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Tuneable reactivity versus PPh₃ and SnX₂ of four- and five-coordinate Pd(II) and Pt(II) complexes containing polyphosphines.

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Abstract

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The reactivity of the unusual d^8 trigonal-bipyramidal systems[MX(PP₃)]X (X=Cl: M = Pd(1a), Pt(2a); X = Br: M = Pd(3a), Pt(4a); X = I: M = Pd(5a), Pt(6a); $PP_3 = tris[2-$ (diphenylphosphino)ethyl]phosphine) in CHCl₃/CH₃OH, the square-pyramidal compounds $[MCl(NP_3)]Cl(M = Pd(7a); Pt(8a); NP_3 = tris[2-(diphenylphosphino)ethyl]amine) in$ CD₃OD/DMF and the distorted square-planar mononuclear [MX(PNP)]X (M= Pd: X= Cl(10a); M = Pt: X = I(10b); PNP = bis[2-(diphenylphosphino)ethyl]amine) and the heteronuclear $[PdAu_2X_4(PP_3)][X = I(9a), Cl(14a), Br(15a)]$ and $[MAuX_2(PP_3)]X[M=Pd: X]$ = Cl(16a); M = Pt: X = Cl(17a), Br(18a)] species in CDCl₃ with PPh₃ + SnX₂ has been explored to establish the factors that influence the nature of the products. With the mononuclear precursors the course of the reaction is strongly dependent on the tripodal or linear arrangement of the polydentate ligand and in the former case on the halogen. Thus, while for chlorides (1a-2a, 7a-8a) and bromides (3a-4a) the reaction led to the trigonalbipyramidal compounds $[M(SnCl_3)(AP_3)][SnCl_3][A = P: M = Pd(1), Pt(2); A = N: M$ =Pd(7), Pt(8)], $[MBr(PP_3)][SnBr_3]$ [M = Pd(4), Pt(6)] containing M-Sn and M-Br bonds, respectively, for iodides (5a-6a) resulted in the unknown neutral square-planar compounds $[MI_2(PP(PO)_2)(SnI_2)_2]$ [M = Pd(9) and Pt(10)] bearing two dangling P=O-SnI₂ units and P_2MI_2 environments. However, complexes of the type [PtCl(PP_2PO)X]X' [X= SnCl_2, X'= $[SnCl_3]^{-}(11)]$ and $[M(PP(PO)_2)_2X_4]X'_2[X=SnCl_2, X'=[SnCl_3]^{-}: M=Pd(12), Pt(13)]$ showing P=O-SnCl₂ arms were obtained by direct reaction of [PtCl(PP₂PO)]Cl (11a) and $[M(PP(PO)_2)_2]Cl_2$ [M = Pd(12a), Pt(13a)] with SnCl₂ in CH₃OH. Although complex 9 was

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also prepared by interaction of the heteronuclear iodide **9a** with PPh₃ + SnI₂ in CDCl₃, the use of the neutral and ionic heteronuclear chlorides and bromides (**14a-18a**) as starting materials afforded the distorted square-planar ionic systems [MAuX'(PP₃)(PPh₃)][SnX₃]₂ [$M = Pd: X = Cl, X' = SnCl_3^{-}(14); X = Br, X' = SnBr_3^{-}(15). M = Pt: X=Cl, X' = SnCl_3^{-}(17); X = Br, X' = SnBr_3^{-}(18)$] containing M-SnX₃ and P-Au-PPh₃ functionalities. It was found that these reactions where the heteronuclear species are the precursors proceed *via* the trigonal-bipyramidal halides not only with X=Cl and Br(**1a-4a**) but also I(**5a**).When the precursors were **10a** and **10b** the reaction occurred with formation of [Pd(PNP)(PPh₃)][SnCl₃]₂(**23**) and [Pt(PNP)(PPh₃)][SnCl₂I]₂ (**24**) showing M-PPh₃ units and trihalostannato counter anions.

Introduction

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Platinum(II) complexes containing PPh₃ and/or Sn(II)-based ligands are of current interest because their applications as catalysts, precursors of new materials and biologically relevant systems.¹⁻³ Tin dichloride is the simplest example of Sn(II)-based ligands that acts as important co-catalyst in various group 10 metal-catalyzed reactions. The Pt(II)-Sn(II) complexes are usually prepared via the insertion of SnCl₂ into a Pt-Cl bond of the Pt(II) starting species. The weak coordination of the resultant SnCl₃⁻ anion and/or its *trans*labilizing effect is used to explain the importance of SnCl₂ as co-catalyst. Given that the exact role of this halide is still unclear, studies dealing with the influence of the geometry, the presence of other metals^{4a-c} and the donor ability of the ligands that complete the coordination sphere of Pt(II) are of interest. Aryl-substituted P,P/P,P,P and P,N/P,N,P donor ligands are capable of positioning two metal centres in close proximity and provide a well defined coordination environment for the Pt(II) centre throughout catalytic cycles avoiding the exchange and dissociation of the monodentate ligands.^{4d-e} However, when a monophosphine interacts with the neutral square-planar systems $[PtCl(SnCl_3)(P_2)](P_2 =$ two monophosphines or chelating diphosphine) the cleavage of the Pt-Sn bond occurs with formation of ionic complexes containing [SnCl₃]⁻ as counter anion.^{4f} In a previous work⁵ we reported ionic square-planar complexes containing a linear triphosphine as [MCl(triphos)]Cl (M=Pd, Pt; triphos = bis[2-(diphenylphosphino)ethyl]phenyl phosphine) that react with PPh₃ and excess SnCl₂ to give [M(triphos)(PPh₃)][SnCl₃]₂. The heterobimetallic complexes [MAuCl₂(PP₃)]Cl (M = Pd, Pt; PP₃ = tris[2-

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(diphenylphosphino)ethyl]phosphine),⁶ with a similar P₃MCl arrangement, react with PPh₃ affording [MAuCl(PP₃)(PPh₃)]Cl₂ with dangling P-Au-PPh₃ units. However, there is no reaction between PPh₃ and the unusual d⁸ trigonal-bipyramidal species [MCl(PP₃)]Cl (M = Pd, Pt) that by subsequent addition of SnCl₂ lead to [M(SnCl₃)(PP₃)][SnCl₃].⁷ With the aim of exploring the behaviour of other halo complexes bearing tripodal and linear polydentate ligands in this work we present a comparative study of the reactivity of ionic trigonal-bipyramidal [MX(PP₃)]X (M = Pd, Pt: X = Cl, Br, I), square-pyramidal [MCl(NP₃)]Cl (M = Pd, Pt; NP₃ = tris[2-(diphenylphosphino)ethyl]amine) and distorted square-planar [MX(PNP)]X (M= Pd: X = Cl; M= Pt: X = I; PNP = bis[2-(diphenylphosphino)ethyl]amine), [MAu₂X₄(PP₃)] and [MAuX₂(PP₃)]X compounds with PPh₃ and SnX₂.

Results and Discussion

Three types of compounds (Scheme 1) were obtained by direct reaction of $[MX(PP_3)]X$ [X= Cl: M=Pd(1a), Pt(2a); X= Br: M=Pd(3a), Pt(4a); X=I: M= Pd(5a), Pt(6a)] with PPh₃ in CHCl₃ and solutions of 2 equiv. of SnX₂ in CH₃OH or suspensions in CHCl₃: a) Complexes with a palladium/platinum-tin bond by tin(II) chloride insertion into M-Cl bonds such as $[M(SnCl_3)(PP_3)][SnCl_3]$ (1, 2); b) Cationic bromo complexes with $[SnBr_3]^$ as counter anion like $[MBr(PP_3)][SnBr_3]$ (4, 6); c) The rare neutral iodides $[MI_2(PP(PO)_2)(SnI_2)_2]$ (9, 10). In absence of PPh₃ there is no insertion in any case affording solids of the type b $[MX(PP_3)][SnX_3]$ (3 – 6) as hydrates. The reaction of the precursors $[MCl(NP_3)]Cl$ (7a, 8a) with PPh₃ and 2 equiv. of SnCl₂ in CD₃OD/DMF led to $[M(SnCl_3)(NP_3)][SnCl_3]$ (7, 8) that belong to type a.

