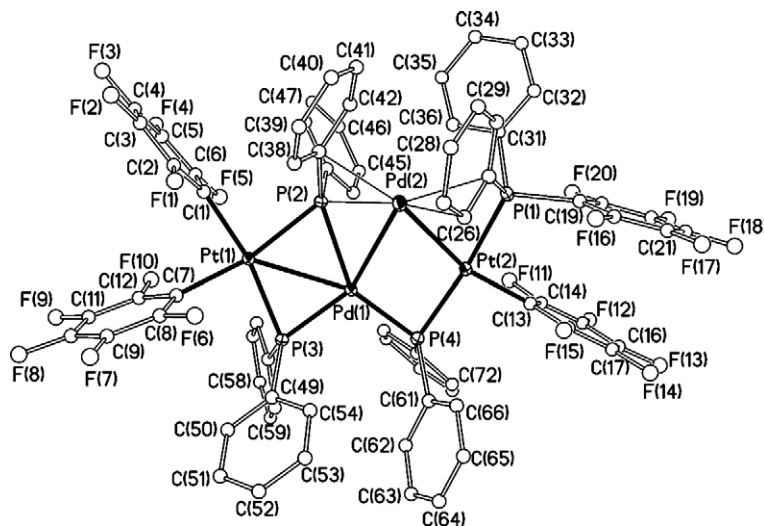


Fig. 1. Molecular structure of [Pt₂Pd₂(μ-PPh₂)₃(C₆F₅)₃(PPh₂C₆F₅)] (**1**). Selected distances: Pt(1)–C(7) 2.059(5), Pt(1)–C(1) 2.066(5), Pt(1)–P(3) 2.2830(14), Pt(1)–P(2) 2.3583(13), Pt(1)–Pd(1) 2.7445(5), Pt(2)–C(13) 2.039(6), Pt(2)–P(4) 2.2526(15), Pt(2)–P(1) 2.2843(15), Pt(2)–Pd(2) 2.7300(5), Pd(1)–P(3) 2.2044(14), Pd(1)–P(4) 2.2356(15), Pd(1)–P(2) 2.3894(14), Pd(1)–Pd(2) 2.7919(6), Pd(2)–P(2) 2.2718(14), Pd(2)–C(37) 2.391(5), Pd(2)–C(26) 2.415(5), Pd(2)–C(25) 2.503(5).

Table 1
Crystal data and structure refinement for [Pt₂Pd₂(μ-PPh₂)₃(C₆F₅)₃-
(PPh₂C₆F₅)] (1)

Empirical formula	C ₇₂ H ₄₀ AgF ₂₀ P ₄ PdPt ₂
Formula weight	2013.37
Unit cell dimensions	
<i>a</i> (Å)	18.5203(11)
<i>b</i> (Å)	14.0172(8)
<i>c</i> (Å)	25.2076(15)
<i>V</i> (Å ³), <i>Z</i>	6544.0(7), 4
Wavelength (Å)	0.71073
Temperature (K)	100(1)
Radiation	Graphite monochromated Mo Kα
Crystal system	Orthorhombic
Space group	<i>Pna</i> 2 ₁
Crystal dimensions (mm)	0.47 × 0.24 × 0.15
Absolute coefficients (mm ⁻¹)	5.027
Diffractometer	Bruker SMART Apex
2θ Range for data collection (°)	3.24–50.08
Number of reflections collected	36974
Number of independent reflections	10289 [0.0399]
[<i>R</i> _{int}]	
Refinement method	Full-matrix least-squares on <i>F</i> ²
Goodness-of-fit on <i>F</i> ^{2a}	1.003
Final <i>R</i> indices (<i>I</i> > 2σ(<i>I</i>)) ^b	<i>R</i> ₁ = 0.0221, <i>wR</i> ₂ = 0.0503
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0228, <i>wR</i> ₂ = 0.0505

$$^a \text{ Goodness-of-fit} = \sum w(F_o^2 - F_c^2) / (n_{\text{obs}} - n_{\text{param}})^{1/2}$$

$$^b R_1 = \sum (|F_o| - |F_c|) / \sum |F_o|, wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}$$

shorter than the Pd(1)–P(2) and Pt(1)–P(2) distances (2.389(1) and 2.358(1) Å, respectively). These data indicate that the P(2)–C(37) bond interacts with the Pd(2) centre giving rise to a 2e–3c bond or an agostic-like interaction of a P–C_{sp}² bond with an unsaturated metal atom, as it has been recently called for related phosphine complexes [26–28].

