Reactivity of Alkynyl Platinum Complexes towards PPh$_2$H and PPh$_2$(O)H: Unexpected Formation of Alkynyl Tetralithium Diplatinum Compounds Stabilized by μ_3-(κ^3P,O,O-PPh$_2$O$^-$) Ligands

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Abstract: The reactivity of Li$_2$[Pt(C$\equiv$CR)$_4$] and *cis*-[Pt(C$\equiv$CR)$_2$COD] (R = *t*Bu **a**, Ph **b**) towards PPh$_2$H and PPh$_2$(O)H has been investigated. The course of the reaction of Li$_2$[Pt(C$\equiv$CR)$_4$] with PPh$_2$H strongly depends not only on the reaction conditions employed, but also on the alkyne subtituent R. Thus, treatment of Li$_2$[Pt(C$\equiv$C*t*Bu)$_4$] with PPh$_2$H (1:3) in an acetone/ethanol mixture affords *trans*-[Pt(C$\equiv$C*t*Bu)$_2$(PPh$_2$H)$_2$] (**1a**) together with an unusual tetralithium diplatinum species [{Pt(C$\equiv$C*t*Bu)$_{2-x}$(PPh$_2$O)$_{2+x}$Li$_2$S$_n$}$_2$] (x = 0, S$_n$ = (H$_2$O)$_3$ **2′a**; x = 1, S$_n$ = (H$_2$O)$_2$ **3′a**) in low yield. Complexes [{Pt(C$\equiv$C*t*Bu)$_2$(PPh$_2$O)$_2$Li$_2$(μ-H$_2$O)(Me$_2$CO)$_2$}$_2$] (**2a**) and [{Pt(C$\equiv$C*t*Bu)(PPh$_2$O)$_3$Li$_2$(H$_2$O)(thf)}$_2$] (**3a**) have been characterized by X-ray diffraction. On the other hand, treatment of Li$_2$[Pt(C$\equiv$CPh)$_4$] with PPh$_2$H (1:3 molar ratio) allows the synthesis not only of the analogous derivatives **1b** and **2′b**, but also of the unexpected, novel mononuclear compound [Pt(C$\equiv$CPh)$_2$(PPh$_2$CHPhCH$_2$PPh$_2$)] (**4b**), which has been characterized by X-ray diffraction and contains *cis*-terminal alkynyl groups and the new chelating ligand 1-phenyl-1,2-bis(diphenylphosphino)ethane. Similar σ-alkynyl complexes *cis*-[Pt(C$\equiv$CR)$_2$(PPh$_2$H)$_2$] **5** are easily prepared by displacement of the cyclooctadiene (COD) ligand from the precursor *cis*-[Pt(C$\equiv$CR)$_2$COD] at low temperature (−30 °C) by PPh$_2$H. The unexpected diplatinum complex [{Pt(C$\equiv$C*t*Bu)(μ-PPh$_2$)(PPh$_2$H)}$_2$] (**6a**), also characterized by X-ray diffraction, is also formed (2% yield) during the synthesis of complex **5a**. By contrast, *cis*-[Pt(C$\equiv$CR)$_2$COD] reacts with PPh$_2$(O)H in CH$_2$Cl$_2$ at low temperature (−40 °C), either in 1:2 or 1:3 molar ratio, to produce novel diphenylphosphinous acid/phosphinite complexes [{Pt(C$\equiv$CR){(PPh$_2$O)$_2$H}(PPh$_2$OH)] **7**, which are precursors of the related neutral compounds [Pt(C$\equiv$CR){(PPh$_2$O)$_2$H}L] (L = PEt$_3$, PPh$_2$H, CN*t*Bu **8–10**) and the ionic (NBu$_4$)[Pt(C$\equiv$CR)(CN){(PPh$_2$O)$_2$H}] (**11**), which are formed through simple PPh$_2$OH substitution reactions. Complexes **7** can also be doubly deprotonated by LiOH to give the corresponding tetralithium diplatinum species **3**; this route is the most convenient one for the synthesis of **3a** and the only one for complex **3b**.

