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| Complete List of Authors: | Ara, Irene; Universidad de Zaragoza,, Departamento de Química Inorgánica, Instituto de Síntesis Química y Catálisis Forniés, Juan; Universidad de Zaragoza, Departamento de Química Inorgánica, Instituto de Síntesis Química y Catálisis Ibañez, Susana; Universidad de Zaragoza, Departamento de Química Inorgánica, Instituto de Síntesis Química y Catálisis Mastrorilli, Piero; Politecnico di Bari, DICATECh Todisco, Stefano; Politecnico di Bari, DICATECh Gallo, Vito; Politecnico di Bari, DICATECh |
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Polynuclear Platinum Phosphanido/Phosphinito Complexes: Formation of P-O and P-O-P Bonds through Reductive Coupling Processes†

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Irene Ara,^a Juan Forniés,^{a,*} Susana Ibáñez,^a Piero Mastrorilli,^{b,c,*} Stefano Todisco,^b and Vito Gallo^b

The mixture of the asymmetric complexes of formula $[(R_F)_2Pt(\mu-PPh_2O)(\mu-PPh_2)Pt(\mu-PPh_2)_2Pt(solV)(solV')]$ (**1-(solV)(solV')**) (solV, solV' = acetone, H₂O, CH₃CN) has been prepared by reaction of $[(R_F)_2Pt^II(\mu-PPh_2)_2Pt^II(\mu-PPh_2)_2Pt^II(NCCH_3)_2]$ with AgClO₄ in CH₃CN/acetone. The lability of the Pt–solvent bonds allows the displacement of the coordinated solvent molecules by dppm or Cl[−] and the isolation of the tri- or hexanuclear phosphanido/phosphinito Pt(II) complexes $[(C_6F_5)_2Pt(\mu-PPh_2)(\mu-PPh_2O)Pt(\mu-PPh_2)_2Pt(dppm)]$ (**2**) or $[NBu_4]_2[(C_6F_5)_2Pt(\mu-PPh_2)(\mu-PPh_2O)Pt(\mu-PPh_2)_2Pt(\mu-Cl)_2Pt(\mu-PPh_2)_2Pt(\mu-PPh_2)(\mu-PPh_2O)Pt(C_6F_5)_2]$ (as a mixture of the two possible isomers **4a+4b**). Complex **2** reacts with AgClO₄ to form the tetranuclear derivative $[(C_6F_5)_2Pt(\mu-PPh_2)(\mu-PPh_2O)Pt(\mu-PPh_2)_2Pt(dppm)Ag(OCIO_3)]$ (**3**), which displays two Pt–Ag donor-acceptor bonds. The mixture of the hexanuclear isomers **4a+4b** reacts with Tl(acac) producing the acetylacetonato complex $[NBu_4]_2[(C_6F_5)_2Pt(\mu-PPh_2)(\mu-PPh_2O)Pt(\mu-PPh_2)_2Pt(acac)]$ (**5**) which, upon reaction with HCl, yields back the mixture of **4a+4b**. The reaction of **4a+4b** with PPh₃ produces $[NBu_4]_2[(C_6F_5)_2Pt(\mu-PPh_2)(\mu-PPh_2O)Pt(\mu-PPh_2)_2Pt(Cl)(PPh_3)]$ (**6**) as a mixture of isomers with the chloro ligand located *syn* (**6a**) or *anti* (**6b**) to the PPh₂O[−] group. Either the reaction of **6a+6b** with AgClO₄ or the treatment of **5** with HPPh₃ClO₄ results in the formation of the species $[(C_6F_5)_2Pt^II(\mu-PPh_2)_2Pt^II(\mu-PPh_2OPPh_2)Pt^II(PPh_3)]$ (**7**) (44 VEC), which can be explained as the consequence of a PPh₂O/PPh₂ reductive coupling and a rearrangement of ligands in the molecule generating a Pt(II),Pt(II),Pt(I) compound. All complexes were characterised in the solid state by XRD (only one of the isomers, in the cases of **4** and **6**) and in solution by NMR spectroscopy.

Introduction

Diorganophosphanido ligands have been used as building blocks for the synthesis of a huge amount of polynuclear complexes since: a) the flexibility of these bridging ligands makes them highly adequate groups to support metal centres located at short or long distances, as required by the number of skeletal electrons; b) the stability of the $M(\mu-PR_2)_xM'$ bridging systems in complexes with this type of bridges allows, in many cases, the polynuclear framework to be retained throughout chemical reactions.²⁻⁹

In the course of our current research on palladium or platinum phosphanido complexes¹⁰⁻²⁰ we observed, as expected, the stability of the $M(\mu-PPh_2)_xM'$ metal skeleton (M, M' = Pd, Pt), and the influence of the number of skeletal electrons on the structure of the polynuclear complex.¹⁰⁻²⁶ In this regard, one of the facts that militate against the preservation of the $(\mu-PPh_2)$ bridging system is the oxidation of the metal centres, since the oxidized Pd or Pt complexes usually evolve, depending on the

reaction conditions, through reductive PPh₂/X coupling processes to produce new complexes containing bridging or terminal X–PPh₂ ligands. Some of these reactions are outlined in Scheme 1.^{10-12, 14, 27-29}

Recently we have prepared, through a reductive coupling process, the dianionic trinuclear derivative $(NBu_4)_2[(R_F)_2Pt^II(\mu-OPPh_2)(\mu-PPh_2)Pt^II(\mu-PPh_2)_2Pt^II(R_F)_2]$ ¹² (see Scheme 1c) which contains two types of bridging ligands, PPh₂[−] and OPPh₂[−], of different nucleophilicity and in this work we describe the chemistry of neutral or monoanionic trinuclear complexes of the type $[(R_F)_2Pt^II(\mu-OPPh_2)(\mu-PPh_2)Pt^II(\mu-PPh_2)_2Pt^II]L_2$.

Results and discussion

The starting material for the synthesis of trinuclear asymmetric complexes containing a P–O[−] bridging ligand is the mixture of solvento species $[(R_F)_2Pt^II(\mu-OPPh_2)(\mu-PPh_2)Pt^II(\mu-PPh_2)_2Pt^II(solV)(solV')]$ (solV, solV' = H₂O, acetone, acetonitrile) (**1-(solV)(solV')**) (Scheme 2) obtained by treatment of the trinuclear Pt(II) derivative $[(R_F)_2Pt^II(\mu-PPh_2)_2Pt^II(\mu-PPh_2)_2Pt^II(NCCH_3)_2]$ ¹¹ (**A**) with AgClO₄, as an oxidant, in acetonitrile and wet acetone (used for reasons of solubility, see Scheme 2).

According to previous observations,¹² complex **1-(solV)(solV')** is in all likelihood formed via two processes. The first one is the oxidation of **A**, a Pt(II),Pt(II),Pt(II) complex, to the corresponding Pt(III),Pt(III),Pt(II) derivative, and the second

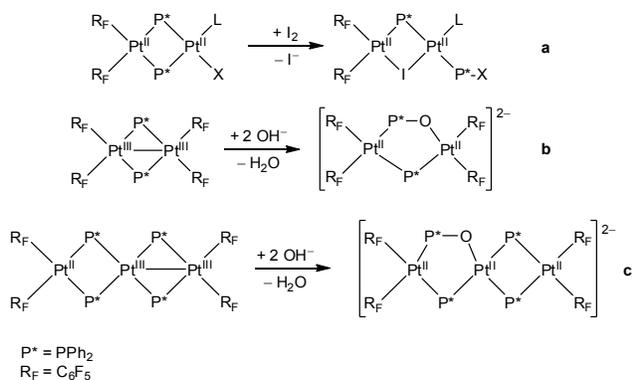
^a Departamento de Química Inorgánica, Instituto de Síntesis Química y Catálisis Homógena, Universidad de Zaragoza - CSIC, 50009 Zaragoza, Spain.

^b Dipartimento di Ingegneria Civile, Ambientale del Territorio, Edile e di Chimica DICATECH del Politecnico di Bari, via Orabona 4, I-70125 Bari, Italy.

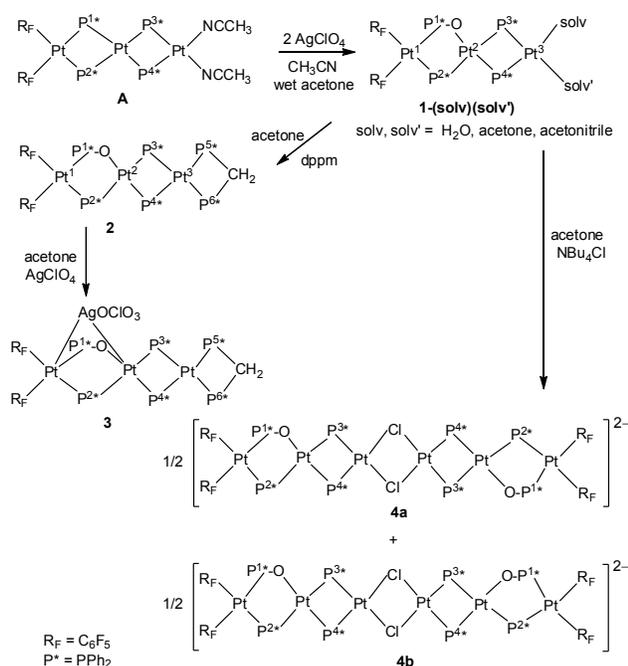
^c Consiglio Nazionale delle Ricerche, Istituto di Chimica dei Composti Organometallici (ICCOM-CNR), Via Orabona 4, 70125 Bari, Italy.

† Polynuclear Homo- or Heterometallic Palladium(II)-Platinum(II) Pentafluorophenyl Complexes Containing Bridging Diphenylphosphido Ligands. 34. For part 33 see reference 1.

For crystallographic data in CIF see DOI: 10.1039/x0xx00000x



Scheme 1 Reductive coupling of bridging phosphanides (X = benzoquinolate, 8-hydroxyquinolate, picolinate, acetylacetonato).



Scheme 2 Synthesis of Phosphanido/Phosphinito Complexes.

process is the formation of the PPh_2O^- ligand which, as has been demonstrated previously,¹² takes place by coordination of the OH^- group to the Pt(III) centre, followed by reductive P-O coupling and formation of the mixture of solvent species **1-(solv)(solv')**, which, in all cases, contain one diphenylphosphinito ligand and all Pt centres in formal oxidation state (II).

The product of reaction between **A** and $AgClO_4$ was characterised as the mixture of solvent species **1-(solv)(solv')** by ESI-MS, NMR, and XRD analyses. The ESI-MS spectrogram of **1-(solv)(solv')** in acetonitrile showed an intense peak ascribable to $[1-(CH_3CN)_2 + H]^+$ ($m/z = 1758.1289$; calculated mass = 1758.1414 Da)⁵ plus several other overlapped peaks ascribable to proton or sodium adducts of solvent species

containing one or two molecules of water and/or acetonitrile. The ^{31}P NMR spectrum in acetone- d_6 showed signals in the region from 125 to 130 ppm ascribable to the bridging diphenylphosphinito P^1 , around 14 ppm for the bridging diphenylphosphanide P^2 and at $\delta -142$ and $\delta -152$ for the bridging diphenylphosphanides P^4 and P^3 respectively. Although it was impossible to assign each resonance to the specific corresponding solvent species, it was ascertained by 1H EXSY and $^{31}P\{^1H\}$ EXSY that the complexes contained H_2O , CH_3CN and acetone as labile ligands bonded to Pt^3 , and that all these solvent species were in equilibrium. In fact, exchange cross peaks between signals at $\delta 2.84$ (free H_2O in acetone) and $\delta 3.37$ (coordinated H_2O), as well as between overlapped signals at $\delta 2.1$ (free acetone but also acetonitrile in acetone) and δ from 2.3 to 2.4 (coordinated acetone and coordinated acetonitrile) were present in the 1H EXSY spectrum of an acetone- d_6 solution of **1-(solv)(solv')** at 298 K. Moreover, the $^{31}P\{^1H\}$ EXSY spectrum of the same solution showed at 298 K, in the phosphinito region, cross peaks between an intense peak at $\delta 126.9$ and weak peaks at: $\delta 124.8$, $\delta 128.8$ and $\delta 129.5$. These results can be explained by considering that the peak at $\delta 126.9$ belongs to the mixed acetone/ H_2O species **1-(acetone)(H_2O)** (the major species in acetone solution), which is in equilibrium with **1-(H_2O)₂**, **1-(acetone)₂** and **1-(acetone)(CH_3CN)**, the latter ones displaying signals at $\delta 124.8$, $\delta 128.8$ and $\delta 129.5$.

By adding a drop of acetonitrile to a solution of the mixture **1-(solv)(solv')** in acetone- d_6 , a single species was obtained, presumably the bis-acetonitrile complex $[(R_F)_2Pt(\mu-Ph_2PO)(\mu-PPh_2)Pt(\mu-PPh_2)_2Pt(NCCH_3)_2] [1-(CH_3CN)_2]$ showing ^{31}P NMR signals, at 263 K, at $\delta 127.1$ (P^1), $\delta 12.8$ (P^2), $\delta -144.3$ (P^4), $\delta -153.7$ (P^3). A complete multinuclear NMR (and ESI-MS) characterisation in solution is reported in the Experimental Part for the analogous bis-benzonitrile complex obtained by dissolving the mixture **1-(solv)(solv')** in benzonitrile.

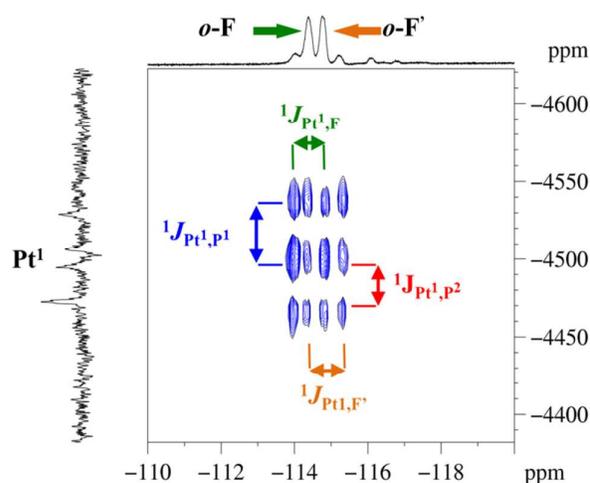


Fig. 1 ^{19}F - ^{195}Pt HMQC spectrum of **1-(PhCN)₂** (PhCN, 298 K).

For $[(R_f)_2Pt(\mu\text{-Ph}_2\text{PO})(\mu\text{-PPh}_2)Pt(\mu\text{-PPh}_2)_2Pt(\text{PhCN})_2]$ [**1**-**(PhCN)**]₂, the ^{195}Pt signals were found at δ -4500 (Pt^1), δ -3900 (Pt^3) and δ -3784 (Pt^2), also by means of ^{19}F - ^{195}Pt HMQC experiments (Figure 1).

