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Triphos as a bidentate ligand: the reactivity of the dangling phosphorus in [$PtMe_2$(triphos-*P*,*P*′)]

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Abstract

Complex [$PtMe_2$(triphos-*P*,*P*′)], (**1**) where the linear triphosphine triphos [= bis(diphenylphosphinoethyl)phenylphosphine] acts as a bidentate ligand, can be easily converted in a variety of new complexes due to the reactivity of the free phosphorus donor. The selective oxidation of the uncoordinated phosphorus gave [$PtMe_2$(triphosPO-*P*,*P*′)] whose X-ray crystal structure is here reported; from the reactions of **1** with platinum and non platinum precursors homotrimetallic [Pt_3Me_4XY(triphos)$_2$] (X = Y = Me, Cl, I, X = Me, Y = Cl) and heterotrimetallic ([$Pt_2PdMe_4Cl_2$(triphos)$_2$] and [Pt_2RhMe_4(cod)(triphos)$_2$]PF_6) complexes were obtained where triphos acts as a chelating/bridging ligand. When **1** was treated with triflic acid in the presence of a neutral electron donor L (L = SMe_2, pyridine, PPh_3), complexes [PtL(triphos)]$^{2+}$ were rapidly recovered in high yields. The protonolysis of **1** in the presence of CO and methanol gave the new organometallic complex [Pt(COOMe)(triphos)]OTf. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Platinum complexes; Triphosphine complexes; Polynuclear complexes

1. Introduction

The linear triphosphine $PPh(CH_2CH_2PPh_2)_2$ (triphos) presents an extensive coordination chemistry with a variety of metals mainly due to its ability to act as a tridentate ligand both in an octahedral [1] and in a square planar environment [2].

Concerning Pt(II) chemistry, great emphasis has been given to Pt(II)–triphos systems where the triphosphine occupies three coordination positions while a monodentate anionic or neutral ligand is bonded in the fourth position (Fig. 1); these complexes represent excellent probes for mechanistic studies of substitution reactions at the metal, small molecule activation and catalytic processes [3].

For example, [PtX(triphos)]$^+$ complexes (X = monodentate anionic ligand) have been used to probe the *trans* influence of a variety of X ligands upon the central phosphorus–metal bond and to establish a sequence of nucleophilicity in the X ligand exchange reactions [4].

We have recently reported that when X is the easily replaceable anion triflate ($OTf^- = CF_3SO_3^-$), complex [PtOTf(triphos)]$^+$ can be regarded as a versatile synthon to a variety of Pt–triphos complexes [5].

During that work, we found that [PtOTf(triphos)]OTf can be most conveniently prepared by treatment of [$PtMe_2$(triphos-*P*,*P*′)] with triflic acid.

Complex [$PtMe_2$(triphos-*P*,*P*′)], (**1**), is an example of bidentate coordination of triphos, whose third phosphorus atom is dangling out the coordination plane.

The bidentate coordination mode of tridentate phosphines has been observed in a few complexes and it can be accomplished in some different ways (Fig. 2): (i) through two of the three equivalent phosphorus atoms as in the tripodal phosphine 1,1,1-tris(diphenylphosphinomethyl)ethane, giving a six membered ring [6]; (ii) through the two terminal phosphino groups as in $PPh(CH_2PPh_2)_2$, giving a six membered ring including three phosphorus atoms [7]; (iii) through the central and

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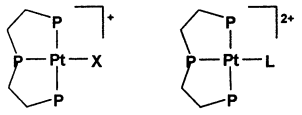


Fig. 1. Pt-complexes with triphos acting as a tridentate ligand.

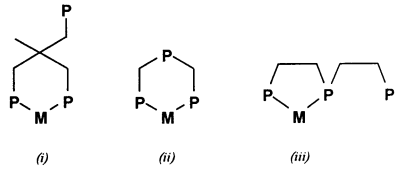


Fig. 2. Some selected coordination modes of tridentate phosphines.

one of the terminal phosphorus atoms giving a five membered ring [8], like triphos in complex **1**. This last mode gives a particularly dynamic character to square planar Pt(II) complexes for two reasons: (a) the length of the pendant arm allows the uncoordinated phosphorus to reach the metal center; (b) the great tendency to form two stable five membered chelate rings [9].

The preparation of **1**, based on the substitution of cod (cod = 1,5-cyclooctadiene) with triphos in [$PtMe_2$(cod)], was first reported by Meek et al. in 1977 [10]. They also described the fluxional behavior of **1** in solution, due to the attack of the uncoordinated phosphorus on platinum leading to a fast exchange between the two external phosphorus atoms of triphos via a five coordinated intermediate, whose geometry is discussed also in a recent paper by us [5b].

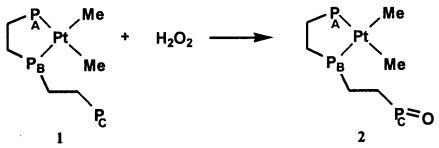
We reasoned that the presence in complex **1** of a free phosphorus with a high tendency to coordinate should be a powerful driving force to a variety of reactions.