Keywords: alkynyl · diphenylphosphine · lithium · phosphinite · platinum

Introduction

Transition metal complexes with σ-acetylide ligands have attracted considerable attention recently,[1] partly because of their close relationship to organometallic vinylidene chemistry,[2] but also because of their role as promising building blocks in the design of species containing linear arrays of delocalized π systems.[3] Investigations in this area range from basic chemical transformations to the synthesis of new materials with enhanced nonlinear optical properties or to the preparation of liquid crystals and polymeric materials.[1–3] As a result of the wide variety of metals and coligands used, the family of acetylide complexes is now quite large.[1] Usually, these complexes are stabilized by innocent neutral ligands, such as tertiary phosphines or arsines (ER$_3$; E = P, As), diphosphines, and so forth. However, as far as we know, similar compounds containing secondary or primary phosphines (PR$_2$H or PRH$_2$) as coligands are very scarce.[4] This could be due in part to the fact that the high reactivity of P–H bonds in these molecules will have restricted the use of the most conventional synthetic methods employed for acetylide compounds.[1–4] On the other hand, it is well established that addition reactions of H–E (E = a heteroatom or group) across unsaturated carbon linkages are an important class of

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reactions from a synthetic viewpoint.[5] However, in spite of recent interest in the metal-catalyzed interaction of P–H bonds with acetylenes,[6] the reactivity of alkynyl complexes towards these acidic phosphines has scarcely been explored,[7] in contrast to the very rich chemistry developed for related acetylene ($R{-}C\equiv CR$) or alkylidyne ($M\equiv CR$) bridging complexes.[8a–e] P–C coupling reactions through the insertion of acetylenes, either at terminal or bridging PR_2 groups, have been also documented.[8f–j] In the context of these molecules it should be noted, however, that many di- and polynuclear complexes stabilized by phosphido ($\mu{-}PR_2^-$) and acetylide (μ-$C\equiv CR^-$) bridges have been prepared through P–C(alkyne) bond cleavage reactions starting from phosphinoacetylene ($PR_2C\equiv CR$) and metal carbonyls.[9]

Following our work on polymetallic alkynyl dibridged platinum complexes,[10] we recently explored the reactivity of diphenylalkynylphosphine compounds *cis*-$[PtX_2(PPh_2C\equiv CR')_2]$ ($X = Cl$[11a] or $C\equiv CR$[11b]; R, R′ = Ph, *t*Bu) towards the labile neutral species *cis*-$[Pt(C_6F_5)_2(thf)_2]$ (thf = tetrahydrofuran) as a possible synthetic route for obtaining hetero-bridged phosphide/acetylide compounds. However, the expected P–C(alkyne) bond cleavage process does not take place and only homo-bridged $(\mu\text{-}X)_2$ ($X = Cl$, $C\equiv CR$), or hetero-bridged (μ-$PPh_2C\equiv CPh$)(μ-X) homo- or hetero-dinuclear complexes resulted from these reactions. These results prompted us to try the preparation of heteroleptic *cis*- or *trans*-$[Pt(C\equiv CR)_2L_2]$ platinum alkynyl complexes containing PR_2H ligands. Such complexes are of interest since it is well-known that upon coordination the P–H bond is reactive and, therefore, could give appropriate precursors for phosphido (PR_2^-) ligands formed by proton transfer reactions or by addition to sources of unsaturated metal fragments.[12] In addition, the combination of these acidic molecules and the alkynyl ligands on a metal center could in principle induce new features and properties not necessarily encountered in their analogues containing tertiary phosphine ligands.