X-ray structure of 1-(acetone)(H₂O)·2.5acetone. Slow diffusion of hexane into a concentrated solution of the crude solid in acetone, allowed the crystallization of one of the complexes constituting the **1**-(**solv**)(**solv'**) mixture, and namely the species having **solv** = acetone and **solv'** = H₂O: $[(C_6F_5)_2Pt(\mu\text{-PPh}_2)(\mu\text{-PPh}_2)_2Pt(\mu\text{-PPh}_2)_2Pt(\text{acetone})(\text{OH}_2)] \cdot 2.5\text{acetone}$. The structure of [**1**-(**acetone**)(**H₂O**)]·2.5acetone was studied by X-ray diffraction and is shown in Figure 2. The solid state structure confirms that it is a trinuclear unsymmetrical complex which contains the “ $(C_6F_5)_2Pt(1)(\mu\text{-OPPh}_2)(\mu\text{-PPh}_2)_2Pt(2)(\mu\text{-PPh}_2)_2Pt(3)$ ” fragment (present in most of the complexes described in this paper) and H₂O and acetone coordinated to Pt(3). Since most of the complexes described in this paper contain the same trinuclear fragment as a part of the molecule, relevant data related with the skeleton of this fragment have been collected in Table 1 to facilitate comparison between different complexes. The three metal atoms are disposed in an almost linear arrangement [$Pt(1)\text{---}Pt(2)\text{---}Pt(3) = 169.29(1)^\circ$]. $Pt(1)$ and $Pt(2)$ are supported by a phosphanido, $P(2)Ph_2$, and a phosphinito, $Ph_2P(1)\text{---}O$, bridging ligand whereas $Pt(2)$ and $Pt(3)$ are supported by two PPh_2 groups, $P(3)$ and $P(4)$. $Pt(1)$ is coordinated to two pentafluorophenyl groups and $Pt(3)$ is coordinated to one water molecule and one acetone molecule. The three platinum atoms display square planar environments, the coordination planes not being coplanar; the dihedral angle between the best $C(1)$, $C(7)$, $Pt(1)$, $P(1)$, $P(2)$ plane and the best $O(1)$, $P(2)$, $Pt(2)$, $P(3)$, and $P(4)$ plane is $148.01(2)^\circ$, and that between the best $O(1)$, $P(2)$, $Pt(2)$, $P(3)$, and $P(4)$ plane and the best $O(2)$, $O(3)$, $Pt(3)$, $P(3)$, and $P(4)$ plane is $173.8(26)^\circ$. The five-membered ring formed by $P(1)\text{---}O(1)$ phosphinite, $P(2)$ phosphanide, $Pt(1)$ and $Pt(2)$ atoms is not planar. The long intermetallic distances [$Pt(1)\cdots Pt(2) = 3.854(6)$ Å, $Pt(2)\cdots Pt(3) = 3.518(6)$ Å] rule out any kind of bonding interaction between the metal centres, as expected for a trinuclear platinum complex with 48 valence electron count (VEC). Other relevant interatomic distances are collected in Table 2.

In **1**-(**solv**)(**solv'**), **solv** and **solv'** are, in all cases, very labile ligands and **1**-(**solv**)(**solv'**) can be used as starting material for the preparation of other pure trinuclear asymmetric

complexes by displacement reactions. Thus, the treatment of **1**-(**solv**)(**solv'**) with bis-(diphenylphosphino)methane (dppm) ($Pt/dppm$ ratio approx. 2/1) gave the neutral asymmetric complex $[(R_f)_2Pt^II(\mu\text{-OPPh}_2)(\mu\text{-PPh}_2)Pt^II(\mu\text{-PPh}_2)_2Pt^II(dppm)]$ (**2**) in good yield (81%), with the dppm coordinated as a chelating ligand to one of the ends of the molecule.

The ^{19}F NMR spectrum of **2** showed six signals due to the *o*-F, *m*-F, and *p*-F of the inequivalent, freely rotating C_6F_5 rings. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2** in 1,2-dichloroethane consisted of six signals, the most deshielded of these being a singlet (broadened by multiple $^{31}\text{P}\text{---}^{19}\text{F}$ and $^{31}\text{P}\text{---}^{31}\text{P}$ small couplings) centred at δ 127.9 and ascribed to the bridging phosphinito P^1 .^{12,30} The three bridging phosphanides gave signals at δ 13.8 (d), δ -134.2 (dd), and δ -142.4 (m). Of these, the doublet at δ 13.8 is ascribed to the P^2 atom involved in a five-membered ring, while the doublets of doublets at δ -134.2 and δ -142.4 are due to the mutually coupled P atoms, involved in the four-membered Pt^2P_2 ring, P^4 and P^3 , respectively. The ^{31}P signals of the coordinated dppm were almost isochronous in the region of around -30 ppm ($\delta_{p_5} -28.3$, $\delta_{p_6} -30.5$). The $^{195}\text{Pt}^2$ and $^{195}\text{Pt}^3$ nuclei gave sharp signals at δ -3584 and δ -4027, while the $^{195}\text{Pt}^1$ signal was very broad and difficult to detect in the monodimensional ^{195}Pt NMR spectrum, due to multiple $^{195}\text{Pt}\text{---}^{19}\text{F}$ and $^{195}\text{Pt}\text{---}^{31}\text{P}$ couplings. However, the resonance of Pt^1 was found at δ -4461 by a $^{19}\text{F}\text{---}^{195}\text{Pt}$ HMQC experiment.

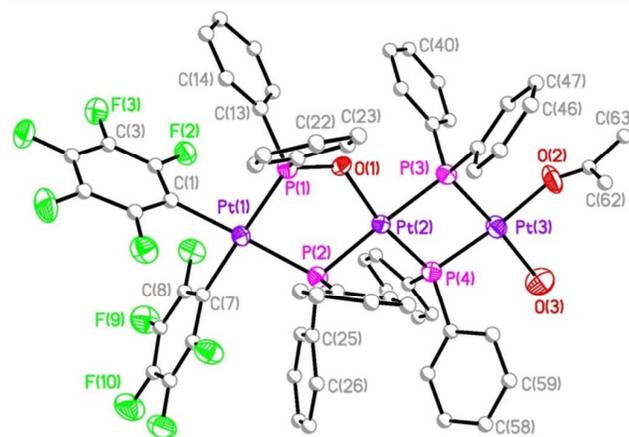


Fig. 2 Molecular structure of the complex $[(C_6F_5)_2Pt(\mu\text{-PPh}_2)(\mu\text{-PPh}_2)_2Pt(\mu\text{-PPh}_2)_2Pt(\text{acetone})(\text{OH}_2)] \cdot 2.5\text{acetone}$ [**1**-(**acetone**)(**H₂O**)]·2.5acetone.

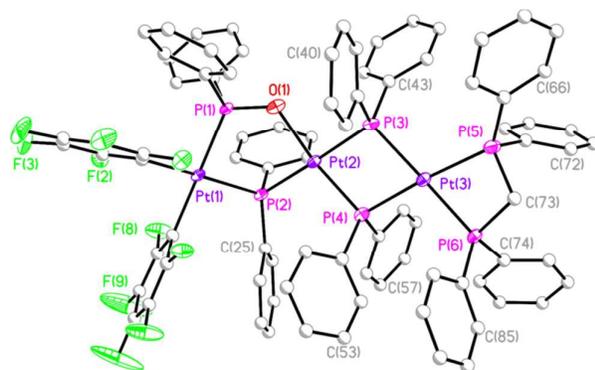
Table 1 Selected structural data for the Pt_3 framework of complexes **1**-**7**.

| | $Pt(1)\text{---}Pt(2)\text{---}Pt(3)$ angle ($^\circ$) | $Pt(1)\text{---}Pt(2)$ distance (Å) | $Pt(2)\text{---}Pt(3)$ distance (Å) | $D^*Pt(1)/Pt(2)$ | $D^*Pt(2)/Pt(3)$ | $Pt(3)\text{---}Pt(3')$ distance (Å) |
|---|---|--|--|------------------|------------------|---|
| 1 -(acetone)(H₂O) | 169.29(1) | 3.8543(6) | 3.5184(6) | 148.01(20) | 173.38(26) | |
| 2 | 155.76(2) | 3.6617(7) | 3.5987(7) | 123.36(19) | 170.76(14) | |
| 3 | 154.55(2) | 3.7316(6) | 3.5827(6) | 134.13(16) | 167.49(14) | |
| 4a | 171.75(1) | 3.9068(5) | 3.5247(5) | 159.32(9) | 168.04(8) | 3.5831 |
| 5 | 171.74(1) | 3.9335(3) | 3.5540(2) | 152.54(4) | 170.47(7) | |
| 6a | 158.81(2) | 3.7696(7) | 3.5810(7) | 135.34(17) | 177.04(16) | |
| 7 | 101.98(2) | 2.7509(6) | 2.2604(6) | | | |

D^* is the dihedral angle between coordination planes

Table 2-Selected Bond Distances (Å) for complexes 1-6.

| | 1·2.5acetone | 2·0.5acetone | 3·0.5CH ₂ Cl ₂ ·4hexane | 4a·2acetone·1.5hexane | 5·acetone | 6a·CH ₂ Cl ₂ ·0.5H ₂ O |
|--------------|--------------|--------------|---|-----------------------|------------|---|
| Pt(1)–C(1) | 2.073(10) | 2.093(12) | 2.082(12) | 2.051(8) | 2.073(4) | 2.065(13) |
| Pt(1)–C(7) | 2.084(10) | 2.050(14) | 2.069(11) | 2.083(8) | 2.096(4) | 2.081(15) |
| Pt(1)–P(1) | 2.273(3) | 2.275(3) | 2.295(3) | 2.257(2) | 2.2619(10) | 2.264(3) |
| Pt(1)–P(2) | 2.315(3) | 2.315(3) | 2.321(3) | 2.304(2) | 2.3220(10) | 2.316(4) |
| Pt(2)–O(1) | 2.080(6) | 2.112(8) | 2.075(8) | 2.098(5) | 2.109(3) | 2.119(8) |
| Pt(2)–P(2) | 2.347(3) | 2.350(3) | 2.352(3) | 2.342(2) | 2.3579(9) | 2.357(3) |
| Pt(2)–P(3) | 2.308(3) | 2.307(3) | 2.328(3) | 2.310(2) | 2.3197(10) | 2.305(3) |
| Pt(2)–P(4) | 2.234(3) | 2.226(3) | 2.257(3) | 2.2352(19) | 2.2400(10) | 2.239(3) |
| P(1)–O(1) | 1.549(7) | 1.549(9) | 1.581(8) | 1.555(6) | 1.560(3) | 1.527(10) |
| Pt(3)–P(3) | 2.234(3) | 2.340(3) | 2.325(3) | 2.2400(19) | 2.2308(10) | 2.303(3) |
| Pt(3)–P(4) | 2.223(3) | 2.338(3) | 2.341(3) | 2.231(2) | 2.2363(10) | 2.270(3) |
| Pt(3)–P(5) | | 2.332(4) | 2.338(3) | | | 2.343(3) |
| Pt(3)–P(6) | | 2.324(3) | 2.331(4) | | | |
| Pt(1)–Ag | | | 2.7596(10) | | | |
| Pt(2)–Ag | | | 2.8741(11) | | | |
| Ag–O(2) | | | 2.350(19) | | | |
| Pt(3)–O(2) | 2.169(8) | | | | 2.096(3) | |
| Pt(3)–O(3) | 2.165(8) | | | | 2.075(3) | |
| Pt(3)–Cl(1) | | | | 2.415(2) | | 2.382(3) |
| Pt(3)–Cl(1A) | | | | 2.4195(18) | | |

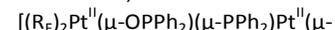
Fig. 3 Molecular structure of the complex $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)(\mu\text{-}PPh_2O)Pt(\mu\text{-}PPh_2)_2Pt(dppm)]\cdot 0.5\text{acetone}$ (**2**·0.5acetone).

X-ray structure of 2. The X-ray structure of **2** is shown in Figure 3 while selected bond distances and angles are collected in Tables 1 and 2. In this molecule the three metal atoms are disposed in an almost linear arrangement [Pt(1)–Pt(2)–Pt(3) = 155.76(2)°]. Pt(1) and Pt(2) are supported by a phosphanido, P(2)Ph₂, and a phosphinito, Ph₂P(1)–O, bridging ligand whereas Pt(2) and Pt(3) are supported by two PPh₂ groups, P(3) and P(4) with the Pt atoms in square-planar environments and without Pt ··· Pt interactions, as expected for a molecule with a 48 VEC skeleton [Pt(1)···Pt(2) = 3.662(1) Å and Pt(2)···Pt(3) = 3.599(1) Å]. The environments of the Pt centres are not coplanar, the dihedral angles between the Pt(1) and Pt(2) coordination planes being 123.4(2)°, while that formed by the Pt(2) Pt(3) coordination planes is 170.8(1)° (Table 1). The dihedral angle formed by the dppm skeleton and the Pt(3) coordination plane is 150.47(57)°.

Reactions of complex 2 with Ag⁺. We have previously reported that Ag⁺ or [Ag(PPh₃)]⁺ can act as oxidants towards binuclear or trinuclear phosphanido Pt(II) or Pd(II) derivatives, affording M(III) or M(III)/M(II) derivatives, but they can also act as electrophiles, resulting in the formation of complexes with M–Ag donor-acceptor bonds.^{1, 32}

Complex $[(R_F)_2Pt^II(\mu\text{-}OPPh_2)(\mu\text{-}PPh_2)Pt^II(\mu\text{-}PPh_2)_2Pt^II(dppm)]$ (**2**) is an excellent candidate to study its reaction with Ag⁺. In fact, considering that complex **2** displays several nucleophilic positions (namely the Pt(II) centres and some of the Pt–(μP), Pt–P or Pt–O bonds) and that the Pt(II) centres could also be oxidized by Ag⁺, different types of complexes could be produced when this reaction is carried out, depending on the process (or processes) which effectively take place.

The reaction between $[(R_F)_2Pt^II(\mu\text{-}OPPh_2)(\mu\text{-}PPh_2)Pt^II(\mu\text{-}PPh_2)_2Pt^II(dppm)]$ (**2**) and AgClO₄ in CH₂Cl₂ at low temperature (253 K) and in the dark, results in the formation of a yellow solid which, according to structural data, is the tetranuclear complex



The solid state structure of the tetranuclear complex **3** was established by an X-ray diffraction study.