We report here the selective oxidation of the uncoordinated phosphorus and the X-ray crystal structure of the oxidation product; the reactions of **1** with platinum and non platinum precursors to form homotrimetallic and heterotrimetallic complexes, respectively, where triphos acts as a chelating/bridging ligand. Finally it will be shown that the addition of L and triflic acid in sequence can easily convert complex **1** into a variety of $[PtL(triphos)]^{2+}$ complexes (L = SMe_2, pyridine, PPh_3), where triphos acts as a tridentate ligand.

2. Results and discussion

2.1. Oxidation of the uncoordinated phosphorus of complex 1

The treatment of **1** in benzene with aqueous H_2O_2 gives complex **2** where only the uncoordinated phosphorus is oxidized, Eq. (1).



(1)

The $^{31}P\{^1H\}$ NMR of **2** shows the presence of three inequivalent phosphorus atoms: P_A appears as a doublet with satellites at 48.6 ppm due to its coupling with P_B ($^2J(P_BP_A) = 4.5$ Hz) and Pt ($^1J(PtP_A) = 1810$ Hz); P_B is a doublet of doublets with satellites at 49.0 ppm being coupled with P_A, with P_C ($^3J(P_CP_B) = 53.2$ Hz) and with platinum ($^1J(PtP_B) = 1803$ Hz). These chemical shifts are in the typical range of phosphorus atoms included in a five membered chelate ring [11]. Finally, P_C is a doublet ($^3J(P_BP_C) = 53.2$ Hz) at 33.2 ppm, which is a typical shift of a phosphine oxide [12].

The coupling constant $^2J(P_BP_A)$ is small compared with $^3J(P_BP_C)$ (4.5 vs. 53.2 Hz). This is due, as previously noted in analogous situations [13], to the two components of J(PP): ^BJ(PP) 'coupling through the backbone' and ^MJ(PP) 'coupling through the metal'. The observed coupling constant is the algebraic sum of ^BJ(PP) and ^MJ(PP): in the case of a five membered ring ^BJ(PP) and ^MJ(PP) have often similar absolute values but opposite signs and, therefore, the observed value is smaller than the coupling $J(P_BP_C)$ occurring only via the backbone.

The recrystallization of crude **2** from $CHCl_3$ and Et_2O gave crystals suitable for X-ray diffraction. Fig. 3 shows the ORTEP view of **2**. The two Pt–P bonds have similar lengths (2.263 and 2.256 Å) and also the two Pt–C

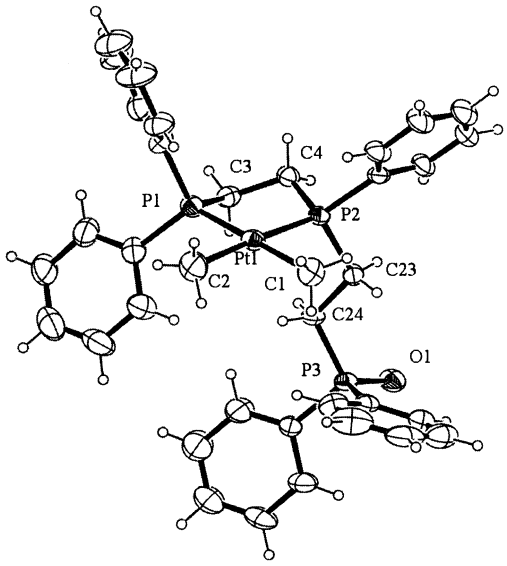


Fig. 3. ORTEP [28] view of compound [$PtMe_2$(triphosPO-P,P')], **2**. Selected bond lengths and angles: Pt1–P1 = 2.268(3); Pt1–P2 = 2.258(3); Pt1–C1 = 2.11(1); Pt1–C2 = 2.09(1) Å; P1–Pt1–P2 = 86.0(1); P1–Pt1–C1 = 179.0(4); P1–Pt1–C2 = 95.4(4); P2–Pt1–C1 = 93.1(4); P2–Pt1–C2 = 177.5(5); C1–Pt1–C2 = 85.4(5)°.

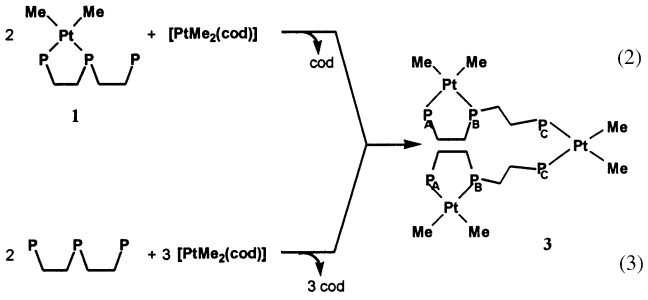
bonds (2.11, 2.09 Å). Pt and the four coordinated atoms lie in a plane and the bond angles at Pt are very near to 90°. The distance between O1 and P3 [Fig. 3, P_C in Eq. (1)] is 1.480 Å; O1 points away from Pt and there are not intramolecular interactions between P_C and Pt.

This oxidation process creates a diphosphine-phosphine oxide ligand on platinum: this species has the potentiality to act as a tridentate ligand exploiting the coordination ability of P=O particularly towards hard metal ions. The formation of the same ligand on palladium has been recently reported by Sadler [12].