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The characterisation of the complexes of the types **a** and **b** is in keeping with a trigonalbipyramidal structure for the cations, M-SnCl₃⁷ and M-X bonds, respectively, and [SnX₃]⁻ counter anions. The ${}^{1}J({}^{31}P^{A}-{}^{195}Pt)$ couplings of **2a** (2505 Hz). **4a** (2485 Hz) and **6a** (2398 Hz), with cations of the type **b** $[PtX(PP_3)]^+$, are in agreement with an increase of the *trans* influence going down in the halogen group in particular from Br to I.⁶ The 195 Pt{ 1 H}NMR of 4a (Figure 1) exhibits an overlapped doublet of quartets centred at δ -4652 with a ¹J(¹⁹⁵Pt - ³¹P^B) coupling of 2580 Hz in agreement with the proposed geometry. From solutions of 4a. 2H₂O in CH₂Cl₂ and 6a. H₂O in CH₂Cl₂/Et₂O single crystals of 4a and [PtI(PP₃)]Cl (6a') were afforded the latter indicating (as previously observed for the square-planar species $[PtCl(triphos)]Cl + KI)^5$ that the (2a + KI) metathesis reaction begins with the chloro ligand substitution. The X-ray crystal structures of 4a and 6a' are shown in Figures 1 and S1, respectively. The anomalous trend in the Pt-P^{ax} bond distances from Cl (2a: 2.2214(2) Å) to Br (4a: 2.2203(17) Å) and I (6a': 2.229(2) Å) can be attributed to prevailing steric over electronic factors with Br and I that contribute to higher chelate-ring strains. The ${}^{31}P{}^{1}H{}NMR$ spectra for 7 and 8 show a singlet at δ 28.1 (7) and 33.5 (8) attributed to the three equatorial P of NP₃ in the trigonal-bipyramidal Cl₃Sn- MNP₃ arrangement, allowing for 7 a ${}^{2}J({}^{117/119}Sn - {}^{31}P^{B})$ coupling constant of 227 Hz, and a peak at δ -4.8, in both cases, due to free PPh₃. Thus, PPh₃ activates the cleavage of M-Cl bonds on the precursors containing NP₃ and PP₃, favours the SnCl₂ insertion and does not coordinate to M in any observable extent.⁷ The behaviour as a Lewis acid of $SnPh_2Cl_2$ versus 1a - 2a or 7a-8a, just binding Cl⁻ excludes the possibility of formation of M-Sn bonds. The SnCl₃⁻

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ligand of **1** and **2** undergoes facile dissociation by reaction with salts such as CuCl and AgCl to form [MM'Cl₃(PP₃)](M'= Cu, Ag)⁹ and by addition of 1 equiv. of [AuCl(tdg)] (tdg = thiodiglycol) in CDCl₃+CH₃OH obtaining the rare heteronuclear ionic systems [M₂Au₂Cl₄(PP₃)₂][SnCl₃]₂ (**19**, **20**) (Equation S1). The ³¹P {¹H}NMR spectra for **19** and **20** (Figure S2) consist of three signals at δ 80.5, 66.3, 30.5 and δ 53.3, 42.7, 29.7, respectively with an 1:1.2 integration ratio attributed to P^D: P^E: P^F (Scheme S1). The ¹J(³¹P^D-¹⁹⁵Pt) = 3519 Hz and ¹J(³¹P^E-¹⁹⁵Pt) = 3625 Hz are characteristic of P *trans* to Cl and confirm a distorted square-planar P₂MCl₂ arrangement with linear P-Au-P fragments involved in a 16-membered chelate ring.¹⁰ PP₃ also induces the SnCl₃⁻ ligand dissociation of **1** and **2** affording [M(PP₃)₂][SnCl₃]₂ (**21**, **22**) with square-planar P₂MP₂ environments (Scheme S1). In both cases the mass spectra show peaks attributable to M(PP₃)(PP₂)(CH₂) fragments in consistence with a 1:2 M to ligand ratio. The couplings ¹J(³¹P^D-¹⁹⁵Pt) = 2471 Hz < ¹J(³¹P^E-¹⁹⁵Pt) = 2584 Hz for **22** are in keeping with two pendant CH₂CH₂PPh₂ arms bound to P^D.¹⁰

The reaction of iodides **5a** and **6a** with two equivalents of SnI₂ proceeds in air in the presence or absence of PPh₃ giving the unusual neutral compounds **9**·3H₂O and **10**·3H₂O where PP₃ is acting as bidentate ligand through the central and one terminal P with the remaining two P being oxidised and bound to SnI₂ moieties. The conductivity measurements for **9**·3H₂O in DMF (0.2 ohm⁻¹cm²mol⁻¹) confirm the non electrolyte behaviour. The mass spectra exhibit peaks attributable to MI₂(PP(PO)₂) fragments in both cases. Their ³¹P {¹H} NMR spectra consist of three resonances at δ 82.3, 65.1 and 32.0 (**9**) and 58.7, 48.8 and 31.5 (**10**, Figure 3). The two peaks at lower field were assigned to the central (P^D) and terminal (P^E) phosphorus bound to M while the signal at higher field was

attributed to the two dangling P^F=O. The ¹J(³¹P^D-¹⁹⁵Pt) and ¹J(³¹P^E-¹⁹⁵Pt) couplings of 3254 and 3417 Hz, respectively are characteristic of P *trans* to I in a distorted square-planar P₂MI₂ environment. The trend in these constants, ¹J(³¹P_{central} - ¹⁹⁵Pt) < ¹J(³¹P_{terminal} - ¹⁹⁵Pt), coincides with that previously found for complexes with 1:1 and 1:2 M to ligand ratio (M= Pd, Pt) possessing dangling P=O, dangling P, a combination of dangling P=O and P-Au-Cl or PP₂M' (M' = Cu, Au) 8-membered and PP₂Au₂P₂P 16-membered cycles such as $[PtI_2(PP(PO)_2)]^{11}$ (3257 < 3406 Hz), $[Pt(PP_3)_2]Cl_2^{10}$ (2187 < 2598 Hz), **22** (*vide supra*), $[PtAuCl_3(PP_2PO)]^{11}$ (3506 < 3639Hz) or $[PtM'_2Cl_4(PP_3)_2]$ (M' = Au: 3378 < 3641 Hz; M' = Cu: 2169 < 2272 Hz)¹⁰ and **20** (*vide supra*) and contrasts with that one for $[PtAu_2Cl_4(PP_3)]^6$ (3653 > 3291 Hz) or $[PtAuCl_3(triphos)]^{12}$ (3600 > 3590 Hz) that contain just dangling P-Au-Cl arms.

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The influence of the halogen on the reactions $1a - 2a (X = Cl)/3a - 4a (X = Br)/5a - 6a (X = I) + PPh_3 + 2 SnX_2$ can be explained on the basis of a mechanism starting with the trigonal-bipyramidal [M(SnX_3)(PP_3)][SnX_3] species that retain the SnX_3⁻ ligand for X = Cl (1, 2) and evolves (Scheme S2) by a deinsertion process due to the higher steric hindrance for Br (4, 6) without changes in the geometry and I (9, 10) by oxidation of two dissociated P with the result of a distorted square-planar arrangement to M.

Since the spontaneous oxidation of phosphorus previous to the formation of P=O-SnX₂ groups only occurred for X = I, the titration of [PtCl(PP₂PO)]Cl (**11a**) and $[M(PP(PO)_2)_2]Cl_2$ (**12a**, **13a**) with SnCl₂ in CDCl₃ + CD₃OD was followed by ³¹P{¹H}NMR and the results compared with those of the titration with SnPh₂Cl₂ (Figures S3 and S4).By direct reaction of **11a** – **13a** with SnCl₂/SnPh₂Cl₂ in CH₃OH the white ionic