X-ray structure of 3. The molecular structure of complex **3** is shown in Figure 4. Relevant structural parameters are collected in Tables 1 and 2. The structure of **3** is the result of the interaction of two of the Pt centres (Pt(1) and Pt(2)) with Ag⁺ through two Pt–Ag donor-acceptor bonds. Thus the Pt skeleton is very similar to that of the starting material and the silver centre is located on the inner side of the “open book”

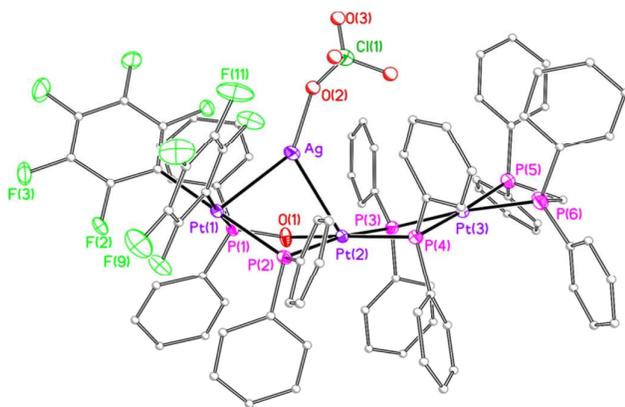


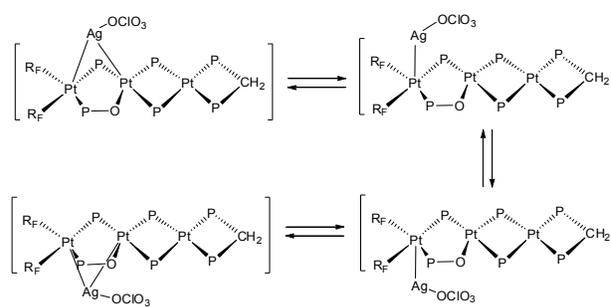
Fig. 4 Molecular structure of the complex $[(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-PPh}_2)(\mu\text{-PPh}_2\text{O})\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\text{dppm})\text{Ag}(\text{OCIO}_3)]\cdot\text{CH}_2\text{Cl}_2$ (**3**·0.5CH₂Cl₂·4hexane).

structure with the Pt atoms in square planar environments. The silver centre completes its coordination sphere with an O atom of the perchlorate ligand. The two square planar coordination planes of the platinum atoms connected to Ag⁺ form a dihedral angle of 134.1(2)° while the dihedral angle formed by the Pt(2) and Pt(3) coordination planes is 167.5(2)°. The Pt–Ag distances are 2.7596(10) and 2.8741(11) Å and, as observed in previous examples, the shorter distance corresponds to the Pt(1) centre, which is bonded to the pentafluorophenyl ligands. Assuming that the shorter Pt–Ag distance should be related to a stronger metal–metal bond, and due to the nature of the donor–acceptor Pt–Ag bonds, it seems plausible to assume that the Pt(1) centre bearing the C₆F₅ groups should probably be the most basic in character. It is remarkable that the dihedral angle formed by the Pt(1) and Pt(2) coordination planes in complexes **2** and **3** are rather similar in spite of the fact that in **3**, Ag⁺ is bonded to the Pt centres, on the inner side of the book, forming two Pt–Ag bonds.^{1, 16, 32}

The ESI-MS(+) analysis of **3** in acetonitrile shows a peak ascribable to $[\mathbf{3} - \text{ClO}_4]^+$ at $m/z = 2168.1084$ (exact mass for $[\mathbf{3} - \text{ClO}_4]^+ = 2168.1070$) indicating that the Ag adduct is stable in solution.

The chemical shift and the multiplicity of the ³¹P NMR signals of **3** are similar to those of **2**, the main difference being the direct coupling constants between Pt^{1/2} and P^{1/2} which are considerably lower in the case of **3**. For instance, the ¹J_{P₂,Pt₁ and ¹J_{P₂,Pt₂ values are 1868 Hz and 1890 Hz for **2** and 1271 Hz and 1376 Hz for **3**, respectively. The ¹⁹⁵Pt NMR features are conclusive that the AgClO₄ is bonded to Pt¹ and Pt². In fact, the ¹⁹⁵Pt NMR signals of Pt¹ and Pt² of **3** were found at δ –3954 and δ –3022, respectively, compared to δ –4461 and δ –3584, respectively, for Pt¹ and Pt² of **2**. The Pt³ NMR resonance of **3** (δ –4058) did not differ significantly from that of **2** (δ –4027). A downfield shift for the ¹⁹⁵Pt nuclei upon Ag bridging coordination has been already observed in the case of (R_F)₂Pt(μ-PPh₂)₂Pt(L-L′) complexes (L-L′ = benzoquinolate, 8-hydroxyquinolate, picolinate).¹}}

The ¹⁹F NMR spectrum of **3** in CD₂Cl₂ (or in acetone-*d*₆) at 258 K showed two broad signals assigned to the *ortho*-F signals of



Scheme 3 Dynamic process involving complex **3** in solution.

the nonequivalent C₆F₅ rings. Given that at low T the pentafluorophenyl ring rotation is expected to block^{1, 20, 28, 32} the equivalence of the *ortho*-F signals of each ring would point to a dynamic process in which the Ag(ClO₄) moiety passes from one face to the other of the complex (Scheme 3). This view is substantiated by the ¹H-³¹P HMQC spectrum that shows only one (averaged) type of *ortho*-phenyl proton bonded to each P atom and not two, as would have been expected if the upper and bottom part of the molecule were differentiated by the steady presence of the Ag(ClO₄).

Synthesis of $[\text{NBu}_4]_2[(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-PPh}_2)(\mu\text{-PPh}_2\text{O})\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\mu\text{-Cl})_2\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\mu\text{-PPh}_2\text{O})\text{Pt}(\text{C}_6\text{F}_5)_2]$ (**4a,b**).

The reaction of acetone solutions of the solvent species **1**-(*sol*v)(*sol*v′) with NBu₄Cl (approx. 1:1 molar ratio) allowed the isolation of the hexanuclear derivatives $[\text{NBu}_4]_2[(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-PPh}_2)(\mu\text{-PPh}_2\text{O})\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\mu\text{-Cl})_2\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\mu\text{-PPh}_2)(\mu\text{-PPh}_2\text{O})\text{Pt}(\text{C}_6\text{F}_5)_2]$ (**4**) (Scheme 2). In this process, the chloride is coordinated to the Pt centre with elimination of the two labile molecules *sol*v, *sol*v′. As observed in some other instances,^{33, 34} the supposed intermediate $[(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-PPh}_2)(\mu\text{-PPh}_2\text{O})\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\text{Cl})_2]^{2-}$, if formed, does not crystallise from the solution, the hexanuclear complex being crystallised instead. The NMR spectra indicate that complex **4** is in fact a mixture of the two expected isomers **4a** and **4b** (see Scheme 2).

The ³¹P{¹H} NMR spectrum of **4a-b** (Figure 5) shows one signal for the phosphinite P¹ (δ 124.9) and for the phosphanide P² (δ 13.0) and two signals each for the phosphanide P atoms P³ (δ –147.9 and δ –148.2, ddd) and P⁴ (δ –138.5 and δ –138.7, d) indicating that, as expected, slight differences in ³¹P chemical shift were found, at 161 MHz, only for of the atoms adjacent to the Pt₂Cl₂ ring (*i.e.* P³ and P⁴) for the two isomers. The phenyl protons bonded to P³ and P⁴ are also differentiated, as indicated by the ¹H-³¹P HMQC spectrum shown in Figure 6. The ¹⁹⁵Pt signals of **4a-b** were detected by combining data from ¹⁹⁵Pt spectrum (δPt² = –3789, δPt³ = –3495) and ¹⁹F-¹⁹⁵Pt HMQC experiments (δPt¹ = –4515). Due to the weakness of the signals, caused by the moderate solubility of the complexes, the expected difference in chemical shift for at least Pt² and Pt³ of **4a-b**, was not seen.

X-ray structure of 4a. The structure of the hexanuclear anion of **4a** is shown in Figure 7 with the six Pt atoms disposed in an almost linear array. Selected bond distances and angles are

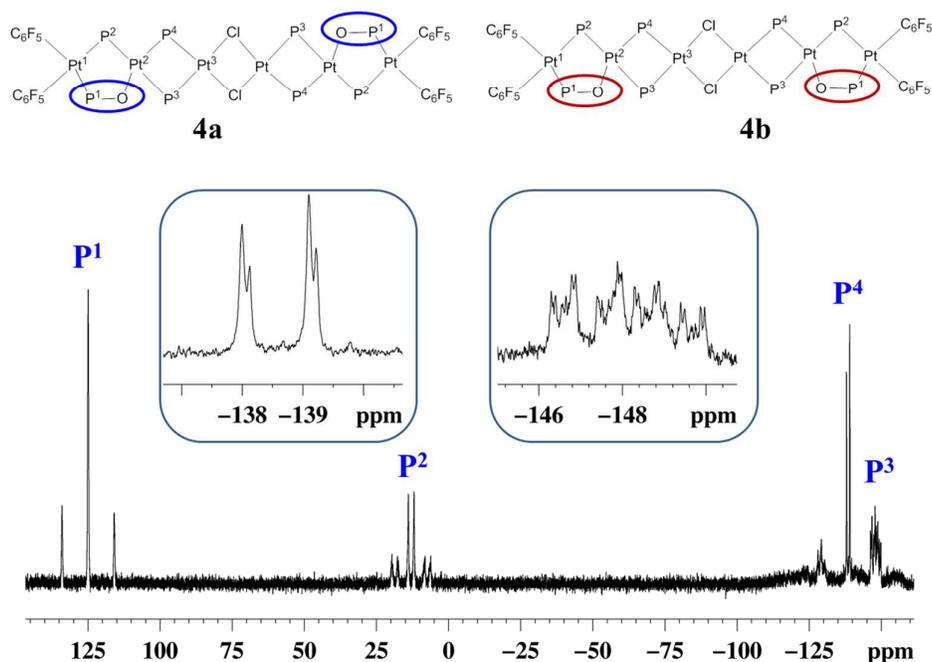


Fig. 5 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **4a-b** (acetone- d_6 , 298 K).

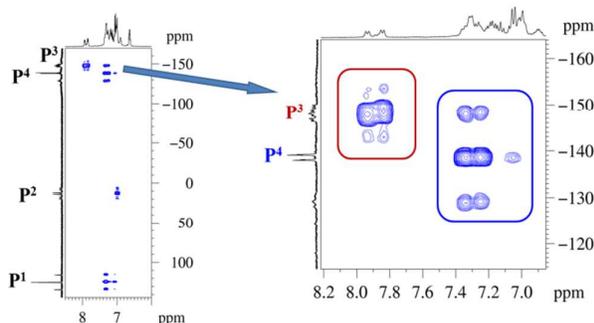


Fig. 6 $^1\text{H}-^{31}\text{P}$ HMQC spectrum of **4a-b** (acetone- d_6 , 298 K).

collected in Tables 1 and 2. The anion has an inversion centre, and thus both halves are equivalent. The six Pt(II) centres are located in approximately square planar coordination environments. In fact, the anion complex consists of two of the abovementioned fragments “ $(\text{C}_6\text{F}_5)_2\text{Pt}(1)(\mu\text{-OPPh}_2)(\mu\text{-PPh}_2)\text{Pt}(2)(\mu\text{-PPh}_2)_2\text{Pt}(3)$ ”, which are connected by two bridging chloro ligands. The Pt...Pt distances range from 3.583(1) Å to 3.907(1) Å excluding any kind of Pt...Pt interactions, as is to be expected for a 96 VEC Pt_3 species. Table 1 shows other distances and dihedral angles of the skeleton that do not show significant differences with the parameters corresponding to complex **2**.

The “ $\text{Pt}(\mu\text{-Cl})_2\text{Pt}$ ” bridging system is expected to be easily split and thus the mixture of isomers **4a** and **4b** represents an

excellent starting material for the synthesis of unsymmetrical trinuclear phosphanido/phosphinito-bridged derivatives.

Reactions of 4 with $\text{Ti}(\text{acac})$ or PPh_3 . The “ $\text{Pt}(\mu\text{-Cl})_2\text{Pt}$ ” bridging system in **4a-b** is expected to be a very reactive point to produce other polynuclear complexes.⁵⁵ Thus, reaction of **4a-b** with $\text{Ti}(\text{acac})$ (1:2 molar ratio) in acetone afforded, after work-up, crystalline $[\text{NBu}_4][(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-PPh}_2)(\mu\text{-PPh}_2)_2\text{Pt}(\text{acac})]$ (**5**) (Scheme 4). Since the incorporated acetylacetonato ligand is symmetric, only one isomer was expected and only one isomer formed. As expected,^{11, 14, 35-38} the acetylacetonato complex **5** reacts with HCl in acetone (1:1 molar ratio) producing acetylacetonato and again, the mixture of the isomers **4a-b**.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **5** in acetone- d_6 showed the phosphinito P^1 signal at δ 125.3, the phosphanido P^2 involved in a five-membered ring at δ 13.9, and the phosphanides P^3

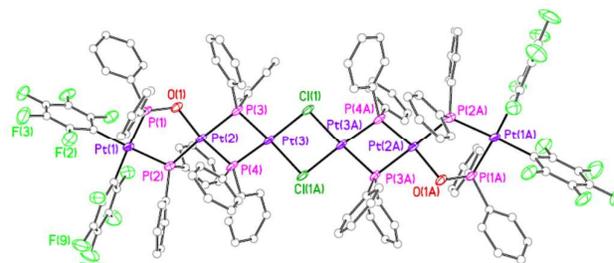
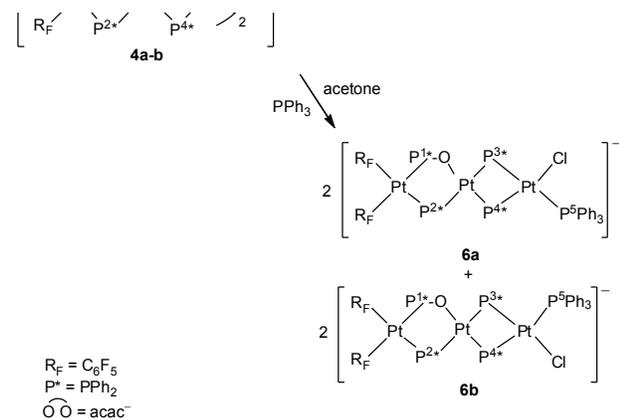


Fig. 7 Molecular structure of the anion of the complex $[\text{NBu}_4]_2[(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-PPh}_2)(\mu\text{-PPh}_2)_2\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\mu\text{-Cl})_2\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\mu\text{-PPh}_2)(\mu\text{-PPh}_2)_2\text{Pt}(\text{C}_6\text{F}_5)_2] \cdot 2\text{acetone} \cdot 1.5n\text{-hexane}$ (**4a**·acetone·1.5*n*-hexane).



Scheme 4 Reactivity of **4** with Tl(acac) or PPh₃.

and P⁴ involved in a four-membered ring at $\delta -150.8$ and $\delta -142.9$, respectively. As expected, on the basis of the different *trans* influence between acetylacetonato and dppm, the direct P^{3/4}-Pt³ coupling constants of **5** ($^1J_{P(3),Pt(3)} = 2636$ Hz, $^1J_{P(4),Pt(3)} = 2832$ Hz) are higher than **2** ($^1J_{P(3),Pt(3)} \approx 1680$ Hz, $^1J_{P(4),Pt(3)} = 1928$ Hz).

X-ray structure of 5. The solid state structure of **5** (Figure 8, relevant bond distances and angles in Tables 1 and 2) confirms that it is a trinuclear unsymmetrical complex resulting from the elimination of the chloro bridging system in **4a-b** and the replacement of these ligands by acac. The “(C₆F₅)₂Pt(μ-PPh₂)(μ-PPh₂O)Pt(μ-PPh₂)₂Pt” fragment is very similar to the analogous fragments found in the complexes described so far. The Pt atoms are located in square-planar environments and no Pt...Pt interactions are detected. The coordination planes of the Pt centres are not coplanar. The acac ligand is planar and almost coplanar with the Pt(3) coordination plane (dihedral angle 12.59(14)°).