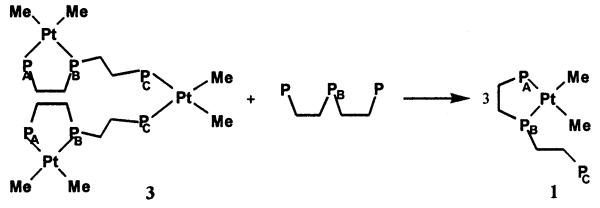
2.2. Coordination of the dangling phosphorus of complex 1. Formation of trinuclear complexes

2.2.1. The homotrimetallic complex $[Pt_3Me_6(triphos)_2]$, (3)

The reaction between **1** and $[PtMe_2(cod)]$ in a 2:1 ratio gives the trinuclear platinum complex **3** which can be alternatively prepared from triphos and $[PtMe_2(cod)]$ in a 2:3 ratio, Eqs. (2) and (3).



When **3** is treated with one equivalent of triphos, **1** is recovered as the only product, Eq. (4).



In this reaction the coordinated P_C of complex **3**, an alkyldiarylphosphine, is replaced by the more nucleophilic P_B of the free ligand (a dialkylarylphosphine); the reaction is favored also by the formation of three chelate rings (3 equiv. of **1**) starting from two (1 equiv. of **3**).

The identification of **3** is based mainly on $^{31}P\{^1H\}$-NMR observations:

i) from their high frequency chemical shifts, it can be deduced that P_A and P_B (48.5 and 47.6 ppm, respectively) are in a five membered ring while the 'normal' shift of P_C (18.5 ppm) is consistent with a monodentate coordination mode;

ii) the size of $^1J(PtP)$ for P_A, P_B and P_C (1801, 1797 and 1891 Hz, respectively) shows that all these three atoms are directly bonded to platinum and *trans* to a group of high *trans* influence like CH_3;

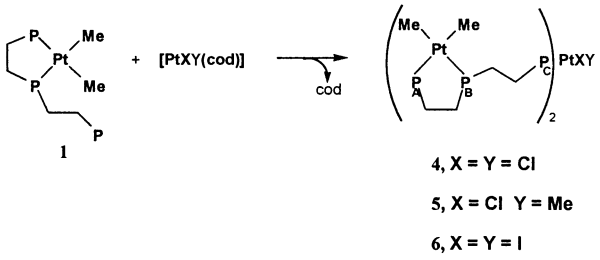
iii) the P donors on the central platinum are *cis* to each other as indicated by $^1J(Pt_{(2)}P_C) = 1891$ Hz (comparable for example with the value of 1878 Hz in *cis*-$[PtMe_2(PPh_3)_2]$ [14]).

The chiral centre at P_B in **3** leads to the prediction of two diastereoisomers (*rac* and *meso*) of **3** and these are indeed observed in the $^{31}P\{^1H\}$ NMR spectra of **3** which shows two sets of signals with the same multiplicity in the ratio of 1:1.

The $^{31}P\{^1H\}$ NMR spectrum changes upon raising the temperature. In DMSO at 20 °C, two sets of signals are observed for P_A P_B and P_C consistent with the presence of *rac* and *meso* diastereomers. These two sets of signals coalesce at higher temperatures and at above 100 °C, only one set of $^{31}P\{^1H\}$ NMR is observed (see Section 3). The variable temperature experiment was run also in toluene to exclude the involvement of the highly coordinating solvent DMSO in the process and also in this case a single set of signals was observed above 90 °C. This result is consistent with the interconversion of the diastereoisomers by inversion at P_B. The Pt–P_B coupling undergoes small changes during the variable temperature experiments (from 1790 Hz at 25 °C to 1763 Hz at 100 °C in toluene, from 1813 Hz at 25 °C to 1784 Hz at 140 °C in DMSO): this seems to indicate that the process does not involve rupture of the Pt–P_B bond. Although the inversion at free phosphino phosphorus at high temperature has been observed long ago [15], to our knowledge the inversion of configuration at phosphorus belonging to a coordinated phosphine has not previously been observed.

2.2.2. Other homotrimetallic complexes

The reaction of **1** with [PtXY(cod)] (X = Y = Cl; X = Cl Y = Me; X = Y = I) gives the homotrimetallic complexes $[Pt_3Me_4Cl_2(triphos)_2]$, **4**, $[Pt_3Me_5Cl(triphos)_2]$, **5**, and $[Pt_3Me_4I_2(triphos)_2]$, **6** with chelating/bridging triphos, Eq. (5).

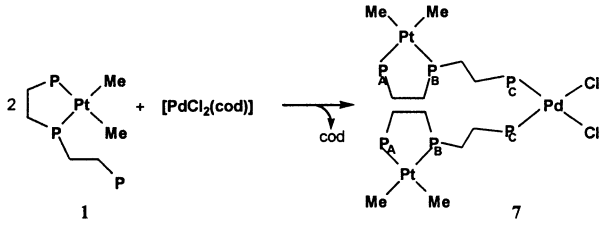


In each case the product was obtained as a 1:1 couple of *rac* and *meso* diastereoisomers.

The coupling constant between P_C and central Pt is diagnostic for the stereochemistry around the central platinum: $^1J(PtP_C)$ has a value of 3654 Hz in **4** indicating a *cis* geometry (compared with 3674 for *cis*-$[PtCl_2(PPh_3)_2]$ [16]), while the values of 3070 in **5** and 2400 Hz in **6** support a *trans* geometry around central platinum in these complexes (compare with 3144 Hz in *trans*-$[PtClMe(PPh_3)_2]$ [17] and 2477 Hz in *trans*-$[PtI_2(PPh_3)_2]$, respectively [18]).