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solids $11 - 13 / 11^* - 13^*$ (Scheme 2) were afforded. The mass spectra exhibit peaks for 11 and 11* due to Pt(PP₂PO)X moieties in agreement with the presence of one P=O-SnCl₂ (11) or P=O-SnPh₂Cl₂ (11^{*}) pendant arm and for $12 - 13/12^* - 13^*$ attributed to $M(PP(PO)_2)_2$ fragments with a 1:2 metal to ligand ratio. The ³¹P{¹H}NMR data in DMSO d_6 consists of three signals attributed from higher to lower field to P^A , P^B , P^C (11 / 11*) and P^{D} , P^{E} , P^{F} (12 – 13/12* - 13*). The ¹HNMR spectra allow averages for ²J(¹H - ^{117/119}Sn) of 101 Hz (11*), 120 Hz (12*) and 115 Hz (13*) consistent with the formation of O-Sn bonds.¹³ From solutions of **13**·4H₂O in DMSO, single crystals of **13a**·(CH₃)₂SO·5.5H₂O were obtained. The X-ray crystal structure consists of discrete units containing one dication (Figure 4) with two bidentate PP₃ ligands and four dangling P=O and two counter anions that are symmetrically placed above and below the P₂PtP₂ coordination plane (Figure S5) significantly closer to the metal (4.177 Å) than for [Pd(PP(PO)₂)₂]Cl₂¹¹ (15.357 Å), [Pd(PP₃)₂]Cl₂¹¹ (12.640 Å) or [Pt(PP₃)₂](NO₃)₂¹⁰ (13.823 Å) and at a comparable distance to that for $[Pd(PP_3)_2]Br_2^{10}$ (4.431 Å). The P-O bond distances (1.485(4) and 1.486(5) Å) are similar to those found for $[PdBr(triphos-O)_2]Br(1.477(9) - 1.457(10) Å)^{14}$ and slightly shorter than for $[Pd(PP(PO_2)_2]Cl_2$ (1.485(6) Å).¹¹ The ³¹P{¹H}NMR spectrum in DMSO-d₆ (Figure S5, Scheme S1) confirms the same structure in solution with ${}^{1}J({}^{31}P^{D}-{}^{195}Pt) = 2254$ $Hz < {}^{1}J({}^{31}P^{E} - {}^{195}Pt) = 2402 Hz$ in the expected range.¹⁰

The rare neutral iodo complex **9** was also afforded in solution in coexistence with the unexpected oxidised forms $[PdI_2(PP(PO)_2)]$ (**9***) (It should be noted that by controlled oxidation of $[PdI(PP_3)]$ I with H_2O_2 the product was $OP(PO)_3^{11}$ instead of **9***) and $[PdI_2(PP(PO)_2(SnI_2)]$ (**9****) by interaction of the neutral square-planar heteronuclear species $[PdAu_2I_4(PP_3)]$ (**9**a) in CDCl₃ with PPh₃ and SnI₂ (Scheme 1, Equation 1)

CDCl₂

Downloaded by UNIVERSITY OF BRIGHTON on 10/05/2013 17:02:34. Published on 10 May 2013 on http://pubs.rsc.org | doi:10.1039/C3DT32611J The ³¹P{¹H}NMR spectrum (Figure S6) shows a peak at δ 27.9 due to [AuI(PPh₃)] (9') and three sets of three and four resonances due to 9- 9* and 9'*, respectively, in accordance with the proposed structures (Schemes 1 and S1). The doublet at δ 36.0 for 9* allows a ³J(³¹P^D, ³¹P^F) = 52 Hz typical of a neutral complex with two dangling P=O groups.¹¹

Given the reaction of **9a** with PPh₃ and SnI₂ leading to **9**, the analogous reactions of the chloro and bromo heteronuclear compounds were explored. It was found that the complexes $[PdAu_2X_4(PP_3)]$ (**14a**, **15a**) and $[MAuX_2(PP_3)]X$ (**16a** – **18a**) react with PPh₃ and SnX₂ in CDCl₃ forming the ionic square-planar systems $[MAu(SnX_3)(PP_3)(PPh_3)][SnX_3]_2$ (**14-15**, **17-18**) containing M-SnX₃ and dangling P-Au-PPh₃ functionalities (Scheme 2) in coexistence for **15**, **17** and **18** with the corresponding (**15***, **17***and **18***) dissociated compounds bearing M-X instead of M-SnX₃ bonds.

Complex 14 was obtained by using both the neutral and ionic heteronuclear species 14a and 16a as precursors. In the former case (Equation 2) 14 coexists with 1 and excess Au(I)

 $CDCl_{3}$ $2[PdAu_{2}Cl_{4}(PP_{3})] + 4PPh_{3} + 5SnCl_{2} \longrightarrow$ $\longrightarrow [Pd(SnCl_{3})(PP_{3})][SnCl_{3}] + [PdAu(SnCl_{3})(PP_{3})(PPh_{3})][SnCl_{3}]_{2} + 3[AuCl(PPh_{3})](2)$

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in [AuCl(PPh₃)] (14'). Indeed, the ³¹P{¹H}NMR spectrum consists of a signal at δ 39.9 due to 14' and two sets of two and three resonances due to 1 and 14, respectively (Figure 5). The couplings ²J(³¹P^B-^{117/119}Sn) = 334 Hz (1), 240 Hz (14) confirm the formation of M-SnX₃ bonds. However, when the precursor was the ionic species 16a (Equation 3) there was no Au(I) left and 14 [²J(³¹P^B, ^{117/119}Sn) = 240 Hz] coexisted just with [PdAuCl(PP₃)(PPh₃)][SnCl₃]₂ (16*).

 $[MAuX_2(PP_3)]X + PPh_3 + 3SnX_2 \xrightarrow[X=Cl,Br]{} [MAu(SnX_3)(PP_3)(PPh_3)][SnX_3]_2 (3)$

Likewise, the neutral precursor **15a** (X = Br) reacts as shown in Equation 4 and Figure S7 to form **15** (${}^{2}J({}^{31}P^{B}, {}^{117/119}Sn) = 200 \text{ Hz}$) that dissociates in part (*vide supra*).

 $[PdAu_{2}Br_{4}(PP_{3})] + PPh_{3} + 3SnBr_{2} \longrightarrow [PdAu(SnBr_{3})(PP_{3})(PPh_{3})][SnBr_{3}]_{2} + AuBr (4)$

If the precursors are the ionic heterobimetallic PtAu-complexes **17a** (X= Cl) and **18a** (X=Br) the reaction (Equation 3) leads to **17** and **18** (Figure 6), respectively. The ${}^{2}J({}^{31}P^{B}-{}^{117/119}Sn) = 261$ Hz (**17**), 227 Hz (**18**) and ${}^{1}J({}^{31}P^{B}-{}^{195}Pt) = 2480$ Hz (**17***), 2574 Hz (**18**) are in the expected range. The coupling ${}^{2}J({}^{31}P^{C}-{}^{31}P^{G}) = 113$ Hz obtained from the resonance at δ 34.1 for **18** is consistent with the predicted P-Au-PPh₃ arrangement.⁶ Therefore, starting from the heteronuclear compounds **14a** - **16a** and **17a** -**18a** new four-coordinate ionic complexes containing M-SnX₃ bonds were afforded for both M= Pd and Pt and not only with X = Cl but also X=Br.

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Downloaded by UNIVERSITY OF BRIGHTON on 10/05/2013 17:02:34. Published on 10 May 2013 on http://pubs.rsc.org | doi:10.1039/C3DT32611J On the other hand, the two insertion products 1 + 14 afforded in the reaction of Equation 2 seem to support an associative mechanism *via* a trigonal-bipyramidal 18electron intermediate^{11,15} for the reaction of the neutral or ionic square-planar heteronuclear halides (Scheme S3) to give the corresponding four-coordinate P₃M-SnX₃ (X = Cl, Br) and P₂MI₂ species. It should be noted that the addition of PPh₃ to the heteronuclear precursors occurs with formation of [AuX(PPh₃)] and a change in the color of the solutions from colorless / pale yellow to red when M =Pd and deep yellow when M = Pt indicating a change from the square-planar to the trigonal-bipyramidal geometry of the compounds 1a – 5a. The reaction of 5a with SnI₂ would proceed, as shown in Scheme S2, *via* oxidation of two dissociated phosphorus while subsequent addition of SnX₂ to 1a-4a would lead to the complexes 1 and 2 in coexistence with 3 and 5 for X= Cl and to 4 and 6 for X = Br that undergo a ring-opening reaction induced by [AuX(PPh₃)] facilitating the SnX₂ insertion into the M-X bonds of the resultant species.

Given that none of the previous processes led to complexes with M-PPh₃ functionalities, the reaction of distorted square-planar complexes containing a linear ligand as [PdCl(PNP)]Cl (**10a**) and [PtI(PNP)]I (**10b**) with PPh₃ and SnCl₂ was followed by ³¹P {¹H}NMR. The reaction was dependent on the solvent (Scheme 3). In CDCl₃ both **10a** and **10b** gave species with M-PPh₃ bonds⁵ as [Pd(PNP)(PPh₃)][SnCl₃]₂ (**23**) and [Pt(PNP)(PPh₃)][SnCl₂I]₂ (**24**). However, by addition of a coordinating solvent as DMF (CDCl₃/DMF = 8/2) **10a** forms [Pd(PNP)(DMF)][SnCl₃]₂ (**23**[•]) and **10b** a mixture of **24**+ [Pt₂(PNP)₃]I₄ (**24**[•]) (Equations S2 and S3). The ³¹P {¹H}NMR spectrum for **10a+PPh₃+2SnCl₂** in CDCl₃ (Figure S8) shows a doblet at δ 43.6 due to P^A, a triplet at δ

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20.6 assigned to P^{G} and a singlet at δ -7.1 due to free PPh₃. The doublet and triplet allow a ${}^{2}J({}^{31}P^{A}-{}^{31}P^{G}) = 21.6$ Hz. The singlets at δ 33.1 and 27.4 for **24** (Figure 7) were assigned to P^{A} and P^{G} , respectively. The coupling ${}^{1}J({}^{31}P^{A}-{}^{195}Pt) = 2626$ Hz is characteristic of P^{A} mutually *trans*.¹⁶ The spectra for reactions of **10a** and **10b** in CDCl₃+DMF are shown in Figure S9.