Abstract in Spanish: *Se han estudiado las reacciones de* $Li_2[Pt(C\equiv CR)_4]$ *y cis*-$[Pt(C\equiv CR)_2COD]$ ($R = tBu$ ***a***, *Ph* ***b***) *con* PPh_2H *y* $PPh_2(O)H$. *El transcurso de la reacción de* $Li_2[Pt(C\equiv CR)_4]$ *con* PPh_2H *depende no solo de las condiciones de reacción usadas, sino también del sustituyente R del alquino. Así, el tratamiento de* $Li_2[Pt(C\equiv CtBu)_4]$ *con* PPh_2H *(1:3) en acetona/etanol da lugar a la formación de trans*-$[Pt(C\equiv CtBu)_2(PPh_2H)_2]$ ***1a*** *junto con las especies* $[\{Pt(C\equiv CtBu)_{2-x}(PPh_2O)_{2+x}Li_2S_n\}_2]$ [$x = 0$, $S_n = (H_2O)_3$ ***2′a***; $x = 1$, $S_n = (H_2O)_2$ ***3′a***] *que se obtienen en bajo rendimiento.* $[\{Pt(C\equiv CtBu)_2(PPh_2O)_2Li_2(\mu\text{-}H_2O)(Me_2CO)_2\}_2]$ ***2a*** *y* $[\{Pt(C\equiv CtBu)(PPh_2O)_3Li_2(H_2O)(thf)\}_2]$***3a*** *han sido caracterizados por difracción de rayos X. Por otro lado, el tratamiento de* $Li_2[Pt(C\equiv CPh)_4]$ *con* PPh_2H *(relación molar 1:3) permite preparar no solo los derivados análogos* ***1b*** *y* ***2′b***, *sino también el compuesto mononuclear* $[Pt(C\equiv CPh)_2(PPh_2CHPhCH_2PPh_2)]$ ***4b***, *caracterizado por difracción de rayos X y que contiene el nuevo ligando 1-fenil-1,2-bis(difenilfosfino)etano. Los complejos del tipo cis*-$[Pt(C\equiv CR)_2(PPh_2H)_2]$ ***5*** *se preparan fácilmente a partir del correspondiente cis*-$[Pt(C\equiv CR)_2COD]$ *por desplazamiento del ligando COD con* PPh_2H *a baja temperatura (−30°C). El complejo dinuclear* $[\{Pt(C\equiv CtBu)(\mu\text{-}PPh_2)(PPh_2H)\}_2]$ ***6a***, *caracterizado por difracción de rayos X, se forma también (2% rendimiento) en el proceso de síntesis de* ***5a***. *cis*-$[Pt(C\equiv CR)_2COD]$ *reacciona con* $PPh_2(O)H$ *en* CH_2Cl_2 *(−40°C), tanto en relación molar 1:2 como 1:3, para formar el complejo* $[Pt(C\equiv CR)\{(PPh_2O)_2H\}(PPh_2OH)]$ ***7***, *precursor de los derivados neutros* $[Pt(C\equiv CR)\{(PPh_2O)_2H\}L]$ ($L = PEt_3$, PPh_2H, *CNtBu* ***8–10***) *o aniónico* $[NBu_4][Pt(C\equiv CR)(CN)\{(PPh_2O)_2H\}]$ ***11*** *relacionados. Los complejos del tipo* ***7*** *pueden ser doblemente desprotonados con LiOH para formar los derivados de tipo* ***3***, *siendo este el camino más conveniente para preparar* ***3a***, *y el único para* ***3b***.

We have previously prepared *trans*-substituted derivatives of the type *trans*-$[Pt(C\equiv CR)_2(PPh_3)_2]$ by treatment of *cis*-$[PtCl_2(PPh_3)_2]$ with classical alkynyl reagents such as $LiC\equiv CSiMe_3$[10b] or $(AgC\equiv CR)_n$ (R = Ph, *t*Bu),[13] although *trans*-$[Pt(C\equiv CtBu)_2(PPh_3)_2]$ can also be obtained in high yield by partial displacement of the alkynyl groups (by PPh_3) from the reactive $Li_2[Pt(C\equiv CtBu)_4]$, prepared *in situ*.[10b] After a few unsuccessful attempts to prepare related derivatives containing the secondary phosphine PPh_2H, by treatment of *cis*-$[PtCl_2(PPh_2H)_2]$ with $MC\equiv CR$ (M = Li, Ag) (the reactions yield very complex mixtures as deduced through ^{31}P NMR spectroscopy), we finally decided to attempt their synthesis by treating $Li_2[Pt(C\equiv CR)_4]$ with PPh_2H. Preliminary results[14] revealed that treatment of $Li_2[Pt(C\equiv CtBu)_4]$ with PPh_2H (1:3 molar ratio) gives not only the expected *trans*-$[Pt(C\equiv CtBu)_2(PPh_2H)_2]$ (**1a**) in low yield (25%), but also a very unusual complex $[\{Pt(C\equiv CtBu)_2(PPh_2O)_2Li_2(\mu\text{-}H_2O)(Me_2CO)_2\}_2]$ (**2a**; 40%), formed by two dianionic *trans*-$^-OPPh_2\{Pt(C\equiv CtBu)_2\}PPh_2O^-$ units connected by four Li^+ centers.

Some preliminary results, in particular the crystal structure of **2a**,[14] have already been reported. We now describe in detail the systematic study that has been undertaken since that report.