2.2.3. Formation of the heterotrimetallic complexes $[Pt_2PdMe_4Cl_2(triphos)_2]$, (7) and $[Pt_2RhMe_4(cod)(triphos)_2]PF_6$, (8)

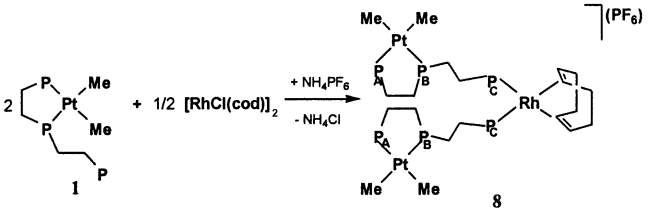
The reaction between **1** and $[PdCl_2(cod)]$ gives the heterotrimetallic complex **7**, $[Pt_2PdMe_4Cl_2(triphos)_2]$ as a 1:1 pair of diastereoisomers, Eq. (6).



(6)

The *cis* geometry around the central Pd is indicated by the presence, in the IR spectrum, of two bands of medium intensity at 295 and 307 cm^{-1} due to the stretching of *cis* Pd–Cl bonds [19].

Complex **1** reacts with 0.5 equiv. of the dimeric chloro-bridged complex $[Rh(cod)Cl]_2$, in the presence of aqueous NH_4PF_6, to give $[Pt_2RhMe_4(cod)(triphos)_2]PF_6$, (**8**), as a couple of diastereoisomers, Eq. (7).



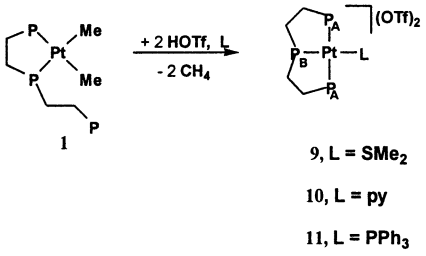
(7)

In the $^{31}P\{^1H\}$ NMR spectrum of **8**, P_C is observed as a doublet of doublets at 28.1 ppm (^1J(RhP) 150 Hz, $^3J(P_BP_C) = 45$ Hz). We did not succeed in isolating **8** as a pure product because of the presence of variable quantities of the side product $[PtMe(triphos)]PF_6$, due to the partial protonolysis of **1** by NH_4^+.

2.3. Formation of mononuclear dicationic complexes via protonolysis of 1

Another consequence of the tendency of the dangling phosphorus to coordinate to a metal is the high susceptibility of **1** to double protonolysis involving both the methyl groups on platinum (Scheme 1) which can be promptly removed (step i and step ii in Scheme 1) using strong coordinating acids like HOTf, *p*-TsOH and CF_3COOH.

We have previously shown that the product of the reaction of **1** with triflic acid, complex [PtOTf(triphos)]OTf, can be regarded as a versatile precursor to a variety of $[PtL(triphos)]^{2+}$ obtainable via OTf substitution [5]. We then observed that the same products can be obtained directly from **1** in a single step: in fact when the protonolysis with HOTf is carried out in the presence of a neutral electron donor L, the product recovered from the process is $[PtL(triphos)]^{2+}$, where triphos acts as a tridentate ligand and L is bonded in the fourth position, Eq. (8).



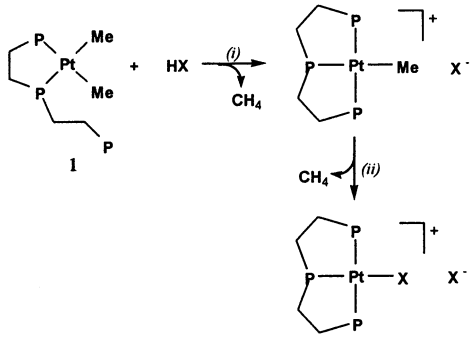
(8)

In Section 3, we describe the new preparation of the known complexes $[Pt(SMe_2)(triphos)]^{2+}$, (**9**), $[Pt(py)(triphos)]^{2+}$, (**10**), and $[Pt(PPh_3)(triphos)]^{2+}$, (**11**).

The preparation and characterization of **9**, **10** and **11** have been previously reported by us [5]; complex **11** has been recently obtained also treating [PtCl(triphos)]Cl with $SnCl_2$ and PPh_3 [3]. The synthetic route here reported for these complexes represents an improvement in terms of both time and yields (see Section 3).

2.4. CO trapping

When a solution containing **1** in CH_2Cl_2 is saturated with carbon monoxide and 2 equiv. of triflic acid are added, the $^{31}P\{^1H\}$ NMR shows the carbonylic complex $[Pt(CO)(triphos)](Otf)_2$ as the only phosphorus containing product [$\delta(P_A) = 49.3$ ppm, $^1J(PtP_A) = 2116$ Hz; $\delta(P_B) = 98.4$ ppm, $^1J(PtP_B) = 2628$ Hz]. Every attempt



Scheme 1.

to isolate this product gave only [PtOTf(triphos)]OTf. As previously noted, this behavior indicates that the equilibrium between [PtOTf(triphos)]OTf and $[Pt(CO)(triphos)](OTf)_2$ favors the CO complex only in the presence of carbon monoxide (saturated solution of CO in CH_2Cl_2), [5].