Conclusions

The reaction of $[MX(AP_3)]X$ (M = Pd, Pt; A= P,N) with PPh₃ and SnX₂ affords trigonalbipyramidal complexes with M-SnX₃ bonds for X = Cl and M-X bonds for X = Br. The complexes $[M(SnCl_3)(PP_3)][SnCl_3]$ undergo elimination of SnCl₂ by addition of CuCl, AgCl, [AuCl(tdg)] or PP₃. The cooperative effect of Au(I) by using the heteronuclear $[PdAu_2X_4(PP_3)]$ and $[MAuX(PP_3)]X$ (M= Pd, Pt) systems as precursors results in the formation of ionic square-planar compounds with P-Au-PPh3 arms and M-SnX3 bonds for X = Cl and Br. When X = I there are no insertions of SnI_2 into M-I neither starting from [MI(PP₃)]I nor [PdAu₂I₄(PP₃)] affording always neutral oxidised species $[MI_2(PP(PO)_2)(SnI_2)_2]$ with two P=O-SnI₂ arms and PP₃ acting as bidentate to M. The preparation of ionic complexes containing P=O-SnCl₂ groups required the reaction between $[PtCl(PP_2PO)]Cl \text{ or } [M(PP(PO)_2)_2]Cl_2$ (with each phosphine adopting the same coordination mode as in iodides) and SnCl₂. The replacement of PP₃ by PNP led to the use of [MX(PNP)]X as starting materials that react with PPh₃ and excess SnX₂ to form squareplanar cationic species $[M(PNP)(PPh_3)]^{2+}$ containing M-PPh₃ bonds and $[SnX_3]^-$ counter anions.

Experimental Section

General Procedures and Instrumentation. Diphenylphosphine, palladium chloride, palladium bromide, potassium tetrachloroplatinate, gold iodide, tin(II) chloride, tin(II) bromide and tin(II) iodide were purchased from Strem Chemicals, tris[2-(diphenylphosphino)ethyl]phosphine, 2,2'-thiodiethanol (tdg thiodiglycol). diphenyltin(IV) chloride, potassium tert-butoxide and triphenylphosphine from Aldrich, sodium chloride, bromide and iodide and H_2O_2 (30% W/v) from Panreac and gold metal from S.E.M.P.S.A. Microanalyses were performed on a Fisons Instrument EA 1108 CHNS-O. Liquid Secondary-Ion (LSI MS) mass spectra were obtained in a Micromass Autospec spectrometer using nitrobenzylic alcohol as the matrix. Infrared spectra were recorded at ambient temperature as KBr pellets (4000-500 cm⁻¹) and Nujol mulls (500-100 cm⁻¹) on a Mattson Cygnus 100 spectrophotometer. The bands are reported as vs = very strong, s =strong, m = medium, w = weak, sh = shoulder, br = broad. ${}^{1}H$, ${}^{31}P{}^{1}H$ and ${}^{195}Pt$ {¹H}NMR spectra were recorded on a Brucker AMX500 spectrometer at 500.1, 202.46 and 107.52 MHz, respectively. A 2s relaxation delay and a 30 degree pulse angle were used to favor measurable integration data. Chemical shifts (δ) are reported in ppm relative to external sodium 3-(trimethylsilyl)propionate (¹H), 85% H₃PO₄ (³¹P) and 1 M Na₂PtCl₆ (^{195}Pt) ; s = singlet, d = doublet, t = triplet, q = quartet, m= multiplet, dd = doublet of doublets, dt = doublet of triplets, br = broad signal, J = coupling constant in Hz. Conductivities were measured at 25°C using 10⁻³M solutions in DMF on a WTW model LF-3 instrument. The crystallizing solvents in the solids were confirmed by infrared and X-

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ray diffraction.

Solutions of Au(I). Solutions containing [AuCl(tdg)] were prepared by procedures similar to those reported.¹²

Preparation of [M(SnCl₃)(PP₃)][SnCl₃] (1, 2), [MX(AP₃)]X (A= P, N; Cl, Br, I) (1a-8a), [PdAu₂I₄(PP₃)] (9a), [PtCl(PP₂PO)]Cl (11a), [Pd(PP(PO)₂)₂]Cl₂ (12a), [PdAu₂X₄(PP₃)] [X= Cl(14a), Br(15a)], [PdAuCl₂(PP₃)]Cl (16a), [PtAuX₂(PP₃)]X [X= Cl (17a), Br (18a)].

Complexes 1, 2, 1a-8a, 9a, 11a-12a, 14a-18a were prepared following procedures previously described.^{6,7,11}

Preparation of $[MX(PP_3)][SnX_3]$ [M = Pd : X= Cl(3), Br(4), M= Pt: X = Cl(5), Br(6)]. Solutions containing [PdCl(PP₃)]Cl (1a·4H₂O) (red color, 0.0998g, 0.1177 mmol), [PtCl(PP₃)]Cl (2a·2H₂O) (yellow color, 0.0752g, 0.0803 mmol), [PdBr(PP₃)]Br (3a·2H₂O) (red color, 0.0926g, 0.0988 mmol) and [PtBr(PP₃)]Br (4a·2H₂O) (yellow color, 0.1039g, 0.1013 mmol) in CHCl₃ (15- 35 mL) were reacted with solutions of SnCl₂ (0.0446g, 0.2354 mmol, 1a), (0.0304g, 0.1606 mmol, 2a) and SnBr₂ (0.0550g, 0.1976 mmol, 3a), (0.0564g, 0.2026 mmol, 4a) in 15 mL of CH₃OH. The bromides 4 and 6 were also prepared in the presence of 1 eq PPh₃ in CHCl₃ (5 mL). After stirring the mixtures for 24h diethyl ether was added. The solids formed were filtered off, washed with ether and dried *in vacuo*. **3**· 2H₂O : Yield: 85%, red solid, mp 210-215 °C.Found: C, 46.5; H, 4.9. C₄₂H₄₆P₄PdSnCl₄O₂ requires: C, 46.9; H, 4.3%. MS (LSIMS): *m*/*z* (rel.intensity) 811 (7.1%, M⁺ - SnCl₃), 776 (1.2 %, M⁺ - SnCl₃ - Cl), 563 (2.7 %, M⁺ - SnCl₃ - Cl –