In polynuclear complexes with a double halide bridging system, the “Pt(μ-Cl)₂Pt” moiety can also be split by treating the complex with neutral ligands. Thus, reacting acetone solutions of **4a-b** with PPh₃ (1:1 molar ratio) yielded a white solid identified, by multinuclear NMR analyses, as a mixture of isomers of formula [NBu₄][(C₆F₅)₂Pt(μ-PPh₂)(μ-PPh₂O)Pt(μ-PPh₂)₂Pt(Cl)(PPh₃)] (**6**), with the chloro ligand located *syn* (**6a**) or *anti* (**6b**) to the PPh₂O⁻ group (Scheme 4). The ³¹P NMR spectrum of **6a-b** shows ten signals, five for each isomer, which, despite the high number of peaks due to different ¹⁹⁵Pt isotopomers present in solution, were easily assigned to **6a** or **6b** by combining ³¹P{¹H} COSY and ¹H-³¹P HMQC data. Figure 9 shows the ¹H-³¹P HMQC spectrum of **6a-b** in CD₂Cl₂. The phosphinito ($\delta 122.6$ for **6a** and $\delta 127.3$ for **6b**) and

phosphanido ³¹P resonances ($\delta 15.2$, P²; $\delta -151.5$, P⁴; $\delta -158.9$, P³ for **6a** and $\delta 11.3$, P²; $\delta -153.0$, P⁴; $\delta -141.2$, P³ for **6b**) gave signals at chemical shifts comparable to those of the other complexes described in this paper. The coordinated triphenylphosphanes gave doublets of doublets at $\delta 25.9$ for **6a** and at $\delta 23.7$ for **6b**.

Monitoring the reaction between the hexanuclear complexes **4a-b** with 1 equiv PPh₃ in CD₂Cl₂ at 298 K by ³¹P NMR, we observed the immediate transformation of the reagents into a mixture consisting of **6a/6b** in a molar ratio of 25/75. On standing in solution the **6a/6b** molar ratio increased progressively, becoming 45/55 after 24 h. This suggests that a dissociative process occurs in solution, transforming the kinetic mixture into a thermodynamic one. The same reaction carried in acetone at 298 K yielded, after 24 h, a mixture consisting of **6a/6b** in a molar ratio of 60/40. Crystallisation of this mixture from dichloromethane/*n*-hexane afforded crystals of **6a** suitable for diffractometric analysis.

X-ray structure of 6a. The structure of the anion of the isomer **6a** is shown in Figure 10. Relevant bond distances and angles are collected in Tables 1 and 2. The structure confirms that **6a** is an unsymmetrical trinuclear complex resulting from the cleavage of the chloro bridging system in **4a-b**. In fact the anion complex consists of the aforementioned fragment “(C₆F₅)₂Pt(1)(μ-OPPh₂)(μ-PPh₂)Pt(2)(μ-PPh₂)₂Pt(3)” with Pt(3) completing its coordination environment with one chloro

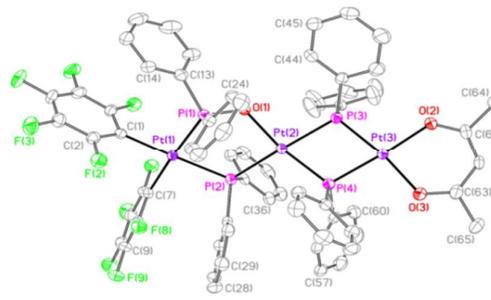


Fig. 8 Molecular structure of the anion of complex [NBu₄][(C₆F₅)₂Pt(μ-PPh₂)(μ-PPh₂O)Pt(μ-PPh₂)₂Pt(acac)]·acetone (**5-acetone**).

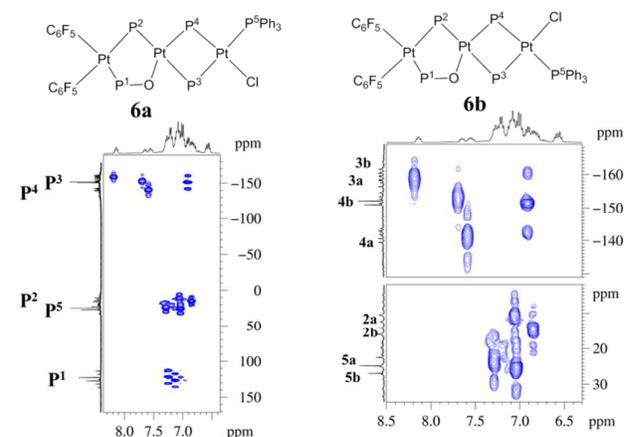


Fig. 9 ¹H-³¹P HMQC spectrum of **6a-b** (CD₂Cl₂, 298 K).

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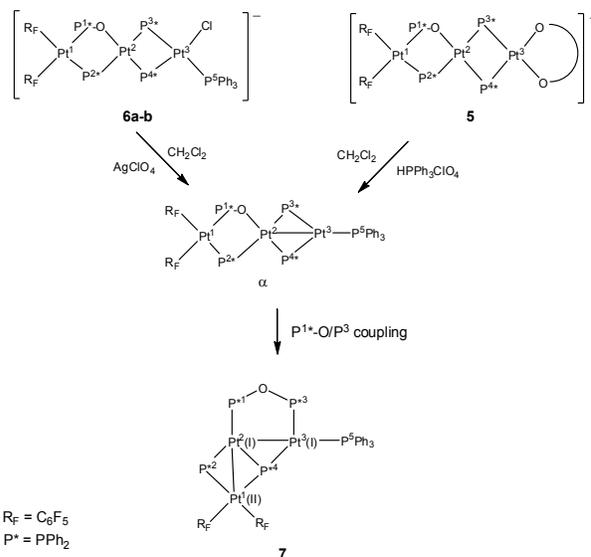
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ligand and one molecule of triphenylphosphine, the PPh₃ ligand being located *anti* to the PPh₂O group. Other relevant data of the skeleton of **6a** (48 VEC) are given in Table 2.

Synthesis of complex 7. Since complexes **6a** and **6b** do not display Pt–Pt bonds (16n valence electron skeleton, 48 e[−]), it would be expected that the elimination of one of the ligands coordinated to Pt(3) would produce a species consisting of a symmetric complex (only one isomer) with a Pt(2)–Pt(3) bond (46 VEC), as observed in other polynuclear phosphanido complexes.^{21, 39,555}

Hence, the addition of AgClO₄ to **6a+6b** (1:1 molar ratio, in the dark) in CH₂Cl₂ resulted in the precipitation of AgCl and the formation of a compound of stoichiometry [(C₆F₅)₂Pt₃(PPh₂)₃(PPh₂O)(PPh₃)] which was isolated from the solution. The same compound was obtained when **5** was treated with [PPh₃H][ClO₄] (1:1 molar ratio) in a non-coordinating solvent (CH₂Cl₂). In the latter experiment it was observed that the pale-yellow colour of the initial solution turned red instantaneously and, after a few minutes, the colour of the solution turned orange. Complex **7** was isolated from the resulting reaction mixture. Surprisingly, complex **7** is not the mere result of eliminating a chloro ligand, although this could well be an intermediate, but rather it results from the reductive coupling between one PPh₂ and one PPh₂O ligand, with formation of a diphosphoxane-bridged ligand, (Scheme 5) and the Pt(II),Pt(I),Pt(I) trinuclear derivative [(C₆F₅)₂Pt¹(μ-PPh₂)₂Pt²(μ-PPh₂OPPh₂)Pt³(PPh₃)] (**7**), as established by XRD and NMR data.

X-ray structure of complex 7. The structure of complex **7** together with the atom-labelling scheme is shown in Figure 11. Relevant bond distances and angles are given in Table 3. The compound is trinuclear, the three platinum atoms being ordered in a triangular array with only two Pt–Pt bonds⁵⁵⁵⁵ and bridged by two diphenylphosphanido and one diphosphoxane ligands which display peculiar structural features. In addition, one triphenylphosphine and two pentafluorophenyl groups are bonded to the metal centres Pt(3) and Pt(1), respectively as terminal ligands. In order to facilitate the understanding of the structural features of complex **7**, this can be considered to form as consequence of the interaction of two fragments **C** and **D** (Scheme 6).



Scheme 5 Syntheses of cluster **7**.

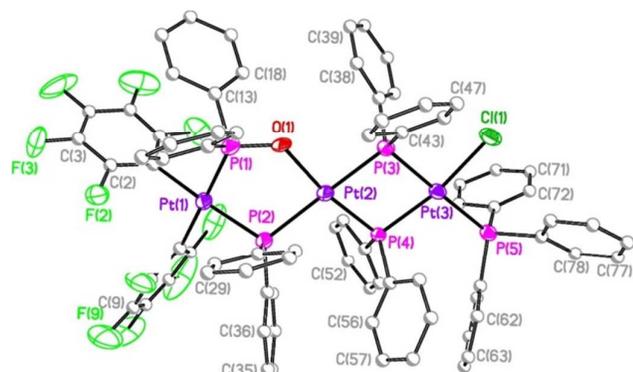


Fig. 10 Molecular structure of the anion of complex [NBu₄][(C₆F₅)₂Pt(μ-PPh₂)(μ-PPh₂O)Pt(μ-PPh₂)₂Pt(Cl)(PPh₃)]·CH₂Cl₂·H₂O (**6a**·CH₂Cl₂·0.5H₂O).

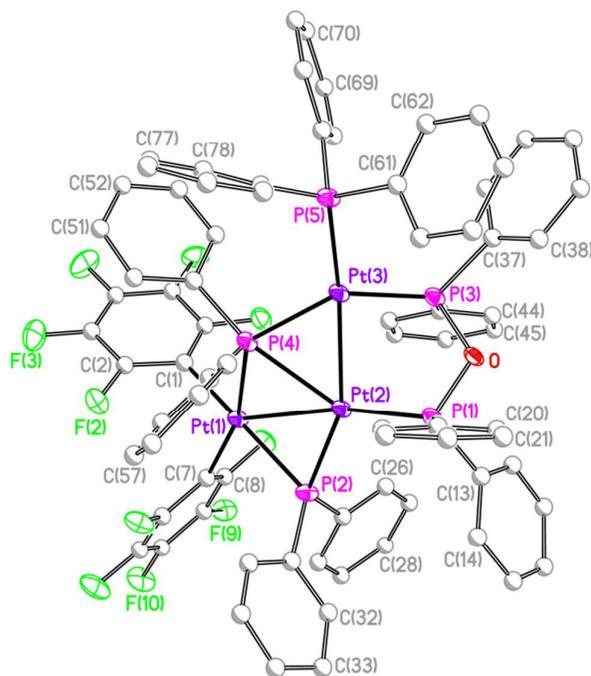
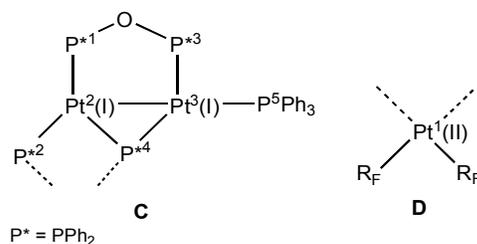


Fig. 11 Molecular structure of the complex [(C₆F₅)₂Pt¹(μ-PPh₂)₂Pt²(μ-PPh₂OPPh₂)Pt³(PPh₃)]·2CH₂Cl₂ (**7**·2CH₂Cl₂).

Fragment **C** is a Pt(I)–Pt(I) fragment formed due to the reductive P–O/P coupling, with a Pt–Pt bond, as is usual in Pt centres with formal oxidation state +1 [Pt(2)–Pt(3) = 2.62204(6) Å] and with bridging P(3)–O–P(4) and P(2)Ph₂ ligands and one terminal P(5)Ph₃. The P(1)Ph₂ ligand displays an unusual structural situation since it is bonded to both Pt(2), completing fragment **C**, and Pt(1) of fragment **D**.



Scheme 6 Fragments constituting cluster 7.

Pd and Pt(II) complexes with structures similar to fragment **C** are well-known.^{31, 40-44}

Furthermore, fragment **D** is formed by the Pt(II)-based synthon "Pt(1)(C₆F₅)₂", which is bonded to the P(2)Ph₂ bridging ligand. This bridging ligand links fragment **C** and **D** through the P(2)-Pt(2) bond but fragment **D** still displays a coordination vacancy that is filled through the donor-acceptor interaction of the P(2)-Pt(2) bond with Pt(1) (a three-centre two-electron bond). This type of bond causes the formation of a metal-metal bond between Pt(1) and Pt(2) [Pt(1)-Pt(2) = 2.7509(3)Å] and causes P(4)Ph₂ to act as a (μ₃-P) ligand bonded to the three Pt centres [Pt(3)-P(4) = 2.319(3), Pt(2)-P(4) = 2.586(3) and Pt(1)-P(4) = 2.455(3)Å].

The μ₃-P coordination of the formally anionic P(2) phosphanido ligand is rather unusual, but has been found previously in other compounds prepared by us, [Pt₂Pd₂(μ-PPh₂)₃(C₆F₅)₃(PPh₂C₆F₅)(CO)],²⁵ [NBu₄][Pt₃(μ-PPh₂)₂(C₆F₅)₅],²⁶ [Pt₄(μ-PPh₂)₄(C₆F₅)₄],²² [NBu₄][Pt₄(μ-PPh₂)₄(C₆F₅)₅]²³ and [Pt₂Pd₂(μ-PPh₂)₃(C₆F₅)₃(PPh₂C₆F₅)].²⁴ Other complexes in which the phosphorus atom of a phosphanido ligand is five coordinated are also known.⁴⁵⁻⁴⁸

Although CCDC reports examples of complexes with the diphosphoxane PPh₂OPPh₂ ligand acting as a bridging⁴⁹⁻⁵³ or chelate ligand,⁵⁴⁻⁵⁸ cluster **7** is the first-reported example of a platinum derivative with this ligand. It is also noteworthy that this ligand is formed via intramolecular reductive PPh₂O/PPh₂ coupling.