We tried to isolate the cation $[Pt(CO)(triphos)]^{2+}$ by precipitating it in methanol as a salt of the non coordinating anion BPh_4^-, excluding in this way the competition between CO and the external anion. The only product we obtained from this reaction was the organometallic complex $[Pt(COOMe)(triphos)]BPh_4$, (**12a**), formed by the nucleophilic attach by methanol on the coordinated CO [20]. In the Section 3 the complete characterization of the new complex [Pt(COOMe)(triphos)]BPh_4, (**12a**), is reported.

$[Pt(COOMe)(triphos)]^+$ can be obtained also as a triflate by adding to a CH_2Cl_2 solution of **1** 2 equiv. of triflic acid, an excess of carbon monoxide and methanol in sequence (Scheme 2). All attempts to isolate the complex from this route led to isolation of [Pt(OTf)(triphos)]OTf, probably generated by the protonolysis of [Pt(COOMe)(triphos)]OTf, (**12b**), by the triflic acid released in step (iii). All the Pt-complexes depicted in Scheme 2 have been identified by $^{31}P\{^1H\}$ NMR [21].

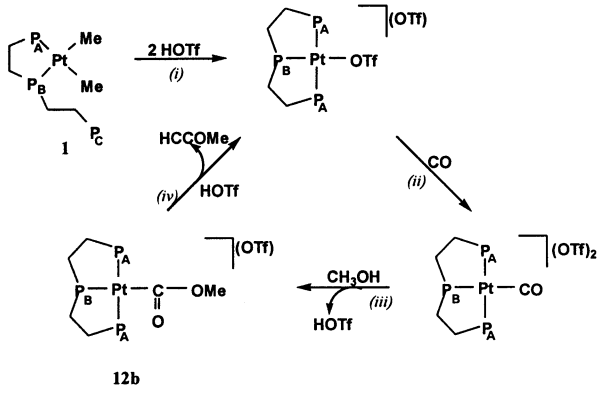
The ability shown by Pt–triphos to uptake and release carbon monoxide may lead to useful catalysis by the system $[Pt(CO)(triphos)](OTf)_2$–[PtOTf(triphos)]OTf and this will be investigated.

3. Experimental

$[PtMe_2(cod)]$, $[PtCl_2(cod)]$, [PtMeCl(cod)], $[PtI_2(cod)]$, $[PdCl_2(cod)]$ and $[RhCl(cod)]_2$ were prepared by literature methods [22–24].

$[PtMe_2(triphos\text{-}P,P')]$, (**1**), was prepared as previously reported [10].

All the other chemicals were purchased (reagent grade) and solvents were distilled before using. Elemental analyses (C, H, N, S) were performed using a Carlo Erba instrument model EA1110. FT-IR spectra were recorded on a Nicolet 510P FT-IR instrument (4000–200 cm^{-1}) in CsI. NMR spectra were run on a Bruker AM spectrometer 200 MHz for ^1H NMR (TMS internal reference) and 81.15 MHz for $^{31}P\{^1H\}$ NMR (H_3PO_4 85% external reference). $^{31}P\{^1H\}$ NMR spectra at variable temperature were recorded on a Varian Gemini 300 spectrometer operating at 121.42 Hz. MS FAB (Fast atomic bombardment) spectra were acquired by a Hewlett–Packard MS engine HP5989 A mass spectrometer using a *p*-nitrobenzylalcohol matrix.



Scheme 2.

3.1. Syntheses

3.1.1. $[PtMe_2(triphosPO\text{-}P,P')]$, (**2**)

a) Eight ml of H_2O_2 (3% in water) were added to a solution containing 57 mg (0.075 mmol) of **1** in 3 ml of benzene and the reaction mixture was stirred for 1 h. The organic phase was separated, dehydrated over Na_2SO_4 and the solvent removed under reduced pressure to leave a white solid (46 mg, 79%).

b) Alternatively the precursor **1** can be generated in situ by dropwise addition of a solution containing $[PtMe_2(cod)]$ (25 mg, 0.075 mmol) in 1 ml of the distilled benzene to a second solution of an equimolar amount of triphos (40 mg, 0.075 mmol) in 2 ml of the same solvent, under nitrogen at room temperature. After 30 min the complete formation of **1** was checked by $^{31}P\{^1H\}$ NMR and the solution was treated with aqueous H_2O_2 and worked up as above. The reaction gave 48 mg of **2** (83%) (Found: C, 55.6; H, 5.1. Calc. for $C_{36}H_{39}OP_3Pt$: C, 55.7; H, 5.1%). ^1H NMR ($CDCl_3$): 0.7 [6H, m, ^2J(PtH) 69.4 Hz, Pt–CH_3], 2.2 [8H, m, P–CH_2], 7.5 [25H, m, aromatics]; $^{31}P\{^1H\}$ NMR (C_6D_6): 48.6 [P_A, d, $^2J(P_BP_A)$ 4.5 Hz, $^1J(PtP_A)$ 1810 Hz], 49.0 [P_B, dd, $^3J(P_CP_B)$ 53.2 Hz, $^2J(P_AP_B)$ 4.6 Hz, $^1J(PtP_B)$ 1803 Hz], 33.2 [P_C, d, $^3J(P_BP_C)$ 53.2 Hz].