 $(CH_2)_2PPh_2$. IR v_{max}/cm^{-1} : (Pd-Cl) 326 vs, (Pd-P) 360w, 370w ,(Sn-Cl)_{as} 290m. $^{31}P{^{1}H}NMR$ (298 K, CDCl₃): $\delta 132.2s$ [1P^A], 29.5s [3P^B]. Λ (DMF)= 85.5 ohm⁻¹cm²mol⁻¹. 4·2H₂O: Yield: 90%, red solid, mp 275-285°C. Found: C, 47.5; H, 4.3. C₄₂H₄₆P₄PdSnBr₄O₂ requires: C, 47.9; H, 4.4%. MS (LSIMS): m/z (rel.intensity) 857 (100%, M⁺- SnBr₃), 776 $(4.0\%, M^+ - SnBr_3 - Br), 563 (16.2\%, M^+ - SnBr_3 - Br - (CH_2)_2PPh_2)$. IR v_{max}/cm^{-1} : (Pd-Br) 216vs. ${}^{31}P{}^{1}H{}NMR$ (298 K, CDCl₃): δ 138.8s [1P^A], 29.6s [3P^B]. Λ (DMF)= 90.1 ohm⁻ ¹cm²mol⁻¹. **5**·H₂O : Yield 84%, yellow solid, mp 255-265°C. Found: C, 44.3; H, 3.9. C42H44P4PtSnCl4O requires: C, 44.1; H, 3.9%. MS (LSIMS): m/z (rel.intensity) 903 (20.1 %, M⁺- SnCl₃). IR ν_{max} /cm⁻¹:(Pt-Cl) 322vs, (Sn-Cl)_{as} 290s. ³¹P{¹H}NMR (298 K, CDCl₃): δ 117.0s [1P^A], 25.0s [3P^B]; ${}^{1}J({}^{31}P^{A}-{}^{195}Pt) = 2536 \text{ Hz}; {}^{1}J({}^{31}P^{B}-{}^{195}Pt) = 2575 \text{ Hz}. \Lambda(DMF) =$ 73.5 ohm⁻¹cm²mol⁻¹. **6**·2H₂O : Yield 73%, vellow solid, mp 290-300°C. Found: C. 44.1: H. 4.0. C₄₂H₄₆P₄PtSnBr₄O₂ requires: C, 44.2; H, 4.0 %. MS (LSIMS): *m/z* (rel.intensity) 944 $(100 \%, M^+-SnBr_3), 865 (2.7\%, M^+-SnBr_3 - Br), 652 (4.1\%, M^+-SnBr_3 - Br (CH_2)_2PPh_2$.IR v_{max}/cm^{-1} :(Pt-Br) 210vs. ³¹P{¹H}NMR (298 K, CDCl₃): δ 121.7s [1P^A], 21.7s $[3P^{B}]$; ${}^{1}J({}^{31}P^{A}-{}^{195}Pt) = 2515 \text{ Hz}$; ${}^{1}J({}^{31}P^{B}-{}^{195}Pt) = 2566 \text{ Hz}$.

Preparation of [MI_2(PP(PO)_2)(SnI_2)_2] [M = Pd(9), Pt(10)] Solutions of $5a \cdot 2H_2O$ (0.1035g, 0.1004mmol) and $6a \cdot H_2O$ (0.1363g, 0.1217 mmol) in CHCl₃ (25-50mL) were treated with SnI₂ [0.0748g, 0.2008 mmol (5a); 0.0907g, 0.2434 mmol(6a)] in CHCl₃ (40mL). The suspensions were stirred for 24h. To the resultant orange solutions diethyl ether (100mL) was added. The solids formed were filtered off, washed with ether and dried *in vacuo*. The preparations were also carried out in the presence of 1 eq. PPh₃ in CHCl₃ (5 mL). **9**·3H₂O: Yield: 94%, brown solid, mp 215-225°C. Found: C, 27.0; H, 2.4.

C₄₂H₄₈P₄PdSn₂I₆O₅ requires: C, 27.1; H, 2.3%. MS (LSIMS): *m/z* (rel.intensity) 1062 (2.3%, M⁺ - 2SnI₂), 935 (100%, M⁺ - 2SnI₂ - I), 579 (12.1% - 2SnI₂ –2I -(CH₂)₂P(O)Ph₂). IR ν_{max} /cm⁻¹:(Pd-I) 187s, (Pd-P) 345w, (P=O) 1184vs. ³¹P{¹H}NMR (298 K, CDCl₃): δ 82.3s [1P^D], 65.1s [1P^E], 32.0s [2P^F=O]. Λ (DMF)= 0.2 ohm⁻¹cm²mol⁻¹. **10**·3H₂O: Yield: 87%, orange solid, mp 190-200°C. Found: C, 25.6; H, 2.4. C₄₂H₄₈P₄PtSn₂I₆O₅ requires: C, 25.9; H, 2.5%. MS (LSIMS): *m/z* (rel.intensity) 1151 (7.2%, M⁺- 2 SnI₂), 1024 (71.8%, M⁺ -2 SnI₂- I), 668 (5.3%, M⁺ - 2SnI₂- 2I - (CH₂)₂P(O)Ph₂). IR ν_{max} /cm⁻¹: (Pt-I) 185s, (P=O) 1183m. ³¹P{¹H}NMR (298 K, CDCl₃): δ 58.7s [1P^D], 48.8s [1P^E], 31.5s [2P^F=O]; ¹J(³¹P^D-¹⁹⁵Pt)= 3254 Hz; ¹J(³¹P^E-¹⁹⁵Pt)= 3417 Hz.

Preparation of [PtCl(PP₂PO)X)]X['] [X= SnCl₂, X[']= [SnCl₃]⁻ (11); X= SnPh₂Cl₂, X['] = [SnPh₂Cl₃]⁻ (11*)]. To solutions of 11a·2H₂O [0.1071g, 0.1124mmol (11); 0.1172g, 0.1230mmol (11*)] in CHCl₃ (30 mL) solutions of SnCl₂ (0.0426g, 0.2248mmol) or SnPh₂Cl₂ (0.0846g, 0.2460 mmol) in CH₃OH were added. The reaction mixtures were stirred for 14h. After that Et₂O (110 mL) was added to complete the precipitation. The solids were filtered off, washed with ether and dried *in vacuo*. 11·2H₂O: Yield: 93%, white solid, mp 290-300°C. Found: C, 36.5; H, 3.3. C₄₂H₄₆P₄PtSn₂Cl₆O₃ requires: C, 36.9; H, 3.5%. MS (LSIMS): *m/z* (rel.intensity) 1070 (7.3%, M⁺- Cl- SnCl₃), 916 (90.9%, M⁺ - SnCl₃ – SnCl₂), 881 (2.4%, M⁺ - Cl - SnCl₃ – SnCl₂). IR v_{max}/cm⁻¹: (Pt-Cl) 315s, (P=O) 1189m. ³¹P{¹H}NMR (298 K, DMSO-d₆): δ 95.3d [1P^A], 46.4s [2P^B], 33.0d [1P^C= O]; ¹*J*(³¹P^A- ¹⁹⁵Pt)= 2960 Hz; ¹*J*(³¹P^B- ¹⁹⁵Pt)= 2508 Hz; ³*J*(³¹P^A- ³¹P^C) = 40Hz. 11* : Yield: 80%, white solid, mp 210-220°C. Found: C, 48.1; H, 3.9. C₆₆H₆₂P₄PtSn₂Cl₆O requires: C, 48.3; H, 3.8%. MS (LSIMS): *m/z* (rel.intensity) 1224 (2.3%, M⁺- Cl- SnPh₂Cl₃), 916

(90.3%, M^+ - SnPh₂Cl₃ – SnPh₂Cl₂), 881 (2.3%, M^+ - Cl - SnPh₂Cl₃ – SnPh₂Cl₂). IR v_{max}/cm^{-1} : (Pt-Cl) 311m, (P=O), 1186m (Sn-C)_{as} 289m, (Sn-C)_s 250m.³¹P{¹H}NMR (298 K, DMSO-d₆): δ 95.3d [1P^A], 46.4s [2P^B], 33.0d [1P^C= O]; ¹J(³¹P^A- ¹⁹⁵Pt)= 2921 Hz; ¹J(³¹P^B- ¹⁹⁵Pt)= 2508 Hz; ³J(³¹P^A- ³¹P^C) = 40Hz.

Preparation of 13a·3CH₂Cl₂ .To a solution of [Pt(PP₃)₂]Cl₂·2H₂O·2CHCl₃ (0.1013g, 0.0630mmol) in CH₂Cl₂ (25mL) excess H₂O₂ (0.5040mmol) was added. The resultant suspension was stirred for 16h. After that Et₂O (10 mL) was added to complete the precipitation. The solid was filtered off, washed with ether and dried *in vacuo*. Yield: 82%, white solid, mp 170-180°C. Found: C, 54.1; H, 4.9. C₈₇H₉₀P₈PtCl₈O₄ requires: C, 54.3; H, 4.7%. MS (LSIMS): *m/z* (rel.intensity) 1599 (8.2%, M⁺- 2Cl), 897 (2.1%, M⁺ -2Cl – P(CH₂CH₂PPh₂)(CH₂CH₂P(O)Ph₂)₂. IR v_{max} /cm⁻¹: (Pt-P) 394m, (P=O) 1184s. ³¹P {¹H}NMR (298 K, DMSO-d₆): δ 52.0s [2P^D], 50.5s [2P^E], 32.2dd [4P^E= O]; ¹J(³¹P^D-¹⁹⁵Pt)= 2254 Hz; ¹J(³¹P^E-¹⁹⁵Pt)= 2402 Hz; ²J(³¹P^D-³¹P^E) = 20Hz; ³J(³¹P^D-³¹P^F) = 42Hz. Λ(DMF)= 87.0 ohm⁻¹cm²mol⁻¹.