Finally it is notable that **7**, which actually is produced from [(R_F)₂Pt^{II}(μ-PPh₂)₂Pt^{II}(μ-PPh₂)₂Pt^{II}(NCCH₃)₂] (**A**), requires two independent reductive coupling processes PPh₂/OH⁻ and PPh₂O⁻/PPh₂⁻, the first one induced by the presence of the nucleophile in the oxidation of **A**, and the second by elimination of a ligand (one pair of electrons) of the skeleton. Multinuclear 1D and 2D NMR analyses of **7** in CD₂Cl₂ indicate that the structure of the cluster in the solid state is preserved in solution. The ³¹P{¹H} NMR spectrum of **7** (Figure 12) shows five multiplets, four of which in the region from 145 to 98 ppm and one centred at δ 24.8. The latter signal is a ddd and is attributed to the coordinated PPh₃, P⁵. The multiplicity of this signal is due to homocouplings with the phosphanido P² nucleus (²J_{P(5),P(2)}} = 70 Hz) and with the phosphinito P¹ and P³ nuclei (²J_{P(5),P(1)}} = 26 Hz, ²J_{P(5),P(3)}} = 5 Hz). The mutually coupled phosphinito P¹ and P³ atoms (²J_{P(1),P(3)}} 14 Hz) gave signals

Table 3. - Selected Bond Distances (Å) and Angles (°) for [(C₆F₅)₂Pt(μ-PPh₂)₂Pt(μ-PPh₂OPPh₂)Pt(PPh₃)] (**7**·2CH₂Cl₂).

| Distances | | |
|---------------------------------|------------------------------|-----------------------|
| Pt(1)-C(7) = 2.067(12) | Pt(2)-P(1) = 2.186(3) | Pt(3)-P(3) = 2.251(3) |
| Pt(1)-C(1) = 2.072(12) | Pt(2)-P(2) = 2.224(3) | Pt(3)-P(5) = 2.299(3) |
| Pt(1)-P(2) = 2.329(3) | Pt(2)-P(4) = 2.586(3) | Pt(3)-P(4) = 2.319(3) |
| Pt(1)-P(4) = 2.455(3) | Pt(2)-Pt(3) = 2.6204(6) | P(1)-O = 1.644(8) |
| Pt(1)-Pt(2) = 2.7509(6) | | P(3)-O = 1.656(8) |
| Angles | | |
| C(7)-Pt(1)-C(1) = 83.2(4) | P(2)-Pt(2)-P(4) = 104.74(11) | |
| C(7)-Pt(1)-P(2) = 85.6(3) | P(1)-Pt(2)-Pt(3) = 89.21(8) | |
| C(1)-Pt(1)-P(2) = 163.7(3) | P(2)-Pt(2)-Pt(3) = 156.46(8) | |
| C(7)-Pt(1)-P(4) = 164.1(4) | P(4)-Pt(2)-Pt(3) = 52.90(6) | |
| C(1)-Pt(1)-P(4) = 87.7(3) | P(1)-Pt(2)-Pt(1) = 168.44(9) | |
| P(2)-Pt(1)-P(4) = 105.75(10) | P(2)-Pt(2)-Pt(1) = 54.60(8) | |
| C(7)-Pt(1)-Pt(2) = 135.0(3) | P(4)-Pt(2)-Pt(1) = 54.68(6) | |
| C(1)-Pt(1)-Pt(2) = 135.6(3) | P(3)-Pt(3)-P(5) = 106.28(11) | |
| P(2)-Pt(1)-Pt(2) = 51.11(7) | P(3)-Pt(3)-P(4) = 140.65(11) | |
| P(4)-Pt(1)-Pt(2) = 59.23(7) | P(5)-Pt(3)-P(4) = 111.99(11) | |
| Pt(2)-P(2)-Pt(1) = 74.30(9) | P(3)-Pt(3)-Pt(2) = 82.34(8) | |
| P(1)-Pt(2)-P(2) = 114.31(12) | P(5)-Pt(3)-Pt(2) = 164.54(8) | |
| P(1)-Pt(2)-P(4) = 136.65(11) | P(4)-Pt(3)-Pt(2) = 62.78(8) | |
| Pt(3)-P(4)-Pt(1) = 121.90(13) | Pt(3)-P(4)-Pt(2) = 64.31(8) | |
| Pt(3)-Pt(2)-Pt(1) = 101.982(19) | Pt(1)-P(4)-Pt(2) = 66.08(8) | |
| O-P(1)-Pt(2) = 112.3(3) | O-P(3)-Pt(3) = 112.6(3) | |

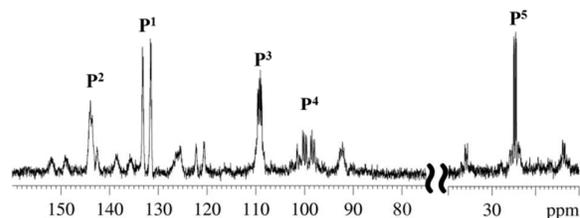
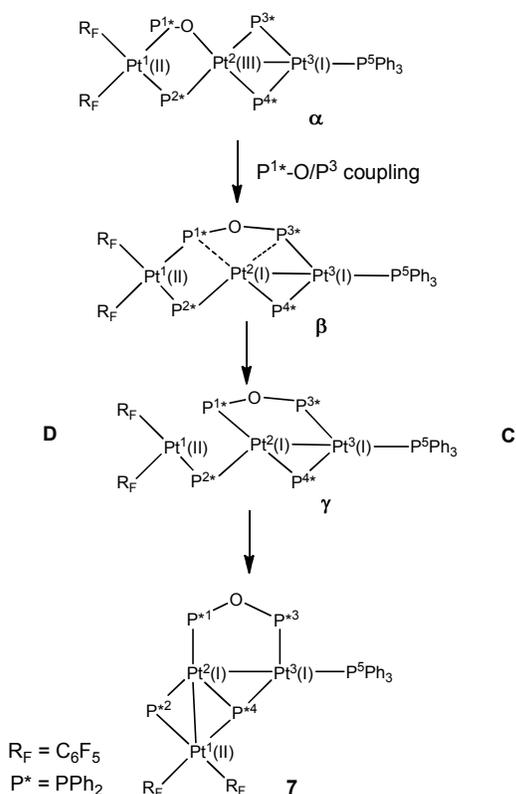


Fig. 12 ³¹P{¹H} NMR spectrum of **7** (CD₂Cl₂, 288 K).

centred at δ 132.3 and δ 109.1, respectively, and showed measurable scalar couplings with all the ³¹P nuclei of the molecule. The bridging phosphanido atoms P² and P⁴ subtending Pt-Pt bonds gave the expected deshielded signals at δ 143.8 and δ 99.1, respectively. The difference in the chemical shifts of these signals presumably reflects the different coordination mode of the P atoms: μ₃ bridging for P⁴ and μ₂ bridging for P². ¹⁹⁵Pt resonances were found at δ -5235 (Pt¹), -5032 (Pt²), and -5183 (Pt³).

The mechanism outlined in Scheme 7 can be proposed to explain the formation of **7**. Both the reaction of the trinuclear compound **6a** with Ag⁺, which results in the precipitation of AgCl, or the reaction of **5** with [PPh₃H]⁺ could generate the species [(C₆F₅)₂Pt^I(μ-PPh₂)(μ-PPh₂O)Pt^{II}(μ-PPh₂)₂Pt^{III}(PPh₃)]/(Pt²-Pt³) (**α**) prone to undergo the P-O/P reductive coupling affording **β**. Intermediate **β** could evolve to **γ** by rupture of the P¹-Pt¹ bond and formation of the P¹-Pt² bond. Finally, coordination of P⁴ to Pt¹ and formation of the Pt¹-Pt² bond yields cluster **7**.



Scheme 7 Proposed mechanism for the synthesis of 7.

The complex $[(C_6F_5)_2Pt(\mu-PPh_2)_2Pt(\mu-PPh_2)_2Pt(PPh_3)]$, analogous to α but with a PPh_2 instead of $P(O)Ph_2$, is formed by reaction of $[NBu_4][[(C_6F_5)_2Pt(\mu-PPh_2)_2Pt(\mu-PPh_2)_2Pt(Cl)(PPh_3)]]$ with Ag^+ or by reaction of $[NBu_4][[(C_6F_5)_2Pt(\mu-PPh_2)_2Pt(\mu-PPh_2)_2Pt(acac)]]$ with H^+/PPh_3 .^{21, 39} However, in the present study the intermediate α was neither isolated, nor detected by NMR monitoring, indicating that such an intermediate is very reactive. A similar situation has been observed in the formation of the heterotrinnuclear Pt/Pd complexes: $[(R_F)_2Pt(\mu-PPh_2)Pd(\mu-PPh_2)(\mu-Ph_2P-PPh_2)Pt(R_F)_2]$,¹⁹ $[(PPh_3)(C_6F_5)_2Pt(\mu-PPh_2)Pd(\mu-PPh_2)(\mu-Ph_2P-PPh_2)Pt(C_6F_5)_2]$ and $[(PEtPh_2)(C_6F_5)_2Pt(\mu-PPh_2)Pd(\mu-PPh_2)(\mu-Ph_2P-PPh_2)Pt(C_6F_5)_2]$,²⁰ which are produced through a PPh_2^-/PPh_2^- reductive coupling but the postulated Pt(III)/Pd(III)/Pt(II) intermediates could not be detected. Furthermore, the structure of intermediate β resembles that of complex $[NBu_4][[(R_F)_2Pt(\mu^3-Ph_2PNPPh_2)(\mu-PPh_2)Pt(\mu-PPh_2)Pt(R_F)_2]]$,¹² which is also formed through a reductive coupling process.

Finally, the outcome of this reaction contrasts with the similar process carried out with $[NBu_4][[(C_6F_5)_2Pt(\mu-PPh_2)_2Pt(\mu-PPh_2)_2Pt(Cl)(PPh_3)]]$ in which the elimination of Cl^- produces $[(C_6F_5)_2Pt(\mu-PPh_2)_2Pt(\mu-PPh_2)_2Pt(PPh_3)]$ similar to the intermediate reported in Scheme 5 and no reductive PPh_2/PPh_2 coupling is observed.

Conclusions

A mixture of the solvento species $[(R_F)_2Pt^{II}(\mu-OPPh_2)(\mu-PPh_2)Pt^{II}(\mu-PPh_2)_2Pt^{II}(solv)(solv')]$ ($solv, solv' = H_2O, acetone, acetonitrile$) **1-(solv)(solv')** is obtained by oxidation of the trinuclear Pt(II) complex $[(R_F)_2Pt^{II}(\mu-PPh_2)_2Pt^{II}(\mu-PPh_2)_2Pt^{II}(NCCH_3)_2]$ with $AgClO_4$ in acetonitrile/wet acetone to the corresponding Pt(III), Pt(III), Pt(II) derivative, followed by a reductive Ph_2P/OH^- coupling. The lability of the Pt–solv bonds allows the displacement of $solv, solv'$ and the formation of pure complexes. For instance, in benzonitrile the mixture **1-(solv)(solv')** is quantitatively transformed into $[(R_F)_2Pt(\mu-PPh_2PO)(\mu-PPh_2)Pt(\mu-PPh_2)_2Pt(PhCN)_2]$ **[1-(PhCN)]₂**. The treatment of **1-(solv)(solv')** with the suitable ligand (dppm or Cl^-) permitted the isolation of $[(R_F)_2Pt^{II}(\mu-OPPh_2)(\mu-PPh_2)Pt^{II}(\mu-PPh_2)_2Pt^{II}(dppm)]$ (**2**) and $[NBu_4]_2[(C_6F_5)_2Pt(\mu-PPh_2)(\mu-PPh_2O)Pt(\mu-PPh_2)_2Pt(\mu-Cl)_2Pt(\mu-PPh_2)_2Pt(\mu-PPh_2)(\mu-PPh_2O)Pt(C_6F_5)_2]$ (**4**), the latter being in fact a mixture of the two possible isomers **4a** (P–O ligands in *transoid* position) and **4b** (P–O ligands in *cisoid* position), as demonstrated by NMR experiments.

The reaction of $[(R_F)_2Pt^{II}(\mu-OPPh_2)(\mu-PPh_2)Pt^{II}(\mu-PPh_2)_2Pt^{II}(dppm)]$ with $AgClO_4$ produces $[(R_F)_2Pt^{II}(\mu-OPPh_2)(\mu-PPh_2)Pt^{II}(\mu-PPh_2)_2Pt^{II}(dppm)Ag(ClO_4)]$ (**3**), a complex in which the starting “(Pt₃dppm)” complex **2** acts as a bidentate Pt donor ligand towards the silver centre forming two Pt–Ag donor-acceptor bonds. Complex **3** is dynamic in solution (¹⁹F NMR and ¹H–³¹P HMQC spectra) with the $Ag(ClO_4)$ moiety passing from one face to the other of the complex. It is also remarkable that no evidence, either in solid state or in solution, of any other behaviour of Ag^+ towards complex **2** (oxidation of some of the Pt centres or insertion reactions into Pt–O or Pt–P bonds that are also well-documented in phosphanido platinum complexes) was obtained.

Additionally, the “Pt($\mu-Cl$)₂Pt” bridging system in the mixture of **4a+4b** is easily eliminated by reaction with $Tl(acac)$ or split by treatment with one equivalent of PPh_3 . In this case, a mixture of the two trinuclear isomers $[NBu_4][[(C_6F_5)_2Pt(\mu-PPh_2)(\mu-PPh_2O)Pt(\mu-PPh_2)_2Pt(Cl)(PPh_3)]]$ (**6a+6b**) with the chloro ligand located *syn* (**6a**) or *anti* (**6b**) to the PPh_2O^- group are obtained.

The XRD studies of **1, 2, 3, 4a, 5, 6a** show that no important differences are observed in the structures of the trinuclear fragment “ $(C_6F_5)_2Pt(\mu-PPh_2)(\mu-PPh_2O)Pt(\mu-PPh_2)_2Pt$ ”, which forms part of all of them.

Finally, the experiments designed for the atom, to eliminate one of the ligands coordinated to it, which were expected to give rise to the formation of a Pt^2-Pt^3 bond (46 VEC), resulted in an unprecedented PPh_2O^-/PPh_2^- reductive coupling with formation of the very unusual trinuclear Pt(II), Pt(I), Pt(I) complex $[(C_6F_5)_2Pt^I(\mu-PPh_2)_2Pt^II(\mu-PPh_2OPPh_2)Pt^I(PPh_3)]$ (**7**), displaying two Pt–Pt bonds (44 VEC).

Experimental

General procedures and Materials

C, H, N analyses were performed with a Perkin–Elmer 2400 CHNS/O Series II microanalyzer. IR spectra were recorded on a Perkin–Elmer Spectrum 100 FT-IR spectrometer (ATR in the range 4000–200 cm^{-1}). Multinuclear NMR spectra were recorded with a Bruker Avance 400 spectrometer (400 MHz for ^1H) at 298 K; chemical shifts are reported in ppm referenced to SiMe_4 for ^1H , CFCl_3 for ^{19}F , 85% H_3PO_4 for ^{31}P and H_2PtCl_6 for ^{195}Pt . Literature methods were used to prepare the starting materials $[(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\text{NCCH}_3)_2]^{11}$ and $[\text{PPh}_3\text{H}][\text{ClO}_4]^{59}$.

Synthesis

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and they should be handled with great caution.

Synthesis of $[(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-PPh}_2)(\mu\text{-PPh}_2\text{O})\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\text{solv})(\text{solv}')] [1\text{-}(\text{solv})(\text{solv}')]$. To a yellow solution of $[(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\text{NCCH}_3)_2]$ (**A**) (0.250 g, 0.15 mmol) in acetone (10 mL) and acetonitrile (5 mL), AgClO_4 (0.060 g, 0.30 mmol) was added. The mixture was stirred in the dark at room temperature for 4 h following which it was filtered through celite and the resulting orange solution evaporated to dryness. Yield: 0.204 g of **1-(solv)(solv')**. The obtained powder was shown to be a mixture of solvent species containing H_2O , acetone or acetonitrile bonded to Pt^3 . By dissolving **1-(solv)(solv')** in benzonitrile the mixture was quantitatively converted into the bis-benzonitrile species of formula $[(\text{R}_f)_2\text{Pt}(\mu\text{-Ph}_2\text{PO})(\mu\text{-PPh}_2)\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\text{PhCN})_2]$ [**1-(PhCN)**]₂ which was characterised in solution by NMR (in benzonitrile) and ESI-MS (in CH_3OH).