3.1.2. $[Pt_3Me_6(triphos)_2]$, (**3**)

a) Ninety one mg (0.12 mmol) of **1** were dissolved in 3 ml of distilled benzene and added dropwise to second solution of $[PtMe_2(cod)]$ (20 mg, 0.06 mmol) in 2 ml of the same solvent. The mixture was kept under stirring at room temperature for 1h and then the solvent was removed in vacuo. The residue was washed with diethyl ether and *n*-pentane, filtered and dried over P_2O_5 (88.4 mg, 85%).

b) Alternatively a solution of $[PtMe_2(cod)]$ (74.6 mg, 0.225 mmol) in 2 ml of distilled benzene was added under nitrogen to a stirred solution of triphos (80 mg, 0.15 mmol) in 2 ml of the same solvent. The

stirring was prolonged for 2 h and then the solvent was removed to leave a white solid which was washed with *n*-pentane. (106 mg, 81%). (Found: C, 51.1; H, 4.9. Calc. for $C_{74}H_{84}P_6Pt_3$: C, 50.9; H, 4.8%). ^{1}H NMR($CDCl_3$): 0.3–0.8 [18H, m, Pt–CH_3], 1.1–1.6 [16H, m, P–CH_2], 7.0–7.7 [50H, m, aromatics].

$^{31}P\{^1H\}$ NMR ($CDCl_3$): two diastereomers distinguishable **D$_1$** 8.5 [P_A, d, $^1J(PtP_A)$ 1801 Hz, $^2J(P_BP_A)$ 5.2 Hz], 47.6 [P_B, dd, $^1J(PtP_B)$ 1797 Hz, $^2J(P_AP_B)$ 5.2 Hz, $^3J(P_CP_B)$ 16.7 Hz], 18.5 [P_C, m, $^1J(PtP_C)$ 1891 Hz]; **D$_2$** 48.4 [P_A, d, $^1J(PtP_A)$ 1802 Hz, $^2J(P_BP_A)$ 4.7 Hz], 47.1 [P_B, dd, $^1J(PtP_B)$ 1796 Hz, $^2J(P_AP_B)$ 4.7 Hz, $^3J(P_CP_B)$ 15.1 Hz], 18.0 [P_C, m, $^1J(PtP_C)$ 1891 Hz]; $^{31}P\{^1H\}$ NMR (DMSO-d_6, 140 °C) 49.4 [P_A, s, $^1J(PtP_A)$ 1803 Hz], 48.0 [P_B, d, $^1J(PtP_B)$ 1784 Hz, $^3J(P_CP_B)$ 35 Hz], 19.3 [P_C, d, $^1J(PtP_C)$ 1866 Hz, $^3J(P_BP_C)$ 35 Hz]. $^{31}P\{^1H\}$ NMR (toluene-d_8, 100 °C) 49.4 [P_A, s, $^1J(PtP_A)$ 1792 Hz], 48.1 [P_B, d, $^1J(PtP_B)$ 1763 Hz, $^3J(P_CP_B)$ 42 Hz], 19.4 [P_C, d, $^1J(PtP_C)$ 1869 Hz, $^3J(P_BP_C)$ 42 Hz].

3.1.3. *[Pt$_3$Me$_4$Cl$_2$(triphos)$_2$], (**4**)*

A solution of [$PtCl_2$(cod)] (28 mg, 0.075 mmol) in 1 ml of distilled benzene was added to a stirred solution of **1** (114 mg, 0.15 mmol). After 20 min of stirring, the volume was reduced to a half in vacuo and the product was precipitated with *n*-pentane. The white powder (94 mg, 70%) was filtered, washed with *n*-pentane and dried over P_2O_5. (Found: C, 48.5; H, 4.6. Calc. for $C_{72}H_{78}Cl_2P_6Pt_3$: C, 48.4; H, 4.4%). IR (CsI) ν_{max} (cm^{-1}) 341 and 292 (Pt–Cl). ^{1}H NMR ($CDCl_3$): 0.4 [6H, m, ^2J(PtH) 70 Hz, Pt–CH_3], 0.55 [6H, m, ^2J(PtH) 69 Hz, Pt–CH_3], 1.7–3.0 [16H, m, P–CH_2], 6.8–8.0 [50H, m, aromatics]; $^{31}P\{^1H\}$ NMR ($CDCl_3$): 48.8 [P_A, m, $^1J(PtP_A)$ 1809 Hz], 49.4 [P_B, m, $^1J(PtP_B)$ 1798 Hz], 9.6 [P_C, m, $^1J(PtP_C)$ 3654 Hz].