Results and Discussion

Reactions of $Li_2[Pt(C\equiv CR)_4]$ (R = *t*Bu, Ph) with PPh_2H: Complex *trans*-$[Pt(C\equiv CtBu)_2(PPh_2H)_2]$ (**1a**) was prepared in low yield (25%) in a way similar to that previously reported for *trans*-$[Pt(C\equiv CtBu)_2(PPh_3)_2]$,[10b] by partial displacement with PPh_2H of the 3,3-dimethylbutynyl ligands of the reactive homoleptic species $Li_2[Pt(C\equiv CtBu)_4]$. Complex **1a** slowly precipitates (~7 h) as a white solid after treatment of the colorless solution obtained by dissolving the species $Li_2[Pt(C\equiv CtBu)_4]$, generated in situ, in an acetone/ethanol mixture with an excess of PPh_2H (Pt/L 1:3), under a nitrogen atmosphere at room temperature. However, prolonged stirring of the resulting filtrate (7 h) under aerobic conditions leads to the formation of a new white precipitate **2′a**. The stoichiometry of this solid is in agreement with a formulation $[\{Pt(C\equiv CtBu)_2(PPh_2O)_2Li_2(H_2O)_3\}_2]$ and its solubility and spectroscopic data (IR, NMR, see below) are clearly different from those of the mononuclear complex **1a**. Recrystallization

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of **2′a** from hot acetone yields a crystalline solid identified by X-ray crystallography as the unexpected tetralithium diplatinum complex $[\{Pt(C{\equiv}CtBu)_2(PPh_2O)_2Li_2(\mu\text{-}H_2O)(Me_2CO)_2\}_2]$ (**2a**; 40 % yield based on Pt). A schematic view of **2a** is given in Scheme 1. The structure and details of the crystallographic study are given in ref. [14] and will not be repeated here. The most interesting feature of this complex is the presence of an unusual linear chain of four lithium ions sandwiched by two square planar dianionic units (*trans*-$^-OPPh_2\{Pt(C{\equiv}CtBu)_2\}PPh_2O^-$) through bridging phosphinite groups, which display a novel μ_3-(κ^3P,O,O) bonding mode. The two inner lithium centers are connected by two (μ-H_2O) bridges, while the outer ones interact with two terminal acetone ligands each. If the second filtrate is stirred, small amounts of yet another new white precipitate (**3′a**) are slowly generated. After 1 d of stirring, the solid **3′a** was filtered and recrystallized from THF/OEt$_2$ giving a microcrystalline solid identified by elemental analysis, spectroscopic data and X-ray crystallography (Figure 1) as the novel tetralithium diplatinum diphenylphosphinite compound $[\{Pt(C{\equiv}CtBu)(PPh_2O)_3Li_2(H_2O)(thf)\}_2]$ **3a**, in very low yield (ca 4 % based on initial Pt). Although at first sight the formulations of **2a** and **3a** are quite different, their overall geometries, in particular the central linear Li$_4$ core, are rather similar. In spite of the large structural diversity found in lithium organyl chemistry,[15] this simple linear Li$_4$ core resulting from the perpendicular disposition of the three four-membered Li$_2$O$_2$ planar rings (apex sharing) is remarkable and contrasts with the more usual cubane (two stacked rings) or stair-shaped