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> Preparation of [M(PP(PO)₂)₂X₄]X[']₂ [M= Pd: X= SnCl₂, X[']= SnCl₃ (12); X= SnPh₂Cl₂, X[']= SnPh₂Cl₃ (12^{*}). M= Pt: X= SnCl₂, X['] = SnCl₃ (13); X= SnPh₂Cl₂, X[']= SnPh₂Cl₃ (13^{*})]

> .To solutions of [M(PP(PO)₂)₂]Cl₂·3CH₂Cl₂, **12a**·3CH₂Cl₂ [(0.1963g, 0.1240 mmol)(**12**); (0.1947g, 0.1230 mmol)(**12***)] and **13a**·3CH₂Cl₂, [(0.2161g, 0.1293 mmol)(**13**); (0.2537g, 0.1230 mmol)(**13***)], in CH₃OH (10mL) solutions of SnCl₂ [(0.1411g, 0.7440 mmol)(**12**); (0.1316g, 0.7758 mmol)(**13**)] and SnPh₂Cl₂ [(0.2537g, 0.7380 mmol)(**12***); (0.2537g,

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0.7380 mmol)(13*)] in CH₃OH (10mL) were added. The resultant suspensions (due to partial precipitation of the products) were stirred for 12-24 h. After that Et₂O (50-80mL) was added to complete the precipitation. The solids were filtered off, washed with ether and dried in vacuo. 12·4H₂O: Yield: 50%, white solid, mp 290-300°C. Found: C, 35.9; H, 3.6. C₄₂H₅₀P₄PdSn₆Cl₁₄O₈ requires: C, 36.1; H, 3.4%. MS (LSIMS): *m/z* (rel.intensity) 1510 M^+ - M^+ (2.7%)4SnCl₂-808(4.7%. $2SnCl_3$). -4SnCl₂-2SnCl₃ P(CH₂CH₂PPh₂)(CH₂CH₂P(O)Ph₂)₂). IR v_{max}/cm⁻¹: (Pd-P) 345w, (Sn-Cl)_{as} 290m, 254m, (P=O) 1176m. ${}^{31}P{}^{1}H{}NMR$ (298 K, DMSO-d₆): δ 61.1s [2P^D], 57.7s [2P^E], 32.5s [4P^F= O]. $\Lambda(DMF) = 75.0 \text{ ohm}^{-1} \text{cm}^{2} \text{mol}^{-1}$. 12*·2Et₂O: Yield: 62%, white solid, mp 200-210°C. Found: C, 41.1; H, 3.7. C₁₆₄H₁₆₄P₈PdSn₆Cl₁₄O₆ requires: C, 40.5; H, 3.5%. MS (LSIMS): m/z (rel.intensity) 1510 (19.1%, M⁺- 4SnPh₂Cl₂- 2SnPh₂Cl₃), 808 (39.5%, M⁺ -4SnPh₂Cl₂- $2SnPh_2Cl_3 - P(CH_2CH_2PPh_2)(CH_2CH_2P(O)Ph_2)_2$. IR v_{max}/cm^{-1} : (P=O) 1184m, (Sn-C)_{as} 291m, (Sn-C)_s 242m, ³¹P{¹H}NMR (298 K, DMSO-d₆): δ 60.9s [2P^D], 57.6s [2P^E], 32.5s $[4P^{F}= O]$. **13**·4H₂O: Yield: 50%, white solid, mp >300°C. Found: C, 34.7; H, 3.4. C₈₄H₉₂P₈PtSn₆Cl₁₄O₈ requires: C, 35.0; H, 3.3%. MS (LSIMS): *m/z* (rel.intensity) 1599 (7.7%, M^+ -4SnCl₂-2SnCl₃), 897(3.0%, M^+ -4SnCl₂- $2SnCl_3$ P(CH₂CH₂PPh₂)(CH₂CH₂P(O)Ph₂)₂). IR v_{max}/cm⁻¹: (Sn-Cl)_{as} 290m, 254m, (P=O) 1177m. ${}^{31}P{}^{1}H{NMR}$ (298 K, DMSO-d₆): δ 53.2s [2P^D], 51.3s [2P^E], 33.7dd [4P^F= O]; ${}^{1}J{}^{(31}P^{D}-$ ¹⁹⁵Pt)= 2232 Hz; ${}^{1}J({}^{31}P^{E}-{}^{195}Pt)= 2365$ Hz; ${}^{2}J({}^{31}P^{D}-{}^{31}P^{E}) = 20$ Hz; ${}^{3}J({}^{31}P^{D}-{}^{31}P^{F}) = 42$ Hz. $\Lambda(DMF) = 87.0 \text{ ohm}^{-1} \text{cm}^{2} \text{mol}^{-1}$. **13***·2Et₂O: Yield: 62%, white solid, mp 200-210°C. Found: C, 39.8; H, 3.5. C₁₆₄H₁₆₄P₈PtSn₆Cl₁₄O₆ requires: C, 39.6; H, 3.5%. MS (LSIMS): *m/z* (rel.intensity) 1599 (11.2%, M⁺- 4SnPh₂Cl₂- 2SnPh₂Cl₃), 897(6.4%, M⁺ -4SnPh₂Cl₂- $2SnPh_2Cl_3 - P(CH_2CH_2PPh_2)(CH_2CH_2P(O)Ph_2)_2)$. IR v_{max}/cm^{-1} : (Pt-P) 355w, (P=O)

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1184m, (Sn-C)_{as} 290m, (Sn-C)_s 252s. ³¹P{¹H}NMR (298 K, DMSO-d₆): δ 52.9s [2P^D], 51.1s [2P^E], 32.2s [4P^F= O]; ¹J(³¹P^D- ¹⁹⁵Pt)= 2239 Hz; ¹J(³¹P^E- ¹⁹⁵Pt)= 2375 Hz; ²J(³¹P^D- ³¹P^E) = 20Hz; ³J(³¹P^D- ³¹P^F) = 42Hz.

Preparation of [M(PP₃)₂][SnCl₃]₂ [M= Pd(21), Pt(22)]

To solutions of $[M(SnCl_3)(PP_3)][SnCl_3]\cdot CHCl_3$, $1\cdot CHCl_3$ (0.0617g, 0.0503 mmol) and $2\cdot CHCl_3$ (0.0990g, 0.0752mmol), in CHCl_3 (50 mL) a solution of PP_3 [0.0337g, 0.0503 mmol (1); (0.0505g, 0.0752 mmol (2)] in CHCl_3 (25mL) was added. The reaction mixtures were stirred for 24h. After that Et₂O (80mL) was added to induce the precipitation. The solids were filtered off, washed with ether and dried *in vacuo*. **21**·2CHCl₃: Yield: 84%, red solid, mp 200-210°C. Found: C, 48.5; H, 4.3. $C_{86}H_{86}P_8PdSn_2Cl_{12}$ requires: C, 48.3; H, 4.1%. MS (LSIMS): m/z (rel.intensity) 776 (11.4%, M⁺-P(CH₂CH₂PPh₂)₃ - 2SnCl₃). IR v_{max}/cm^{-1} : (Sn-Cl)_{as} 289s, 249s. ${}^{31}P\{{}^{1}H\}$ NMR (298 K, DMSO-d₆): δ 61.3s [2P^D], 35.4s [2P^E], -11.5br [4P^F]. Λ (DMF)= 85.5 ohm⁻¹cm²mol⁻¹. **22**·3CHCl₃: Yield: 84%, yellow solid, mp 200-210°C. Found: C, 44.8; H, 3.9. $C_{87}H_{87}P_8PtSn_2Cl_{15}$ requires: C, 44.5; H, 3.7%. MS (LSIMS): m/z (rel.intensity) 865 (6.9%, M⁺- P(CH₂CH₂PPh₂)₃ - 2SnCl₃). IR v_{max}/cm^{-1} : (Pt-P) 343m, (Sn-Cl)_{as} 303s, 252m. ${}^{31}P\{{}^{1}H\}$ NMR (298 K, DMSO-d₆): δ 54.1s [2P^D], 34.1s [2P^E]; ${}^{1}J({}^{31}P^{D}-{}^{195}Pt)= 2471$ Hz; ${}^{1}J({}^{31}P^{E}-{}^{195}Pt)= 2584$ Hz. Λ (DMF)= 85.5 ohm⁻¹cm²mol⁻¹.