HRMS(+), exact mass for the cation $[\text{C}_{67}\text{H}_{45}\text{F}_{10}\text{NNAOP}_4\text{Pt}_3]^+$: 1801.1213. Measured m/z : 1801.1046, $[\text{M}-\text{PhCN}+\text{Na}]^+$. ^1H NMR (PhCN, 298 K, 400 MHz): δ 7.94 (m, *o*-Ph bonded to P^3), 7.63–7.04 (m, *Ph*). ^{19}F NMR (PhCN, 298 K, 376.5 MHz): δ –114.4 (broad, 2 *o*-F, $^3J_{\text{F,Pt}} = 283$ Hz), –114.8 (broad, 2 *o*-F, $^3J_{\text{F,Pt}} = 329$ Hz), –164.8 (m, 2 *m*-F), –165.3 (m, overlapped 2 *m*-F + 1 *p*-F), –166.0 (t, $^3J_{\text{F,F}} = 19$ Hz, 1 *p*-F). $^{31}\text{P}\{^1\text{H}\}$ NMR (PhCN, 298 K, 161 MHz): δ 130.2 (broad s, P^1 , $^1J_{\text{P}(1),\text{Pt}(1)} = 2914$ Hz), 13.6 (broad d, P^2 , $^2J_{\text{P}(2),\text{P}(3)} = 325$ Hz, $^1J_{\text{P}(2),\text{Pt}(1)} = 1809$ Hz, $^1J_{\text{P}(2),\text{Pt}(2)} = 1906$ Hz) – 141.3 (d, P^4 , $^2J_{\text{P}(4),\text{P}(3)} = 166$ Hz, $^1J_{\text{P}(4),\text{Pt}(2)} = 3270$ Hz, $^1J_{\text{P}(4),\text{Pt}(3)} = 2576$ Hz), –150.0 (dd, P^3 , $^2J_{\text{P}(3),\text{P}(2)} = 325$ Hz, $^2J_{\text{P}(3),\text{P}(4)} = 166$ Hz, $^1J_{\text{P}(3),\text{Pt}(2)} = 1766$ Hz, $^1J_{\text{P}(3),\text{Pt}(3)} = 2374$ Hz). ^{195}Pt NMR (PhCN, 298 K, 86 MHz): δ –3792 (Pt^2), –3875 (Pt^3), –4500 (Pt^1).

Synthesis of $[(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-PPh}_2)(\mu\text{-PPh}_2\text{O})\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\text{dppm})]$ (2**).** To a yellow solution of $[(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\text{NCCH}_3)_2]$ (**A**) (0.250 g, 0.15 mmol) in acetone (10 mL) and acetonitrile (5 mL), AgClO_4 (0.060 g, 0.30 mmol) was added. The mixture was stirred in the dark at room temperature for 4 h and then was filtered through celite and the resulting solution was evaporated to ca. 1 mL, *i*-PrOH (5 mL) was added. The resulting white solid was dissolved in 20 mL of acetone and bis(diphenylphosphanyl)methane (dppm) (0.059 g, 0.15 mmol) was added. The mixture was stirred at

room temperature for 1 h. The resulting yellow solution was evaporated to ca. 1 mL and Et_2O (2 mL) was added. Complex **2** crystallised as a yellow solid, which was filtered, washed with Et_2O (2 \times 2 mL) and vacuum-dried. Yield: 0.233, 81 %. Anal. Found (Calcd for $\text{C}_{85}\text{H}_{62}\text{F}_{10}\text{OP}_6\text{Pt}_3$): C, 49.52 (49.55); H, 2.98 (3.03). IR (cm^{-1}): 951 (s), 781 (m, d), $\text{C}_6\text{F}_5^{60}$ 689 (s), 496 (s) (dppm), ν (PPh₂-O) should appear in the 1025(m)–998(m) region^{61–63} however, internal absorptions of the C_6F_5 groups preclude unambiguous assignment of this absorption.

HRMS(+), exact mass for the cation $[\text{C}_{85}\text{H}_{63}\text{F}_{10}\text{OP}_6\text{Pt}_3]^+$: 2060.2185. Measured m/z : 2060.1873, $[\text{M}+\text{H}]^+$. ^1H NMR (CD_2Cl_2 , 298 K, 400 MHz): δ 7.60–6.53 (m, *Ph*, 60 H), 4.48 (dt, $^2J_{\text{H-H}} = 66$ Hz, $^2J_{\text{H-P}} = 10$ Hz, CH dppm, 1 H), 4.44 (broad dt, $^2J_{\text{H-H}} = 66$ Hz, $^2J_{\text{H-P}} = 10$ Hz, CH dppm, 1 H). ^{19}F NMR (acetone-*d*₆, 298 K, 376.5 MHz): δ –115.1 (m, 4 overlapped *o*-F, $^3J_{\text{F,Pt}} \approx 320$ Hz), –167.0 (m, 2 *m*-F), –167.5 (m, 2 *m*-F), –167.7 (t, $^3J_{\text{F,F}} = 20$ Hz, 1 *p*-F), –168.3 (t, $^3J_{\text{F,F}} = 19$ Hz, 1 *p*-F). $^{31}\text{P}\{^1\text{H}\}$ NMR ($\text{C}_2\text{H}_4\text{Cl}_2$, 298 K, 161 MHz): δ 127.9 (s, P^1 , $^1J_{\text{P}(1),\text{Pt}(1)} = 2925$ Hz), 13.8 (broad d, P^2 , $^2J_{\text{P}(2),\text{P}(3)} = 307$ Hz, $^1J_{\text{P}(2),\text{Pt}(1)} = 1868$ Hz, $^1J_{\text{P}(2),\text{Pt}(2)} = 1890$ Hz), –28.3 (dd, P^5 , $^2J_{\text{P}(5),\text{P}(4)} = 323$ Hz, $^2J_{\text{P}(5),\text{P}(6)} = 23$ Hz, $^1J_{\text{P}(5),\text{Pt}(3)} = 1740$ Hz), –30.5 (m, P^6 , $^2J_{\text{P}(6),\text{P}(3)} = 284$ Hz, $^2J_{\text{P}(6),\text{P}(5)} = ^2J_{\text{P}(6),\text{P}(2)} = 23$ Hz, $^1J_{\text{P}(5),\text{Pt}(3)} = 1550$ Hz), –134.2 (dd, P^4 , $^2J_{\text{P}(4),\text{P}(5)} = 323$ Hz, $^2J_{\text{P}(4),\text{P}(3)} = 161$ Hz, $^1J_{\text{P}(4),\text{Pt}(2)} = 3070$ Hz, $^1J_{\text{P}(4),\text{Pt}(3)} = 1928$ Hz), –142.4 (m, P^3 , $^2J_{\text{P}(3),\text{P}(6)} = 343$ Hz, $^2J_{\text{P}(3),\text{P}(2)} = 307$ Hz, $^2J_{\text{P}(3),\text{P}(4)} = 161$ Hz, $^1J_{\text{P}(3),\text{Pt}(2)} \approx ^1J_{\text{P}(3),\text{Pt}(3)} \approx 1680$ Hz). ^{195}Pt NMR ($\text{C}_2\text{H}_4\text{Cl}_2$, 298 K, 86 MHz): δ –3584 (Pt^2), –4027 (Pt^3), –4461 (Pt^1).

Synthesis of $[(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-PPh}_2)(\mu\text{-PPh}_2\text{O})\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\text{dppm})\text{Ag}(\text{ClO}_4)]$ (**3**)

To a yellow solution of $[(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-PPh}_2)(\mu\text{-PPh}_2\text{O})\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\text{dppm})]$ (**2**) (0.050 g, 0.02 mmol) in CH_2Cl_2 (5 mL), AgClO_4 (0.005 g, 0.02 mmol) was added. The mixture was stirred at 253 K in the dark for 6 h. The resulting orange solution was evaporated to dryness and the residue was washed with cold toluene. Complex **3** was obtained as a yellow solid, which was filtered, washed with cold toluene (2 \times 2 mL) and vacuum-dried. Yield: 0.033, 61 %. Anal. Found (Calcd for $\text{C}_{85}\text{H}_{62}\text{AgClF}_{10}\text{O}_5\text{P}_6\text{Pt}_3$): C, 45.00 (45.02); H, 2.72 (2.76). IR (cm^{-1}): 951 (s) 784 (s) (C_6F_5), 689 (f), 500 (f) (dppm), 1092 (f), 620 (f) ClO_4 . HRMS(+), exact mass for the cation $[\text{C}_{85}\text{H}_{62}\text{AgF}_{10}\text{OP}_6\text{Pt}_3]^+$: 2168.1070. Measured m/z : 2168.1084, $[\text{M}-\text{ClO}_4]^+$. ^1H NMR (CD_2Cl_2 , 258 K, 400 MHz): δ 7.89–5.74 (m, *Ph*, 60 H), 4.46 (m, CH_2 dppm, 2 H). ^{19}F NMR (CD_2Cl_2 , 258 K, 376.5 MHz): δ –116.2 (m, 2 *o*-F, $^3J_{\text{F,Pt}} = 320$ Hz), δ –116.6 (m, 2 *o*-F, $^3J_{\text{F,Pt}} = 352$ Hz), –165.7 (m, 2 *m*-F), –166.0 (t, $^3J_{\text{F,F}} = 20$ Hz, 1 *p*-F), –166.3 (m, 2 *m*-F), –166.8 (t, $^3J_{\text{F,F}} = 19$ Hz, 1 *p*-F). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 253 K, 161 MHz): δ 123.5 (s, P^1 , $^1J_{\text{P}(1),\text{Pt}(1)} = 2435$ Hz), 15.1 (d, P^2 , $^2J_{\text{P}(2),\text{P}(3)} = 287$ Hz, $^1J_{\text{P}(2),\text{Pt}(1)} = 1271$ Hz, $^1J_{\text{P}(2),\text{Pt}(2)} = 1376$ Hz), –27.5 (ddd, P^5 , $^2J_{\text{P}(5),\text{P}(4)} = 331$ Hz, $^2J_{\text{P}(5),\text{P}(6)} = 35$ Hz, $^2J_{\text{P}(5),\text{P}(3)} = 21$ Hz, $^1J_{\text{P}(5),\text{Pt}(3)} = 1663$ Hz), –28.9 (m, P^6 , $^2J_{\text{P}(6),\text{P}(3)} = 299$ Hz, $^2J_{\text{P}(6),\text{P}(5)} = 35$ Hz, $^1J_{\text{P}(6),\text{Pt}(3)} = 1784$ Hz), –132.3 (dd, P^4 , $^2J_{\text{P}(4),\text{P}(5)} = 331$ Hz, $^2J_{\text{P}(4),\text{P}(3)} = 161$ Hz, $^1J_{\text{P}(4),\text{Pt}(2)} = 2784$ Hz, $^1J_{\text{P}(4),\text{Pt}(3)} = 1972$ Hz), –145.9 (ddd, P^3 , $^2J_{\text{P}(3),\text{P}(2)} = 287$ Hz, $^2J_{\text{P}(3),\text{P}(6)} = 299$ Hz, $^2J_{\text{P}(3),\text{P}(4)} = 161$ Hz, $^1J_{\text{P}(3),\text{Pt}(2)} \approx ^1J_{\text{P}(3),\text{Pt}(3)} \approx 1700$ Hz). ^{195}Pt NMR (CD_2Cl_2 , 253 K, 86 MHz): δ –3022 (Pt^2), –4058 (Pt^3), –3954 (Pt^1).

Synthesis of $[\text{NBu}_4]_2[(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-PPh}_2)(\mu\text{-PPh}_2\text{O})\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\mu\text{-Cl})_2\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\mu\text{-PPh}_2)(\mu\text{-PPh}_2\text{O})\text{Pt}(\text{C}_6\text{F}_5)_2]$ (**4a-b**).

To a yellow solution of $[(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\text{NCCH}_3)_2]$ (**A**) (0.250 g, 0.15 mmol) in acetone (10 mL) and acetonitrile (5 mL), AgClO_4 (0.060 g, 0.30 mmol) was added. The mixture was stirred in the dark at room temperature for 4 h and then was filtered through celite. The resulting solution was evaporated to ca. 1 mL and *i*-PrOH (5 mL) was added. The white solid obtained was dissolved in 40 mL of acetone and NBu_4Cl (0.042 g, 0.15 mmol) was added. The mixture was stirred at room temperature for 24 h. The solution was evaporated to ca. 1 mL and *i*-PrOH (5 mL) was added. A mixture of two isomers (**4a-b**) crystallised as a white solid, which was filtered, washed with *i*-PrOH (2 × 2 mL) and vacuum-dried. Yield: 0.189, 69 %. Anal. Found (Calcd for $\text{C}_{152}\text{H}_{152}\text{Cl}_2\text{F}_{20}\text{N}_2\text{O}_2\text{P}_8\text{Pt}_6$): C, 46.69 (46.71); H, 3.92 (3.92); N, 0.71 (0.72). IR (cm^{-1}): 950 (s), 779 (s) (C_6F_5), 880 (d) (NBu_4^+). HRMS(-), exact mass for the anion $[\text{C}_{60}\text{H}_{40}\text{ClF}_{10}\text{OP}_4\text{Pt}_3]^-$: 1711.0507. Measured m/z : 1711.0381, $[\text{M}/2]^-$. ^1H NMR (acetone- d_6 , 298 K, 400 MHz): δ 7.87 and 7.77 (**4a-b**, partially overlapped dd, *o*-Ph bonded to P^3 , $^3J_{\text{H,P}} = 11$ Hz, $^3J_{\text{H,H}} = 8$ Hz), 7.40-6.54 (m, *Ph*), 3.44 (m, CH_2N NBu_4^+), 1.83 (m, $\text{CH}_2\text{CH}_2\text{N}$, NBu_4^+), 1.43 (m, CH_3CH_2 , NBu_4^+ , $^3J_{\text{H,H}} = 7.3$ Hz), 0.97 (t, CH_3CH_2 , NBu_4^+ , $^3J_{\text{H,H}} = 7.3$ Hz). ^{19}F NMR (acetone- d_6 , 298 K, 376.5 MHz): δ -114.81 and -114.84 (**4a-b**, m, 2 overlapped *o*-F, $^2J_{\text{F,Pt}} \approx 272$ Hz), -115.07 (**4b**, m, 1 *o*-F, $^3J_{\text{F,F}} = 23$ Hz, $^3J_{\text{F,P}} = 11$ Hz, $^2J_{\text{F,Pt}} = 340$ Hz), -115.13 (**4a**, m, 1 *o*-F, $^3J_{\text{F,F}} = 23$ Hz, $^3J_{\text{F,P}} = 11$ Hz, $^2J_{\text{F,Pt}} = 348$ Hz), -167.1 (**4b**, m, 2 *m*-F), -167.5 (**4a**, m, 2 *m*-F), -168.1 (**4a-b**, t, $^3J_{\text{F,F}} = 19$ Hz, 1 *p*-F), -168.6 (t, $^3J_{\text{F,F}} = 19$ Hz, 1 *p*-F). $^{31}\text{P}\{^1\text{H}\}$ NMR (acetone- d_6 , 298 K, 161 MHz): δ 124.9 (**4a-b**, P^1 , $^3J_{\text{P(1),P(4)}} = 14$ Hz, $^1J_{\text{P(1),Pt(1)}} = 2928$ Hz), 13.0 (**4a-b**, P^2 , $^2J_{\text{P(2),P(3)}} = 321$ Hz, $^1J_{\text{P(2),Pt(2)}} = 1872$, $^1J_{\text{P(2),Pt(1)}} = 1766$ Hz), -138.5 and -138.7 (**4a-b**, overlapped d, P^4 , $^2J_{\text{P(4),P(3)}} = 178$ Hz, $^1J_{\text{P(4),Pt(3)}} = 2840$ Hz, $^1J_{\text{P(4),Pt(2)}} = 3200$ Hz), -147.9 and -148.2 (**4a-b**, overlapped ddd, P^3 , $^2J_{\text{P(3),P(2)}} = 321$ Hz, $^2J_{\text{P(3),P(4)}} = 178$ Hz, $^2J_{\text{P(3),P(1)}} = 14$ Hz, $^1J_{\text{P(3),Pt(2)}} = 1736$, $^1J_{\text{P(3),Pt(3)}} = 2729$ Hz). ^{195}Pt NMR (acetone- d_6 , 298 K, 86 MHz): δ -3495 (Pt^3), -3789 (Pt^2), -4515 (Pt^1).