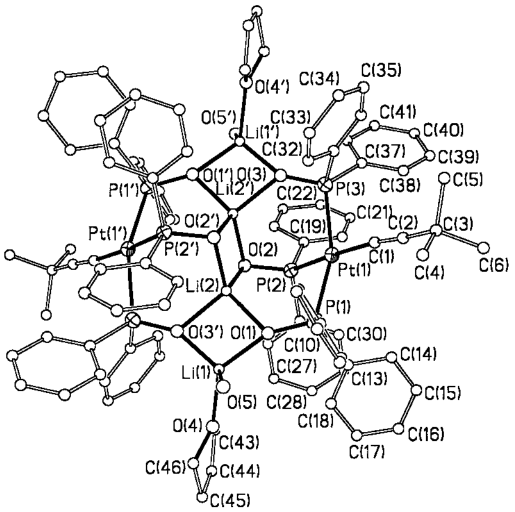
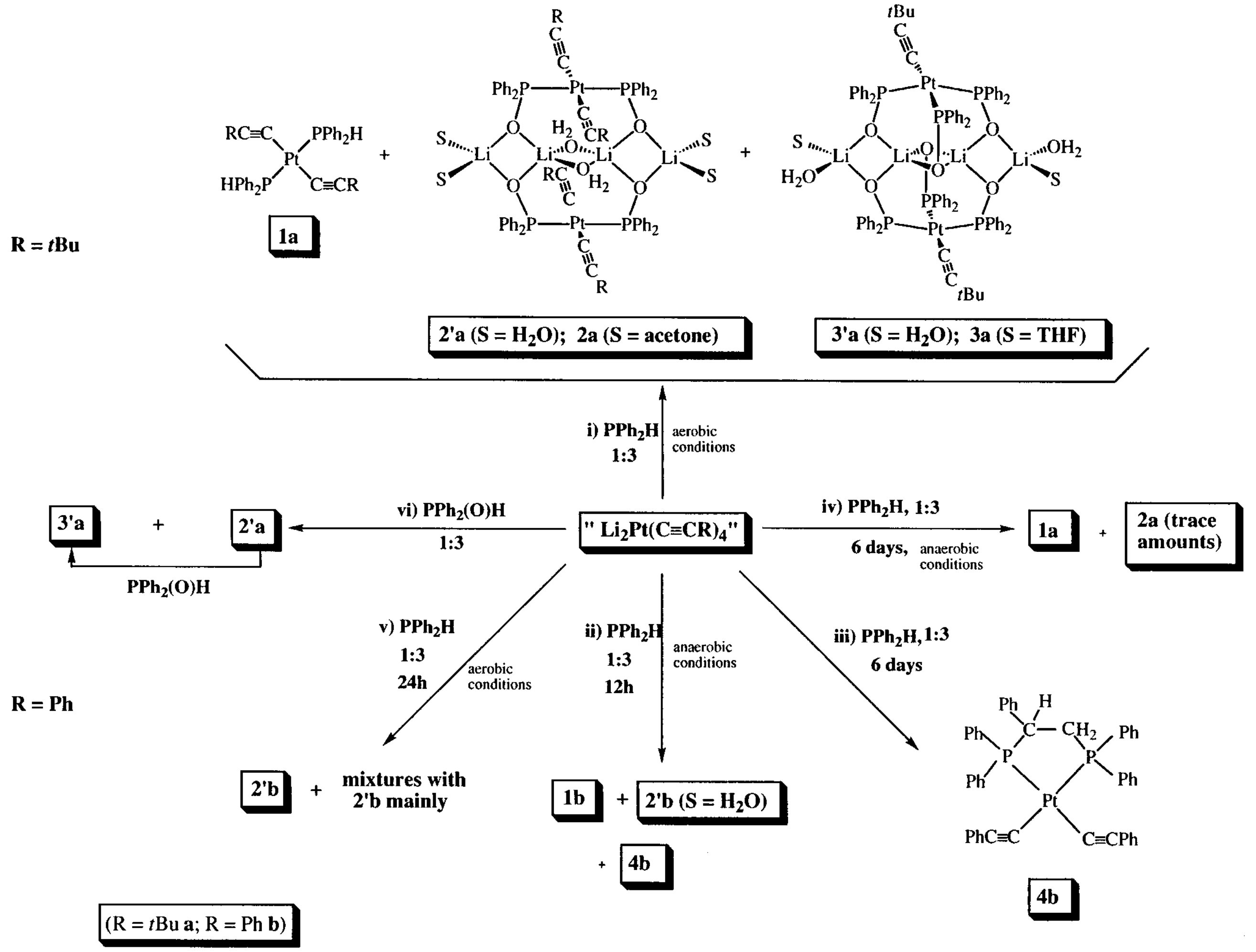
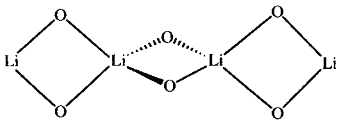


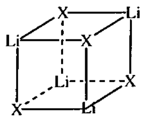
Figure 1. View of the molecular structure of $[\{Pt(C{\equiv}CtBu)(PPh_2O)_3Li_2(thf)(H_2O)\}_2]$ **3a** with the atom numbering scheme.