3.1.4. *[Pt$_3$Me$_5$Cl(triphos)$_2$], (**5**)*

The complex was obtained from 0.15 mmol (114 mg) of **1** dissolved in 3 ml of distilled benzene and 0.075 mmol (26 mg) of [PtMeCl(cod)] in 3 ml of the solvent. The work up was the same as previous. The final product was obtained as a white solid (125 mg, 95%). (Found: C, 49.6; H, 4.8. Calc. for $C_{73}H_{81}ClP_6Pt_3$: C, 49.7; H, 4.6%). ^{1}H NMR ($CDCl_3$): −0.03 [3H, t, ^2J(PtH) 80 Hz, $Pt_{(2)}$–CH_3], 0.6 [12H, m, ^2J(PtH) 68.2 Hz, Pt–CH_3], 1.7–3.2 [16H, m, P–CH_2], 7.3–7.8 [50H, m, aromatics]; $^{31}P\{^1H\}$ NMR ($CDCl_3$): 49.5 [P_B, m, $^1J(PtP_B)$ 1799 Hz], 48.7 [P_A, m, $^1J(PtP_A)$ 1810 Hz], 24.5 [P_C, m, $^1J(PtP_C)$ 3070 Hz].

3.1.5. *[Pt$_3$Me$_4$I$_2$(triphos)$_2$], (**6**)*

The complex was obtained from 0.15 mmol (114 mg) of **1** dissolved in 3 ml of distilled benzene and 0.075 mmol (42 mg) of [PtI_2(cod)] in 3 ml of the solvent. The mixture was treated as above. The final product was obtained as a white solid (114 mg, 77%). (Found: C, 44.1; H, 4.2. Calc. for $C_{72}H_{78}I_2P_6Pt_3$: C, 44.0; H, 3.9%). ^{1}H NMR ($CDCl_3$): 0.55 [6H, m, ^2J(PtH) 70 Hz, Pt–CH_3], 0.6 [6H, m, ^2J(PtH) 69.4 Hz, Pt–CH_3], 1.7–3.0 [16H, m, P–CH_2], 7.3–7.7 [50H, m, aromatics]; $^{31}P\{^1H\}$ NMR ($CDCl_3$): 48.8 [P_A, m, $^1J(PtP_A)$ 1800 Hz], 49.4 [P_B, m, $^1J(PtP_B)$ 1791 Hz], 5.7 [P_C, m, $^1J(PtP_C)$ 2400 Hz].

3.1.6. *[Pt$_2$PdMe$_4$Cl$_2$(triphos)$_2$], (**7**)*

A solution of [$PdCl_2$(cod)] (21 mg, 0.075 mmol) in 1 ml of distilled benzene was added to a stirred solution of **1** (114 mg, 0.15 mmol) in 3 ml of the same solvent. After 15 min of stirring at room temperature, the reaction was worked as above and the final product was isolated as a pale yellow solid (81 mg, 64%). (Found: C, 50.8; H, 4.7. Calc. for $C_{72}H_{78}Cl_2P_6PdPt_2$: C, 50.9; H, 4.8%). IR (CsI) ν_{max} (cm^{-1}) 307 and 295 (Pd–Cl). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 48.6 [P_A, m, $^1J(PtP_A)$ 1804 Hz], 49.4 [P_B, m, $^1J(PtP_B)$ 1825 Hz], 18.4 [P_C, m].

3.1.7. *[Pt$_2$RhMe$_4$(cod)(triphos)$_2$]PF$_6$, (**8**)*

A solution of $[RhCl(cod)]_2$ (25 mg, 0.05 mmol) in 1 ml of distilled CH_2Cl_2 was added under nitrogen to a stirred deoxygenated aqueous solution (2 ml) of NH_4PF_6 (50 mg, 0.3 mmol). A solution of **1**, generated in situ by 0.2 mmol of [$PtMe_2$(cod)] and 0.2 mmol of triphos in 3 ml of distilled CH_2Cl_2 as checked by $^{31}P\{^1H\}$ NMR, was added to this biphasic system. After few min. of stirring, the organic yellow phase was separated, dehydrated, taken to dryness in vacuo and the yellow residue was washed with *n*-pentane. $^{31}P\{^1H\}$ NMR shows that this product is always contaminated by variable quantities of the side product [PtMe(triphos)]PF_6 and other species due to rapid decomposition; for this reason a complete characterization was not possible.

$^{31}P\{^1H\}$ NMR ($CDCl_3$): 49.3 [P_A, d, $^1J(PtP_A)$ 1797 Hz, $^2J(P_BP_A)$ 5 Hz], 48.9 [P_B, dd, $^1J(PtP_B)$ 1782 Hz, $^3J(P_CP_B)$ 45 Hz, $^2J(P_AP_B)$ 5 Hz], 28.1 [P_C, dd, $^1J(RhP_C)$ 150 Hz, $^3J(P_BP_C)$ 45 Hz].

3.2. *Conversion of **1** into [PtL(triphos)](OTf)$_2$, L = SMe$_2$, pyridine, PPh$_3$*

In a typical reaction, 0.112 mmol of **1** have been generated by adding a solution of [$PtMe_2$(cod)] (37 mg, 0.112 mmol) in 2 ml of distilled CH_2Cl_2 to a second solution containing triphos (60 mg, 0.112 mmol) in 2 ml of the same solvent. After few minutes of stirring, the complete formation of **1** was checked by $^{31}P\{^1H\}$ NMR and then 0.135 mmol (1.2 equiv.) of L (**9** L = SMe_2, **10** L = pyridine, **11** L = PPh_3) and HOTf (0.021 ml, 0.236 mmol, 2.1 equiv.) were added in this order. After 15 min of stirring at room temperature, the solution was taken

to dryness in vacuo. The solid residue was washed with diethyl ether and dried over P_2O_5.