Synthesis of $[\text{NBu}_4][(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-PPh}_2)(\mu\text{-PPh}_2\text{O})\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\text{acac})]$ (**5**)

To a colourless solution of **4a-b** (0.100 g, 0.02 mmol) in acetone (40 mL), $\text{Ti}(\text{acac})_3$ (0.015 g, 0.05 mmol) was added. The mixture was stirred at room temperature for 24 h and filtered through celite. The solution was evaporated to ca. 1 mL and *i*-PrOH (5 mL) was added. Complex **5** crystallised as a white solid, which was filtered, washed with *i*-PrOH (2 × 2 mL) and vacuum-dried. Yield: 0.05 g, 48% Anal. Found (Calcd for $\text{C}_{81}\text{H}_{83}\text{F}_{10}\text{NO}_3\text{P}_4\text{Pt}_3$): C, 48.22 (48.22); H, 4.15 (4.15); N, 0.69 (0.69). IR (cm^{-1}): 1500 (s) *acac*; 951 (s), 792 (s), 780 (sh) C_6F_5 ; 880 (d) (NBu_4^+). HRMS(-), exact mass for the anion $[\text{C}_{65}\text{H}_{47}\text{F}_{10}\text{O}_3\text{P}_4\text{Pt}_3]^-$: 1774.1262. Measured m/z : 1774.1307 $[\text{M}^-]$. ^1H NMR (acetone- d_6 , 298 K, 400 MHz): δ 8.06 (dd, $^2J_{\text{H-H}} = 7.9$ Hz, $^3J_{\text{H-P}} = 10.8$ Hz, *ortho*-Ph bonded to P^3 , 4 H) 7.46-7.36 (m, *ortho*-Ph bonded to P^1 + *ortho*-Ph bonded to P^4 , 8 H), 7.30-7.12 (m, *para*-Ph bonded to P^1 , *para*-Ph bonded to P^3 , *para*-Ph bonded to P^4 , *meta*-Ph bonded to P^3 , 10 H), 7.05 (m, *ortho*-Ph bonded to P^2 + *meta*-Ph bonded to P^1 + *meta*-Ph bonded to P^4 ,

12 H), 6.87 (t, *para*-Ph bonded to P^2 , $^2J_{\text{H-H}} = 7.3$ Hz, 2 H) 6.61 (td, *meta*-Ph bonded to P^2 , $^4J_{\text{H-P}} = 1.5$ Hz, $^2J_{\text{H-H}} = 7.8$ Hz, 4 H), 5.17 (s, 1 H, C-H, *acac*), 3.45 (m, CH_2N NBu_4^+), 1.83 (m, $\text{CH}_2\text{CH}_2\text{N}$, NBu_4^+), 1.74 (s, 3 H, C- CH_3 , *acac*), 1.51 (s, 3 H, C- CH_3 , *acac*), 1.43 (m, CH_3CH_2 , NBu_4^+ , $^3J_{\text{H,H}} = 7.4$ Hz), 0.98 (t, CH_3CH_2 , NBu_4^+ , $^3J_{\text{H,H}} = 7.4$ Hz). ^{19}F NMR (acetone- d_6 , 298 K, 376.5 MHz): δ from -114.6 to -115.0 (m, 4 overlapped *o*-F), -167.1 (ddd, $^2J_{\text{F,F}} = 23$ Hz, $^3J_{\text{F,F}} = 20$ Hz, $^4J_{\text{F,P}} = 8$ Hz, 2 *m*-F), -167.4 (ddd, $^3J_{\text{F,F}} = 22$ Hz, $^3J_{\text{F,F}} = 20$ Hz, $^4J_{\text{F,P}} = 11$ Hz, 2 *m*-F), -168.1 (t, $^3J_{\text{F,F}} = 20$ Hz, 1 *p*-F), -168.7 (t, $^2J_{\text{F,F}} = 20$ Hz, 1 *p*-F). $^{31}\text{P}\{^1\text{H}\}$ NMR (acetone- d_6 , 298 K, 161 MHz): δ 125.3 (m, P^1 , $^1J_{\text{P(1),Pt(1)}} = 2937$ Hz), 13.9 (d, P^2 , $^2J_{\text{P(2),P(3)}} = 320$ Hz, $^1J_{\text{P(2),Pt(1)}} = 1869$ Hz, $^1J_{\text{P(2),Pt(2)}} = 1750$ Hz), -142.9 (d, P^4 , $^2J_{\text{P(4),P(3)}} = 171$ Hz, $^1J_{\text{P(4),Pt(2)}} = 3189$ Hz, $^1J_{\text{P(4),Pt(3)}} = 2832$ Hz), -150.8 (ddd, P^3 , $^2J_{\text{P(3),P(2)}} = 320$ Hz, $^2J_{\text{P(3),P(4)}} = 171$ Hz, $^2J_{\text{P(3),Pt(1)}} = 16$ Hz, $^1J_{\text{P(3),Pt(2)}} = 1843$ Hz, $^1J_{\text{P(3),Pt(3)}} = 2636$ Hz). ^{195}Pt NMR (acetone- d_6 , 298 K, 86 MHz): δ -3310 (Pt^3), -3824 (Pt^2), -4509 (Pt^1).

Synthesis of $[\text{NBu}_4][(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-PPh}_2)(\mu\text{-PPh}_2\text{O})\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\text{Cl})(\text{PPh}_3)]$ (**6a-b**).

To a colourless solution of the mixture of isomers $[\text{NBu}_4]_2[(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-PPh}_2)(\mu\text{-PPh}_2\text{O})\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\mu\text{-Cl})_2\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\mu\text{-PPh}_2)(\mu\text{-PPh}_2\text{O})\text{Pt}(\text{C}_6\text{F}_5)_2]$ (**4a-b**) (0.150 g, 0.38 mmol) in acetone (40 mL), PPh_3 (0.020 g, 0.77 mmol) was added. The mixture was stirred at room temperature for 24 h. The resulting solution was evaporated to ca. 1 mL and *i*-PrOH (5 mL) was added. A mixture of complexes (**6a-b**), crystallised as a white solid, which was filtered, washed with *i*-PrOH (2 × 2 mL) and vacuum-dried. Yield: 0.124, 73 %. Anal. Found (Calcd for $\text{C}_{94}\text{H}_{91}\text{ClF}_{10}\text{NOP}_5\text{Pt}_3$): C, 50.97 (50.94); H, 4.13 (4.14); N, 0.62 (0.63). IR (cm^{-1}): 951 (s), 781 (s) C_6F_5 ; 880 (d) (NBu_4^+). HRMS(-), exact mass for the anion $[\text{C}_{78}\text{H}_{55}\text{ClF}_{10}\text{OP}_5\text{Pt}_3]^-$: 1973.1434. Measured m/z : 1973.1470 $[\text{M}^-]$. ^1H NMR (acetone- d_6 , 298 K, 400 MHz): δ from 8.14 to 6.50 (m, *Ph*), 3.42 (m, CH_2N NBu_4^+), 1.81 (m, $\text{CH}_2\text{CH}_2\text{N}$, NBu_4^+), 1.41 (m, CH_3CH_2 , NBu_4^+ , $^3J_{\text{H,H}} = 7.3$ Hz), 0.96 (t, CH_3CH_2 , NBu_4^+ , $^3J_{\text{H,H}} = 7.3$ Hz). ^{19}F NMR (acetone- d_6 , 298 K, 376.5 MHz): δ from -114.4 to -115.3 (m, overlapped *o*-F, $^3J_{\text{F,Pt}} \approx 340$ Hz), -167.2 (m, overlapped *m*-F), -167.5 (m, $^3J_{\text{F,F}} = 23$ Hz, $^3J_{\text{F,P}} = 19$ Hz, $^4J_{\text{F,P}} = 11$ Hz, overlapped *m*-F), -168.2 (t, $^2J_{\text{F,F}} = 20$ Hz, 1 *p*-F), -168.3 (t, $^3J_{\text{F,F}} = 20$ Hz, 1 *p*-F), -168.8 (t, $^3J_{\text{F,F}} = 20$ Hz, 1 *p*-F), -168.9 (t, $^3J_{\text{F,F}} = 20$ Hz, 1 *p*-F). $^{31}\text{P}\{^1\text{H}\}$ NMR (acetone- d_6 , 298 K, 161 MHz): **6a**: δ 122.6 (m, P^1 , $^1J_{\text{P(1),Pt(1)}} = 2937$ Hz), 25.9 (dd, P^5 , $^2J_{\text{P(5),P(4)}} = 339$ Hz, $^2J_{\text{P(5),P(4)}} = 3$ Hz, $^1J_{\text{P(5),Pt(3)}} = 2089$ Hz), 15.2 (d, P^2 , $^2J_{\text{P(5),P(4)}} = 303$ Hz, $^1J_{\text{P(2),Pt(1)}} = 1730$ Hz, $^1J_{\text{P(2),Pt(2)}} = 1840$ Hz), -151.5 (d, P^4 , $^2J_{\text{P(4),P(3)}} = 185$ Hz, $^1J_{\text{P(4),Pt(2)}} = 3082$ Hz, $^1J_{\text{P(4),Pt(3)}} = 2762$ Hz), -158.9 (dddd, P^3 , $^2J_{\text{P(3),P(5)}} = 339$ Hz, $^2J_{\text{P(3),P(2)}} = 303$ Hz, $^2J_{\text{P(3),P(4)}} = 185$ Hz, $^2J_{\text{P(3),Pt(1)}} = 12$ Hz, $^1J_{\text{P(3),Pt(2)}} = 1714$ Hz, $^1J_{\text{P(3),Pt(3)}} = 1816$ Hz). ^{195}Pt NMR (acetone- d_6 , 298 K, 86 MHz): δ -3674 (Pt^2), -4006 (Pt^3), -4522 (Pt^1). **6b**: δ 127.3 (m, P^1 , $^1J_{\text{P(1),Pt(1)}} = 2934$ Hz), 23.7 (m, P^5 , $^2J_{\text{P(5),P(4)}} = 379$ Hz, $^2J_{\text{P(5),P(3)}} = 13$ Hz, $^1J_{\text{P(5),Pt(3)}} = 1970$ Hz), 11.3 (d, P^2 , $^2J_{\text{P(5),P(4)}} = 319$ Hz, $^1J_{\text{P(2),Pt(1)}} = 1737$, $^1J_{\text{P(2),Pt(2)}} = 1832$ Hz), -141.2 (ddd, P^4 , $^2J_{\text{P(4),P(5)}} = 379$ Hz, $^2J_{\text{P(4),P(3)}} = 187$ Hz, $^3J_{\text{P(4),Pt(1)}} = 11$ Hz, $^1J_{\text{P(4),Pt(2)}} = 2974$ Hz, $^1J_{\text{P(4),Pt(3)}} = 1910$ Hz), -153.0 (ddt, P^3 , $^2J_{\text{P(3),P(2)}} = 319$ Hz, $^2J_{\text{P(3),P(4)}} = 187$ Hz, $^2J_{\text{P(3),P(5)}} = 2J_{\text{P(3),Pt(1)}} = 13$ Hz, $^1J_{\text{P(3),Pt(2)}} = 1508$ Hz, $^1J_{\text{P(3),Pt(3)}} = 2243$ Hz). ^{195}Pt NMR (acetone- d_6 , 298 K, 86 MHz): δ -3729 (Pt^2), -4083 (Pt^3), -4506 (Pt^1).

Reaction of [NBu₄][(C₆F₅)₂Pt(μ-PPh₂)(μ-PPh₂O)Pt(μ-PPh₂)₂Pt(acac)] (5) with HCl

To a yellow solution of **5** (0.150 g, 0.074 mmol) in acetone (10 mL) was added 0.31 mL (0.074 mmol) of HCl (HCl/H₂O, 0.24 M). The solution was stirred for 24 h and evaporated to ca. 1 mL and *i*-PrOH (10 mL) was added. A mixture of **4a-b** crystallised upon stirring and was filtered off, washed with *i*-PrOH (2 × 1 mL) and vacuum-dried (0.072 g, 50% yield).

Synthesis of [(C₆F₅)₂Pt(μ-PPh₂)₂Pt(μ-PPh₂OPPh₂)Pt(PPh₃)] (7)

Method A

To a colourless solution of the mixture of isomers [NBu₄][(C₆F₅)₂Pt(μ-PPh₂)(μ-PPh₂O)Pt(μ-PPh₂)₂Pt(Cl)(PPh₃)] (**6a-b**) (0.100 g, 0.039 mmol) in dry CH₂Cl₂ (40 mL), protected from the light, AgClO₄ (0.009 g, 0.039 mmol) was added. The mixture was stirred in the dark at room temperature for 5 h. The resulting solution was evaporated to ca. 1 mL and *i*-PrOH (5 mL) was added. Complex **7** crystallised as an orange solid, which was filtered, washed with *i*-PrOH (2 × 2 mL) and vacuum-dried. Yield: 0.044, 57%.

Method B

To a colourless solution of [NBu₄][(C₆F₅)₂Pt(μ-PPh₂)(μ-PPh₂O)Pt(μ-PPh₂)₂Pt(acac)] (**5**) (0.050 g, 0.025 mmol) in CH₂Cl₂ (20 mL), HPPH₃ClO₄ (0.009 g, 0.025 mmol) was added. The colour of the solution changed immediately to dark red and in a few minutes to orange. This mixture was stirred at room temperature for 1 h. The solution was evaporated to ca. 1 mL and *i*-PrOH (5 mL) was added. Complex **7** crystallised as an orange solid, which was filtered, washed with *i*-PrOH (2 × 2 mL) and vacuum-dried. Yield: 0.037, 77%.