Summarizing, the most relevant data of complex **1** are: (a) as a consequence of the intramolecular reductive coupling the formal oxidation state of the metal centres have to be fractionary (1.5) or in others words, the cluster is built up around the formal [Pt₂Pd₂]⁶⁺ entity; (b) The Pd(2) centre is connected to the rest of the cluster in a very peculiar way: two M–M' bonds, one Pd–η²-phenyl interaction and another η²-interaction with the Pd–P–C_{ipso} bond; (c) The total valence electron count in **1** is 58 and thus only three metal–metal bonds are present. As previously described, the compound displays three short M–M distances (2.730(1), 2.745(1) and 2.792(1) Å) while the other is longer (Pt(2)–Pd(1)) 3.004(1) Å).

The chemical shift of the P atoms of phosphido ligands in **1**, 261.8, 190.6 and 139.6 ppm [1], can be assigned to P(3), P(2) and P(4), respectively, while the higher field signal, 5.7 ppm, is due to the phosphine ligand, P(1). Moreover the ca. 360 and 71 Hz couplings [1] can be assigned to J_{P(1)–P(4)} and J_{P(2)–P(4)}, respectively. It is noteworthy that the P(4) signal appears in the range usually observed for a system containing single phosphido bridging ligands that support bonded metal centres [2,8,29]. This fact suggests that the interaction between the P(2)–C(37) bond

and Pd(2) could disappear in solution while the metal atoms of the “Pt(μ-P(4)Ph₂)Pd” fragment approaches each other.

The observed evolution of **3** to **1** prompted us to test if the homodinuclear complexes [(C₆F₅)₂M(μ-PPh₂)₂M(NCCH₃)₂] (M = Pt **4**, Pd **5**) evolve in a similar way. A white suspension of the platinum complex **4** remains unchanged when it is stirred in CH₂Cl₂ at room temperature for 24 h. In order to increase its solubility, acetone was added and an orange solution was obtained at reflux temperature, from which an orange solid identified (IR, ¹⁹F and ³¹P NMR spectroscopy) as a mixture of the starting material **4** and the tetranuclear cluster [Pt₄(μ-PPh₂)₄(C₆F₅)₄], **2**, was isolated. Compound **2** had been obtained earlier [2], as for **1** through the elimination of chloro ligands, as AgCl from the homotetranuclear anionic compound [(C₆F₅)₂Pt(μ-PPh₂)₂Pt(μ-Cl)]₂²⁻. The homodinuclear yellow complex **5** evolves quickly in CH₂Cl₂. Nevertheless, the spectroscopic study of the resulting brown solid reveals it to be a mixture of complexes, which we have not been able to separate nor identify.

The coordination chemistry of tertiary phosphines was largely thought to be only possible in a terminal mode, until 1989 when it was predicted that a bridging mode was possible [30]. Some very rare examples of polynuclear complexes in which the sp³-hybridised P atom can adopt a bridging bonding mode are known [10,28,31–39]. The bridging mode shown by the P(1)Ph₂(C₆F₅) ligand in **1**, in which the phosphorous atom clearly interacts with only one metal centre and the other metal is bonded through a η²-C=C interaction of a P-phenyl fragment, are more frequent but not usual [1,11–15,40]. The classical coordination mode for phosphido groups (PR₂) is as bridging ligand between two metal centres through the phosphorous atom [41]. Nevertheless, significant examples of μ₃-PR₂ metal transition complexes with like-fivecoordinated P atoms have been reported [30,42–51]. In all our complexes in which a PPh₂ group acts as bridging ligand between three platinum or palladium centres, one η²-arene coordination of one of the phenyl groups of the phosphido is also observed [1,2,7,52], as in complex **2** (Scheme 1). However, **1** shows a rare case of an unsymmetrical bridging μ₃-PR₂ ligand caused by an agostic-like interaction of a P–C_{sp}² bond with an unsaturated palladium centre. The isolation of complexes with bridging PR₃ ligands is relevant as reaction intermediates in the syntheses of μ₂-PR₂ phosphido derivatives from the corresponding μ₂-PR₃ tertiary phosphine complexes through the oxidative addition of the P–C bond to a metal centre [53–58], as well as to rationalize the intramolecular migration of the phosphine ligands. In the same context, the interaction between the P(2)–C(37) bond and the Pd(2) centre in **1** can provide a structural model as intermediates in phosphido transfer processes and even for the syntheses of μ₃-PR phosphinidene derivatives from the corresponding μ₂-PR₂ phosphido complexes.