*3.2.1. [Pt(SMe$_2$)(triphos)](OTf)$_2$, (**9**)*

(107 mg, 87%) Found: C, 41.7; H, 3.65; S, 8.9. Calc. for $C_{38}H_{39}F_6O_6P_3PtS_3$: C, 41.87; H, 3.60; S, 8.82%). ^{1}H NMR (CD_3OD): 1.9 (6H, d, ^3J(PtH) 35 Hz, ^4J(PH) 3.7 Hz, S(CH_3)$_2$), 2.9, 3.7 (8H, 2m, CH_2–CH_2), 7.4–8.0 (25H, m, aromatics); ^{31}P{^{1}H} NMR (CD_3OD): 48.7 [P_A, s, ^1J(PtP$_A$) 2393 Hz], 94.2 [P_B, s, ^1J(PtP$_B$) 2705 Hz)].

*3.2.2. [Pt(py)(triphos)](OTf)$_2$, (**10**)*

(116 mg, 93% yield). Found: C, 44.6; H, 3.45; N, 1.3; S, 5.6. Calc. for $C_{41}H_{38}F_6NO_6P_3PtS_2$: C, 44.49; H, 3.46; N, 1.26; S, 5.79%). ^{31}P{^{1}H} NMR (CD_3OD): 49.4 [P_A, s, ^1J(PtP$_A$) 2408 Hz], 81.4 [P_B, s, ^1J(PtP$_B$) 2825 Hz].

*3.2.3. [Pt(PPh$_3$)(triphos)](OTf)$_2$, (**11**)*

(130 mg, 89%). (Found: C, 49.85; H, 3.55; S, 4.88. Calc. for $C_{54}H_{48}F_6O_6P_4PtS_2$: C, 50.28; H, 3.75; S, 4.97%). ^{31}P{^{1}H} NMR ($CDCl_3$): 12.7 [PPh_3, dt, ^2J(P$_B$P) 297.6 Hz, ^2J(P$_A$P) 22.2 Hz, ^1J(PtP) 2570 Hz], 44.5 [P_A, d, ^1J(PtP$_A$) 2398 Hz], 94.0 [P_B, d, ^1J(PtP$_B$) 2146 Hz].

*3.3. Synthesis of [Pt(COOMe)(triphos)]BPh$_4$, (**12**)*

A solution of [$PtMe_2$(cod)] (75 mg, 0.23 mmol) in 3 ml of distilled CH_2Cl_2 was added to a stirred solution of triphos (123 mg, 0.23 mmol) in 4 ml of the same solvent. The solution was saturated with CO by bubbling for 10 min and then 2.2 equiv. of HOTf (45 μl) were added. The volume was reduced to 2 ml using a continuous flow of CO, and the solution diluted with 3 ml of methanol. A solution containing an excess of $NaBPh_4$ in methanol (120 mg, 0.35 mmol in 3 ml) was finally added to precipitate a white solid which was filtered and washed with methanol (210 mg, 82%). (Found: C, 64.70; H, 4.95. Calc. for $C_{60}H_{56}BO_2P_3Pt$: C, 64.98; H, 5.05%). ^{1}H NMR ($CDCl_3$): 3.25 (3H, s, $OOCH_3$), 1.2–3.2 (8H, m, CH_2–CH_2), 6.6–7.7 (45H, m, aromatics); ^{31}P{^{1}H} NMR ($CDCl_3$): 37.6 [P_A, t, ^1J(PtP$_A$) 2676 Hz, ^2J(P$_B$P$_A$) 7 Hz], 86.8 [P_B, d, ^1J(PtP$_B$) 1584 Hz, ^2J(P$_A$P$_B$) 7 Hz]. MS-FAB: 788 m/z, [Pt(COOMe)-(triphos)]$^+$.

*3.4. X-ray crystal structure of [PtMe$_2$(triphosPO-P,P′)], (**2**)*

Crystals of **2** were obtained from $CHCl_3$ and Et_2O.

$C_{36}H_{39}OP_3Pt\cdot 1/2(C_4H_{10}O)$, $M = 812.73$, colorless crystal, Enraf Kappa CCD diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å, graphite monochromatized). $T = 295$ K. Monoclinic, space group $C2/c$, $a = 15.8194(2)$, $b = 13.2054(2)$, $c = 34.5578(6)$ Å, $\beta = 93.9560(5)^\circ$, $U = 7202.0(2)$ Å^3, $Z = 8$, $D_c = 1.490$ g cm^{-3}. 13 205 reflections collected ($3 \leq \theta \leq 26^\circ$), 6703 unique reflections ($R_{int} = 0.070$), $\mu = 4.059$ mm^{-1}. Empirical absorption correction using the program SORTAV [25]. The crystal includes molecules of solvent (diethyl ether) which show a high degree of disorder around twofold axes. The structure was solved by direct methods (SIR92, [26]) and refined by the full-matrix least-squares method based on F^2 (SHELXL-97, [27]) with all non-hydrogen atoms anisotropic and hydrogens in calculated positions. Final R [$F^2 \geq 2\sigma(F^2)$] = 0.079 and wR (F^2, all reflections) = 0.203.

4. Supplementary material

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication N. CCDC 173567. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336 033; e-mail: deposit@ccdc.cam.ac.uk).

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