Titrations of 7a-9a, 10a-10b and 14a-18a with SnX₂ in the presence of PPh₃

Titrations of 7a-8a

Solutions containing [MCl(NP₃)]Cl [M= Pd(7a), Pt(8a)] in CD₃OD/DMF were treated with one and two equivalents of PPh₃ and SnCl₂, respectively, and stirred for 12h. After that, the ³¹P{¹H}NMR spectra of the solutions were recorded. ³¹P{¹H}NMR [298 K, CD₃OD/DMF (8/2)] : (7a + PPh₃ + 2SnCl₂) δ 28.1s [3P^B, 7], - 4.8s [PPh₃]; ²J(³¹P^B-^{117/119}Sn) = 227 Hz. (8a + PPh₃ + 2SnCl₂) δ 33.5s [3P^B, 8], - 4.8s [PPh₃].

Titrations of 9a

To a solution of [PdAu₂I₄(PP₃)] (**9a**) in CDCl₃ (0.6mL) two and four equivalents of PPh₃ in CDCl₃ (0.1mL) and SnI₂ as solid, respectively, were added in the presence of air. The reaction mixture was stirred for 18h and the ³¹P{¹H}NMR of the red solution formed was recorded. ³¹P{¹H}NMR (298 K, CDCl₃): (**9a** +**2** PPh₃ + **4SnI₂** + **O₂**) δ 77.6br [1P^D], 65.0br [1P^E], 32.1br [2P^F=O-SnI₂] (**9**); δ 74.0br [1P^D], 65.4br [1P^E], 36.0d [2P^F=O], ³J(³¹P^D-³¹P^F) = 52 Hz (**9***); δ 74.0br [1P^D], 65.4br [1P^E], 37.3s [1P^F=O], 32.1br [1P^F=O-SnI₂] (**9***); δ 27.9br (**9***).

Titrations of 10a-10b

Solutions of [PdCl(PNP)]Cl (**10a**) and [PtI(PNP)]I (**10b**) in CDCl₃/DMF (8/2) were reacted with one and two equivalents of PPh₃ and SnCl₂, respectively. After stirring for 12h the ³¹P{¹H}NMR spectra were recorded. ³¹P{¹H}NMR (298 K, CDCl₃): (**10a** + **PPh₃** + **2SnCl₂**) δ 43.6d [2P^A, **23**], 20.6t[1P^G, **23**], -7.2 [PPh₃]; ²J(³¹P^A- ³¹P^G) = 21.6 Hz. (**10b** + **PPh₃ + 2SnCl₂**) δ 33.1s [2P^A, **24**], 27.4s [1P^G, **24**]; ¹J(³¹P^A- ¹⁹⁵Pt) = 2626 Hz. ³¹P{¹H}NMR (298 K, CDCl₃/DMF): (**10a** + **PPh**₃ + **2SnCl**₂) δ 33.1s [2P^A, **23**[']], -8.6s [PPh₃] . (**10b** + **PPh**₃ + **2SnCl**₂) δ 32.1s[2P^A, **24**], 23.0s [1P^G, **24**], -10.1 br [PPh₃]; δ 37.2s [4P^A, **24**[']], -9.9s [2P^B, **24**[']]; ¹J(³¹P^A- ¹⁹⁵Pt) = 2250/1617 Hz (**24/24**[']).

Titrations of 14a-18a

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To solutions of [PdAu₂X₄(PP₃)] [X= Cl (14a), Br (15a)] and [MAuX₂(PP₃)]X [M= Pd: X= Cl (16a); M= Pt: X= Cl(17a), Br (18a) in CDCl₃ (0.6mL), PPh₃ in CDCl₃ (0.2 mL) and SnX_2 as solid were added. After stirring for 18h the ${}^{31}P{}^{1}H{}NMR$ spectra of the solutions were recorded. ${}^{31}P{}^{1}H{NMR}$ (298 K, CDCl₃): (14a + 2PPh₃ + 4SnCl₂) δ 112.7br [1P^A], 43.1brs $[2P^{B}]$, 40.0br $[1P^{C}+1P^{G}]$; ${}^{2}J({}^{31}P^{B}-{}^{117/119}Sn) = 240 \text{ Hz}$ (14); δ 40.0br (14'); δ 160.4s $[1P^{A}], 44.8s [3P^{B}]; {}^{2}J({}^{31}P^{B}-{}^{117/119}Sn) = 334 \text{ Hz} (1). (15a + PPh_{3} + 3SnBr_{2}) \delta 44.6br$ $[2P^{B}]$, 35.6s $[1P^{C}]$, 34.3br $[1P^{G}]$; ${}^{2}J({}^{31}P^{B}-{}^{117/119}Sn) = 200 \text{ Hz}$ (15); δ 110.4br $[1P^{A}]$, 44.6[2P^B], 35.6[1P^C], 33.5 s [1P^G] (15*). (16a + PPh₃ + 3SnCl₂) δ 116.0s [1P^A], 43.0br $[2P^{B}]$, 41.8br $[1P^{C}]$, 32.4br $[1 P^{G}]$; ² $J(^{31}P^{B}-^{117/119}Sn) = 240 \text{ Hz}$ (14); δ 106.0br $[1P^{A}]$, 40.3br $[2P^{B}]$, 34.0br $[1P^{C}]$, 31.4br $[1 P^{G}]$ (16*). (17a + PPh₃ + 3SnCl₂) δ 39.6s $[2P^{B}]$, 37.4br $[1P^{C}]$, 31.4br $[1 P^{G}]$; ${}^{2}J({}^{31}P^{B}-{}^{117/119}Sn) = 261Hz$ (17); δ 84.0br $[1P^{A}]$, 41.8s $[2P^{B}]$, 36.7br $[1P^{C}]$, 31.4br $[1P^{G}]$; ${}^{1}J({}^{31}P^{B}-{}^{195}Pt) = 2480 \text{ Hz}$ (17*). (18a + PPh₃ + 3SnBr₂) δ 35.6s $[2P^{B}]$, 34.1br [1P^C], 33.5br [1 P^G]; ${}^{1}J({}^{31}P^{B}-{}^{195}Pt) = 2754$ Hz; ${}^{2}J({}^{31}P^{B}-{}^{117/119}Sn) = 227$ Hz; ${}^{2}J({}^{31}P^{C}-{}^{31}P^{G}) = 113 \text{ Hz} (18); \delta 87.2 \text{ br} [1P^{A}], 40.3 \text{ br} [2P^{B}], 33.9 \text{ br} [1P^{C}], 33.5 \text{ br} [1 P^{G}];$ ${}^{1}J({}^{31}P^{A}-{}^{195}Pt) = 2996 \text{ Hz} (18^{*}).$

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Titrations of 1 and 2 with [AuCl(tdg)]

Solutions of $[M(SnCl_3)(PP_3)][SnCl_3]$ [M= Pd(1), Pt(2)] in CDCl₃ were treated with 1,2 and 3 equivalents of [AuCl(tdg)] in CH₃OH. The resultant mixtures were stirred for 24h and the ³¹P{¹H}NMR spectra were recorded. ³¹P{¹H}NMR (298 K, CDCl₃ + CH₃OH): (1 + 1 eq [AuCl(tdg)]) δ 80.5br [2P^D], 66.3s [2P^E], 30.5d [4P^F] (19). (2 + 1 eq [AuCl(tdg)]) δ 53.3t [2P^D], 42.7s [2P^E], 29.7d [4P^F]; ¹J(³¹P^D-¹⁹⁵Pt) = 3519Hz; ¹J(³¹P^E-¹⁹⁵Pt) = 3625Hz (20).

Preparation of crystals

Single crystals of **4a** were afforded from a solution of **4a**·2H₂O (0.0125 mmol) in CH₂Cl₂ (1.0 mL), collected by filtration, washed with ether and dried *in vacuo*. Crystals of [PtI(PP₃)]Cl (**6a**') were prepared by recrystallization of a sample (0.0185 mmol) of **6a**·H₂O (K₂PtCl₄ + KI in H₂O + PP₃ in CHCl₃) in 2mL of CH₂Cl₂/Et₂O, filtered off, washed with ether and dried *in vacuo*. Crystals of **13a**·(CH₃)₂SO·5.5H₂O, used for X-ray diffraction, were prepared by addition of 6 equivalents of SnCl₂ to **13a**·3 CH₂Cl₂ (0.0150 mmol) in CH₃OH (2 mL), removal of the white solid formed and recrystallization in DMSO (2mL).