3. Conclusion

The elimination of two acetonitrile ligands from the dinuclear phosphido $[(C_6F_5)_2Pt(\mu-PPh_2)_2M(NCCH_3)_2]$ ($M = Pd, Pt$) is a way to synthesize tetranuclear clusters. For $M = Pd$ the process is fast and takes place through a rare reductive coupling rendering **1**, a cluster that shows the $[Pt_2Pd_2]^{6+}$ entity along with a phosphine and a phosphido ligands in nonclassical bonding modes.

4. Experimental

C and H analyses, IR and NMR spectra were performed as described elsewhere [57]. Complexes $[(C_6F_5)_2M(\mu-PPh_2)_2M'(NCCH_3)_2]$ ($M = Pt, M' = Pd$ **3**; $M = M' = Pt$, **4**, Pd **5**) were prepared as described in the references [3,59].

*Reaction of $[(C_6F_5)_2M(\mu-PPh_2)_2M'(NCCH_3)_2]$. $M = Pt, M' = Pd$ **3**.* A yellow suspension of **3** (0.060 g, 0.055 mmol) in CH_2Cl_2 (10 mL) was stirred for 2 h. The purple solution was evaporated to ca. 1 mL and hexane (4 mL) was added. Cluster **1** crystallized as a purple solid, which was filtered off and washed with hexane (2×1 mL). 0.015 g, 27% yield. $M = M' = Pt$, **4**. A white suspension of **4** (0.100 g, 0.085 mmol) in CH_2Cl_2 (15 mL) and acetone (2 mL) was refluxed for 4 h. The resulting orange solution was evaporated to 0.5 mL and Et_2O (10 mL) was added. A white solid crystallized and was filtered off and characterized as the starting material **4**. The orange solution was evaporated to ca. 1 mL and $iPrOH$ (3 mL) was added. An orange solid crystallized, and was filtered off and washed with $iPrOH$ (2×0.5 mL). The resulting solid, 0.035 g, was characterized (IR and ^{19}F and ^{31}P NMR spectroscopy) as a mixture of **4** and **2**.

Crystal structure analysis of (1). Crystal data and other details of the structure analysis are presented in Table 1. Suitable crystals for X-ray diffraction studies were obtained by slow diffusion of *n*-hexane into concentrated solutions of the complex in 2 mL of CH_2Cl_2 . A single crystal was mounted on a quartz fiber in a random orientation and held in place with a fluorinated oil. Data collection was performed at 100 K temperature on a Bruker Smart CCD diffractometer using graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). The diffraction frames were integrated using the SAINT package [60] and corrected for absorption with SADABS [61]. Lorentz and polarisation corrections were applied. The structure was solved by direct methods. All non-hydrogen atoms of the complex were assigned anisotropic displacement parameters. The hydrogen atoms were constrained to idealised geometries and assigned isotropic displacement parameters equal to 1.2 times the U_{iso} values of their respective parent atoms. C(13), C(14) and C(18) atoms were refined with a common set of anisotropic displacement parameters. Full-matrix least-squares refinement of this model against F^2 converged to final residual indices given in Table 1.

Supplementary material

CCDC 625745 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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