HRMS(+), exact mass for the cation [C₇₈H₅₅F₁₀OP₅Pt₃]⁺: 1938.1737. Measured *m/z*: 1938.1844 [M]⁺. IR (cm⁻¹): 952 (s), 737 (s) C₆F₅; Anal. Found (Calcd for C₇₈H₅₅F₁₀OP₅Pt₃): C, 48.36 (48.33); H, 2.82 (2.86). ¹H NMR (CD₂Cl₂, 298 K, 400 MHz): δ 7.45 (dd, 4H, *o*-H bonded to P⁴, ³J_{H,P} = 12.4 Hz, ³J_{H,H} = 7.7 Hz), 7.41 (dd, 4H, *o*-H bonded to P¹, ³J_{H,P} = 11.2 Hz, ³J_{H,H} = 8.0 Hz), 7.32 (t, 2H, *p*-H bonded to P¹, ³J_{H,H} = 7.5 Hz), 7.28 (t, 2H, *p*-H bonded to P³, ³J_{H,H} = 7.5 Hz), 7.18 (pseudo t, 4H, *m*-H bonded to P¹, ³J_{H,H} = 7.4 Hz), from 7.13 to 6.94 (overlapped, 14H, *m*-H bonded to P³, *p*-H bonded to P², *p*-H bonded to P⁵, *p*-H bonded to P⁴, *o*-H bonded to P³), 6.88 (pseudo t, 4H, *m*-H bonded to P⁴, ³J_{H,H} = 7.5 Hz), 6.84 (pseudo t, 4H, *m*-H bonded to P⁵, ³J_{H,H} = 7.9 Hz), 6.82 (pseudo t, 4H, *m*-H bonded to P², ³J_{H,H} = 7.8 Hz), 6.72 (dd, 4H, *o*-H bonded to P², ³J_{H,H} = 8.0 Hz, ³J_{H,P} = 10.4 Hz), 6.66 (dd, 4H, *o*-H bonded to P⁵, ³J_{H,H} = 8.0 Hz, ³J_{H,P} = 12.6 Hz). ¹⁹F NMR (CD₂Cl₂, 298 K, 376.5 MHz): δ -116.7 (d, 2 *o*-F, ³J_{F,F} = 29 Hz, ³J_{F,Pt} = 340 Hz), δ -117.0 (d, 2 *o*-F, ³J_{F,F} = 32 Hz, ³J_{F,Pt} = 340 Hz), δ -163.9 (t, 1 *p*-F, ³J_{F,F} = 20 Hz), -165.1 (m, 2 *m*-F, ⁴J_{F,Pt} = 82 Hz), -165.8 (m, 2 *m*-F, ⁴J_{F,Pt} = 92 Hz), -166.1 (t, 1 *p*-F, ³J_{F,F} = 20

Hz). ³¹P{¹H} NMR (CD₂Cl₂, 298 K, 161 MHz): δ 143.8 (m, P², ³J_{P(2),P(5)} = 70 Hz, ³J_{P(2),P(3)} = 41 Hz, ²J_{P(2),P(4)} = 36 Hz, ¹J_{P(2),Pt(1)} = 1702 Hz, ¹J_{P(2),Pt(2)} = 2620 Hz), 132.3 (ddd, P¹, ²J_{P(1),P(4)} = 264 Hz, ²J_{P(1),P(5)} = 26 Hz, ²J_{P(1),P(3)} = 14 Hz, ¹J_{P(1),Pt(2)} = 3547 Hz), 109.1 (dddd, P³, ²J_{P(3),P(4)} = 90 Hz, ³J_{P(3),P(2)} = 41 Hz, ²J_{P(3),P(1)} = 14 Hz, ²J_{P(3),P(5)} = 5 Hz, ¹J_{P(3),Pt(3)} = 5474 Hz, ²J_{P(3),Pt(2)} = 205 Hz), 99.1 (ddd, P⁴, ²J_{P(4),P(1)} = 264 Hz, ²J_{P(4),P(3)} = 90 Hz, ²J_{P(4),P(2)} = 36 Hz, ¹J_{P(4),Pt(1)} = 2652 Hz), 24.8 (ddd, P⁵, ²J_{P(5),P(2)} = 70 Hz, ²J_{P(5),P(1)} = 26 Hz, ²J_{P(5),P(3)} = 5 Hz, ²J_{P(3),P(1)} = 12 Hz, ¹J_{P(5),Pt(3)} = 3623 Hz, ²J_{P(5),Pt(2)} = 298 Hz). ¹⁹⁵Pt NMR (CD₂Cl₂, 288 K, 86 MHz): δ -5235 (Pt¹), -5032 (Pt²), -5183 (Pt³).

X-ray Structure Determinations

Crystal data and other details of the structure analyses are collected in Tables 4 and 5. Suitable crystals of **1**-(acetone)(H₂O)·2.5acetone, **2**·0.5acetone, **4a**·2acetone·1.5hexane, **3**·0.5CH₂Cl₂·4hexane, **5**·acetone, **6a**·CH₂Cl₂·0.5H₂O and **7**·2CH₂Cl₂ were obtained by slow diffusion of *n*-hexane into acetone (**1**-(acetone)(H₂O), **2**, **4a** and **5**) or CH₂Cl₂ (**3**, **6a** and **7**) solutions of the complexes. The crystals were mounted at the end of quartz fibres in a random orientation and held in place with fluorinated oil. In all cases the diffraction data were collected with a Bruker Smart Apex diffractometer. The diffraction frames were integrated using the SAINT package⁶⁴ and corrected for absorption with SADABS.⁶⁵ The structures were solved by direct methods. All non-hydrogen atoms of the complexes were assigned anisotropic displacement parameters and refined without positional constraints. H atoms were added at calculated positions with equivalent isotropic displacement parameters set equal to 1.2 or 1.5 times those of the corresponding parent atoms. Areas of residual electron density were modelled as lattice solvent (**1**: 3 molecules of acetone, one of them at 0.5 occupancy; **2**: a molecule of acetone at 0.5 occupancy; **4a**: 2 molecules of acetone at full occupancy and 3 molecules of *n*-hexane at 0.5 occupancy each; **3**: a molecule of CH₂Cl₂ at 0.5 occupancy. In addition an analysis of the solvent region has been performed using the SQUEEZE program⁶⁶ and, as a result, 4 *n*-hexane molecules have been added to the calculations; **5**: a molecule of acetone; **6a**: a molecule of CH₂Cl₂ with one of the Cl atoms disordered over two positions at 0.75 and 0.25 occupancy each and 2 water molecules at 0.25 occupancy each; **7**: 3 molecules of CH₂Cl₂ at full, 0.5 and 0.5 occupancy respectively). Final difference electron density maps showed some peaks above 1 e Å⁻³, all of them are close to the heavy metal atoms with no chemical meaning or in the solvent areas. The structures were refined using the SHELXL-97 program.⁶⁷



Journal Name

Table 4. Crystal data and structure refinement parameters for $[(C_6F_5)_2Pt(\mu\text{-PPh}_2)(\mu\text{-PPh}_2O)Pt(\mu\text{-PPh}_2)_2Pt(\text{acetone})(H_2O)]$ (**1**-2.5acetone), $[(C_6F_5)_2Pt(\mu\text{-PPh}_2)(\mu\text{-PPh}_2O)Pt(\mu\text{-PPh}_2)_2Pt(dppm)]$ -0.5acetone (**2**-0.5acetone), $[(C_6F_5)_2Pt(\mu\text{-PPh}_2)(\mu\text{-PPh}_2O)Pt(\mu\text{-PPh}_2)_2Pt(dppm)Ag(OCIO_3)]$ -CH₂Cl₂ (**3**-0.5CH₂Cl₂-4hexane) and $[NBu_4]_2[(C_6F_5)_2Pt(\mu\text{-PPh}_2)(\mu\text{-PPh}_2O)Pt(\mu\text{-PPh}_2)_2Pt(\mu\text{-Cl})_2Pt(\mu\text{-PPh}_2)_2Pt(\mu\text{-PPh}_2)(\mu\text{-PPh}_2O)Pt(C_6F_5)_2]$ -2acetone-1.5hexane (**4a**-2acetone-1.5hexane).

| Complex | 1-2.5acetone | 2-0.5acetone | 3-0.5CH ₂ Cl ₂ -4hexane | 4a-2acetone-1.5hexane |
|---------------------------------------|--|--|---|---|
| formula | C _{70.5} H ₆₃ F ₁₀ O _{5.50} P ₄ Pt ₃ | C _{86.5} H ₆₅ F ₁₀ O _{1.50} P ₆ Pt ₃ | C _{109.5} H ₁₁₉ AgCl ₂ F ₁₀ O ₅ P ₆ Pt ₃ | C _{83.5} H _{92.50} ClF ₁₀ NO ₂ P ₆ Pt ₃ |
| M _t [g mol ⁻¹] | 1897.36 | 2089.47 | 2654.91 | 2076.69 |
| T [K] | 100(2) | 100(2) | 200(2) | 100(2) |
| λ [Å] | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| cryst syst | orthorhombic | triclinic | triclinic | triclinic |
| space group | P2(1)2(1)2(1) | P-1 | P-1 | P-1 |
| a [Å] | 15.6938(7) | 13.2595(8) | 14.1168(7) | 11.7673(6) |
| b [Å] | 17.0520(8) | 15.3410(9) | 19.3240(10) | 14.5107(7) |
| c [Å] | 26.2736(12) | 21.3535(13) | 19.3754(10) | 26.1772(13) |
| α [deg] | 90 | 76.5992(8) | 81.887(1) | 97.756(1) |
| β [deg] | 90 | 83.0608(8) | 73.116(1) | 95.676(1) |
| γ [deg] | 90 | 67.1476(8) | 82.839(1) | 97.024(1) |
| V [Å ³] | 7031.1(6) | 3891.4(4) | 4987.5(4) | 4365.3(4) |
| Z | 4 | 2 | 2 | 2 |
| ρ [g cm ⁻³] | 1.792 | 1.783 | 1.768 | 1.580 |
| μ [mm ⁻¹] | 6.120 | 5.574 | 4.611 | 4.963 |
| F(000) | 3656 | 2020 | 2622 | 2035 |
| 2θ range [deg] | 1.51-25.00 | 1.67-25.00 | 1.07-25.00 | 1.53-25.00 |
| no. of reflns collected | 38349 | 29108 | 37463 | 32602 |
| no. of unique reflns | 12365 | 13584 | 17412 | 15258 |
| R(int) | 0.0401 | 0.0618 | 0.0435 | 0.0335 |
| Final R indices [>2σ(I)] | R1 = 0.0426, wR2 = 0.0993 | R1 = 0.0637, wR2 = 0.1309 | R1 = 0.0701, wR2 = 0.1627 | R1 = 0.0469, wR2 = 0.1098 |
| R indices (all data) | R1 = 0.0475, wR2 = 0.1018 | R1 = 0.0979, wR2 = 0.1456 | R1 = 0.0887, wR2 = 0.1706 | R1 = 0.0657, wR2 = 0.1178 |
| GOF | 1.057 | 1.094 | 1.103 | 1.073 |

Table 5. Crystal data and structure refinement for (NBu₄)[(C₆F₅)₂Pt(μ-PPH₂)(μ-PPH₂O)Pt(μ-PPH₂)₂Pt(acac)]·acetone (**5**·acetone), [NBu₄][(C₆F₅)₂Pt(μ-PPH₂)(μ-PPH₂O)Pt(μ-PPH₂)₂Pt(Cl)(PPH₃)]·CH₂Cl₂·H₂O (**6a**·CH₂Cl₂·0.5H₂O) and [(C₆F₅)₂Pt(μ-PPH₂)₂(μ-PPH₂OPPh₂)Pt(μ-PPH₂)₂Pt(PPH₃)]·2CH₂Cl₂ (**7**·2CH₂Cl₂).

| Complex | 5 ·acetone | 6a ·CH ₂ Cl ₂ ·0.5H ₂ O | 7 ·2CH ₂ Cl ₂ |
|--|--|--|---|
| formula | C ₈₄ H ₈₉ F ₁₀ NO ₄ P ₄ Pt ₃ | C ₉₅ H ₉₂ Cl ₃ F ₁₀ NO _{1.5} P ₃ Pt ₃ | C ₈₀ H ₅₉ Cl ₄ F ₁₀ OP ₅ Pt ₃ |
| M _r [g mol ⁻¹] | 2075.71 | 2308.17 | 2108.19 |
| T [K] | 100(2) | 100(2) | 100(2) |
| λ [Å] | 0.71073 | 0.71073 | 0.71073 |
| cryst syst | triclinic | monoclinic | monoclinic |
| space group | P-1 | P2 ₁ /n | P2 ₁ /n |
| a [Å] | 12.3303(6) | 13.1529(8) | 15.5689(8) |
| b [Å] | 16.2895(7) | 50.083(3) | 25.4115(13) |
| c [Å] | 20.5648(9) | 13.8499(9) | 19.2739(10) |
| α [deg] | 81.226(1) | 90 | 90 |
| β [deg] | 82.861(1) | 97.620(1) | 96.108(1) |
| γ [deg] | 86.775(1) | 90 | 90 |
| V [Å ³] | 4047.6(3) | 9042.8(10) | 7582.0(7) |
| Z | 2 | 4 | 4 |
| ρ [g cm ⁻³] | 1.703 | 1.695 | 1.847 |
| μ [mm ⁻¹] | 5.323 | 4.875 | 5.838 |
| F(000) | 2032 | 4524 | 4056 |
| 2θ range [deg] | 1.50–26.00 | 1.54–25.00 | 1.54–25.00 |
| no. of refls collected | 43980 | 69176 | 56999 |
| no. of unique refls | 15829 | 15937 | 13341 |
| R(int) | 0.0264 | 0.0475 | 0.0573 |
| Final R indices [I>2σ(I)] ^a | R1 = 0.0254, wR2 = 0.0594 | R1 = 0.0770, wR2 = 0.1498 | R1 = 0.0616, wR2 = 0.1465 |
| R indices (all data) | R1 = 0.0313, wR2 = 0.0626 | R1 = 0.0868, wR2 = 0.1534 | R1 = 0.0786, wR2 = 0.1543 |
| GOF on F ^{2b} | 1.045 | 1.290 | 1.160 |

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Notes and references

§Throughout the paper, the calculated (exact mass) and the experimental (accurate) *m/z* values have been compared considering the principal ion (which gives the most intense peak) of the isotope pattern.

§§In fact, an equilibrium between **4a** and **4b** was revealed by an ¹H EXSY experiment in acetone at 298 K, which can be explained in terms of breaking and re-forming of one of the Pt–Cl bonds.

§§§The expected complex should be the one represented in Scheme 5 as **α**.

§§§§ Compound **7** has a total valence electron count of 44, which is consistent with the presence of two Pt–Pt bonds between the Pt centres

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Polynuclear Platinum Phosphanido/Phosphinito Complexes: Formation of P-O and P-O-P Bonds through Reductive Coupling Processes

Irene Ara,^a Juan Forniés,^{a,*} Susana Ibáñez,^a Piero Mastrorilli,^{b,c,*} Stefano Todisco,^b and Vito Gallo^b

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Reductive $\text{PPh}_2^-/\text{OH}^-$ coupling processes allow the preparation of tri- or hexanuclear Pt(II) complexes with PPh_2^- and PPh_2O^- bridging ligands. By creating unsaturation on the metal skeleton of complexes $[\text{NBu}_4][(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-PPh}_2)(\mu\text{-PPh}_2\text{O})\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\text{Cl})(\text{PPh}_3)]$ or $[\text{NBu}_4][(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-PPh}_2)(\mu\text{-PPh}_2\text{O})\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\text{acac})]$ a new $\text{PPh}_2^-/\text{OH}^-$ reductive coupling occurs, resulting in the trinuclear mixed oxidation state Pt(II),Pt(I),Pt(I) complex $[(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\mu\text{-PPh}_2\text{OPPh}_2)\text{Pt}(\text{PPh}_3)]$ featuring two Pt–Pt bonds.