X-ray Crystallography

Yellow and colorless prisms of **4a** and **13a**·(CH₃)₂SO·5.5H₂O, respectively, and orange plates of **6a**' were mounted on glass fibers and used for data collection. Crystal data were collected at 220 and 293K using a Stoe Stadi4 four-circle (with an Oxford Cryosystem variable Temperature device) and a BRUKER SMART CCD 1000 diffractometer, respectively. Graphite monochromated MoK_{α} radiation was used throughout. The data were processed with SAINT.¹⁷ Absorption corrections for **4a** (with crystal dimensions rather

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similar) were not applied and for 13a and 6a' were made using SADABS and (ψ -scan).¹⁸ The structures were solved by direct methods using the SIR- 92^{19} and refined by full-matrix least-squares techniques against F^2 using SHELXL-97.²⁰ Data were not corrected with SQUEEZE/PLATON programs. The voids, that for 4a and 6a' (Figure S1) are considered to be generated in the crystal packing of the molecules, contain disordered solvent (DMSO and H₂O) molecules for 13a (Figure S5). Positional and anisotropic displacement parameters were refined for all non-hydrogen atoms. Hydrogen atoms were placed geometrically, and positional parameters were refined using a riding model. C33, C41 and some C atoms of phenyl groups for 13a are affected with a considerable disorder degree there being not possible in the phenyl groups a better location. The problem of disorder around the some C and solvent site gave rise to rather elongated ellipsoids. Final refinement included the bond-length restrains SADI for S1S-C1S and S1C-C2S to force these bonds to be equal distances. The H atoms of four water molecules (O1W to O4W) cannot be located and their positions cannot be calculated or predicted from geometrical considerations. Atomic scattering factors were obtained with the use of International Tables for Crystallography.²¹ Graphics were carried out with DIAMOND.²²

Acknowledgements

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Electronic supplementary information (ESI) available: Equations S1-S3; Schemes S1-S3, Figures S1-S9 and CIFs Comments.

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Complex	4a	6a'	13a (CH ₃) ₂ SO·5.5H ₂ O
Empirical formula	$C_{42}H_{42}Br_2P_4Pt$	C ₄₂ H ₄₂ IClP ₄ Pt	C ₈₆ H ₁₀₁ Cl ₂ O _{10.5} P ₈ PtS
Formula weight	1025.55	1028.08	1848.48
Temperature (K)	220(1)	220(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal size (mm)	0.35 x 0.35 x 0.32	0.35 x 0.35 x 0.19	0.31 x 0.14 x 0.03
Colour/habit	Yellow/prisms	Orange/plates	Colorless/prisms
Crystal system	Triclinic	Triclinic	Triclinic
Space group	P-1	P-1	P-1
a (Å)	10.268(4)	10.259(3)	11.756(2)
b (Å)	10.538(4)	10.609 (3)	13.916(3)
c (Å)	20.356(8)	20.307(6)	15.594(3)
α (°)	102.51(2)	102.299(16)	105.645(3)
β (°)	96.79(3)	96.27(2)	99.023(3)
γ (°)	104.38(2)	105.010(18)	102.653(3)
Volume (Å ³)	2048.2(14)	2053.9(10)	2332.8 (8)
Ζ	2	2	1
Calculated density (Mg/m^3)	1.663	1.662	1.316
Absorption coefficient (mm ⁻¹)	5.561	4.417	1.773
F(000)	1044	1004	949
θ range for data collection (°)	2.53 to 24.97	2.53 to 24.98	1.58 to 26.43
Index ranges	$-12 \le h \le 12$	$-12 \le h \le 12$	$-14 \le h \le 14$
	$-12 \le k \le 12$	$-12 \le k \le 12$	$-17 \le k \le 16$
	$0 \le l \le 24$	$0 \le l \le 24$	$0 \le l \le 19$
Reflections collected	10087	9154	27072
Independent reflections	7181 [$R_{int} = 0.0346$]	7208 [$R_{int} = 0.0935$]	$9519 [R_{int} = 0.0335]$
Max. and min. transmission		0.4874 and 0.3070	0.9487 and 0.6094
Data / restraints / parameters	7181 / 0 / 442	7208 / 0 / 442	9519 / 1 / 529
Goodness of fit on F^2	1.019	1.011	1.120
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0357$	$R_1 = 0.0426$	$R_1 = 0.0383$
L (/ J	$wR_2 = 0.0725$	$wR_2 = 0.0888$	$wR_2 = 0.1042$
Largest diff.peak and hole(eÅ ⁻³)	0.786 and -1.150	2.078 and – 1.133	1.073 and -0.540

Table 1. Summary of Crystal Parameters, Data Collection, and Refinement for 4a, 6a'and 13a

Pt(1)-P(1) Pt(1)-P(2) Pt(1)-P(3)	2.2203(17)	2 220(2)		
Pt(1)-P(2) Pt(1)-P(3)	2 27(0(17)	$\angle . \angle \angle 9(\angle)$	2.3217 (10)	
Pt(1)-P(3)	2.3/68(1/)	2.382(2)	2.3199(10)	
	2.3382(16)	2.338(2)		
Pt(1)-P(4)	2.3880(16)	2.390(2)		
$Pt(1)-X(1)^a$	2.5495(13)	2.7091(11)		C S
P(3)-O(1)			1.485(4)	
P(4)-O(2)			1.486(5)	5
P(1)-Pt(1)-P(2)	85.10(6)	85.06(7)	83.89(4)	S
P(1)-Pt(1)-P(3)	84.26(6)	84.13(7)		D
P(1)-Pt(1)-P(4)	84.68(6)	84.70(7)		g
P(2)-Pt(1)-P(4)	113.03(6)	112.30(7)		a a
P(3)-Pt(1)-P(2)	123.47(6)	123.54(7)		2
P(3)-Pt(1)-P(4)	120.92(6)	121.53(7)		Т
P(1)-Pt(1)-P(2 1)			96.11(4)	Ū
$P(2).Pt(1)-P(2^{-1})$			180.00(5)	ot
P(1)-Pt(1)-Cl(1)	177.36(4)	177.30(5)		U
P(2)-Pt(1)Cl(1)	95.42(5)	95.82(5)		Ö
P(3)-Pt(1)-Cl(1)	93.31(5)	93.27(5)		0
P(4)-Pt(1)-Cl(1)	97.48(5)	97.30(5)		4

Table 2. Selected Distances (Å) and Angles (deg.) for 4a, 6a' and 13
--

^aX=Br(4a), I(6a'). Pt(1)·····Cl(1) = 4.177(2) Å (13a).

Scheme and Figure Captions

Scheme 1 Reactivity of 1a-6a with PPh₃ + SnX₂ and 1-2 with [AuCl(tdg)] and PP₃

Scheme 2 Formation of P=O- Sn and M-SnX₃ bonds by reaction of **11a-13a** and **14a-18a** with SnCl₂/SnPh₂Cl₂ and PPh₃ + SnX₂, respectively.

Scheme 3 Reactivity of 10a and 10b with PPh₃ + SnCl₂

Figure 1. ¹⁹⁵Pt{¹H}NMR Spectrum (r.t.) for **4a** (top) and crystal structure for **4a**-cation (bottom).

Figure 2. ³¹P{¹H}NMR spectrum (r.t.) for $7a + PPh_3 + 2SnCl_2$ in CD₃OD + DMF giving 7 and free PPh₃.

Figure 3. ${}^{31}P{}^{1}H{}NMR$ Spectrum (r.t.) in CDCl₃ for 10·3H₂O

Figure 4. Crystal structure for 13a-cation with anions solvents and two dangling arms of one ligand removed for clarity.

Figure 5. ${}^{31}P{}^{1}H{}NMR$ Spectrum (r.t.) for $14a + 2PPh_3 + 4SnCl_2$ in CDCl₃ giving $14 + 1 + [AuCl(PPh_3)]$ (14').

Figure 6. ³¹P{¹H}NMR Spectrum (r.t.: 30-47 ppm) for **18a** + **PPh₃** + **3 SnBr₂** in CDCl₃ giving **18** + **18***

Figure 7. ${}^{31}P{}^{1}H{}NMR$ Spectrum (r.t.) for 10b + PPh₃ + 2SnCl₂ in CDCl₃ giving 24.

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Scheme 1



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Scheme 2



M=Pd:X=Cl(14), Br(15) M=Pt:X=Cl(17), Br(18)

Scheme 3









Figure 1

5





Figure 2





Figure 3





Figure 4





Figure 5



Figure 6

10





Figure 7

Table of contents entry



This work describes the formation of M-SnX₃,P=O- Sn and M-PPh₃ functionalities starting from five- and four-coordinate complexes containing tripodal and linear ligands.