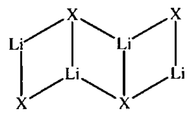
Scheme 1. Reactions of Li$_2$Pt(C≡CR)$_4$ with PPh$_2$H.



Linear Li_4 core found in 2a, 3a



Cubane



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(ladder of three rings) arrangements found in other tetralithium derivatives. The latter have been elegantly rationalized from ring-stacking or laddering ideas.[15] To our knowledge only the recently reported lithium gallium phosphonate $Li_4[(MeGa)_6(\mu_3\text{-}O)_2(tBuPO_3)_6]\cdot(THF)_4$ shows a similar linear tetralithium core.[16] A schematic view of the structure of **3a** (Figure 1) is also given in Scheme 1. As can be observed, the similarity between **2a** and **3a** is clear. The most notable difference is the presence on each Pt center in **3a** of a third phosphinite group, which in turn bridges the two inner lithium centers and displaces the two μ-H_2O observed in complex **2a**. As in **2a**,[14] the crystal structure determination reveals the presence of two independent, but similar half-molecules per asymmetric unit and, therefore, discussion will be limited to only one (denoted A), for which selected bond distances and angles are listed in Table 1. As can be seen in Figure 1, each centrosymmetric hexanuclear Pt_2Li_4 molecule is made up by two identical and staggered (180°) dianionic platinate $Pt(C{\equiv}CtBu)(PPh_2O)_3^{2-}$ fragments, which sandwich a one-dimensional lithium wire consisting of four Li^+ ions linked through the oxygen atoms of the phosphinite groups. The inner lithium centers [Li(2), Li(2′)] achieve the usual fourfold coordination through bonding to four oxygen atoms from four different PPh_2O^- ligands (two from each platinum fragment), while the peripheral lithium centers [Li(1), Li(1′)] interact with only two oxygen atoms of two different PPh_2O^- ligands (one from each Pt unit) and complete their coordination spheres with two different solvent molecules each (THF and H_2O). However, in spite of this structural difference, the Li–O bond distances [range 1.95(2) – 2.00(2) Å for Li(2) and 1.90(2) – 1.99(2) Å for Li(1)] are similar and comparable with those found in **2a**[14] and in other lithium compounds containing pseudotetrahedral LiO_4 units.[15–16] While in **2a** the outer Li_2O_2 rings possess bridging H_2O, in **3a** these rings are bound by the oxygen atoms [O(2), O(2′)] of the PPh_2O^- groups *trans* to C≡C*t*Bu ligands. As a consequence, the Li ··· Li separation and angles at the oxygen atoms in the external rings [Li(1)–Li(2) = 2.62(3) Å, 85.4(9)° at O(1) and 84.4(8)° at O(3)] are similar to those found in **2a** [Li(1)–Li(2) = 2.610(13) Å, angles at O, 84.5(4)° average], but they are very different in the central Li_2O_2 ring [Li(3) ··· Li(2) 2.57(4) Å in **3a** vs 2.848(13) Å in **2a**; Li(2)–O(2)–Li(2′) = 82.1(9) in **3a** vs. Li(2)–O(5) Li(2′) = 88.1(4)° in **2a**).

Another remarkable structural feature in complex **3a** is the presence, as in complex **2a**, of phosphinite ligands displaying an unusual μ_3-(κ^3P,O,O') bonding mode. Although a variety of metal coordination modes have been observed[17] for PR_2O^- ligands, (monodentate P- or O-bonded and bridging μ-P,O), to our knowledge these complexes are the first examples in which this type of ligand connects three centers. Each PPh_2O^- ligand is P-bonded to the soft Pt center [Pt(1)–P(1,2,3) 2.307(3), 2.290(3), 2.315(3) Å] and O-bridging to two lithium centers. All P-μ_3-O bond lengths vary over a small range [1.527(8) – 1.543(8) Å] and are comparable with those observed in **2a** [average 1.538(4) Å]. These distances are also similar to those reported for $[\{Me_3Si_2N\}Cd\{(mes)_2P{-}O\}_2\text{-}Li(thf)_2]$ [1.512(8), 1.526(8) Å],[18] which is the only previously reported structure containing metal and Li centers connected by phosphinite bridging ligands $\{\mu_2\text{-}P(mes)_2O\}$, and only slightly larger than those seen in $Ph_3P{=}O$ [1.461, 1.484(1) Å],[19] suggesting that the interaction with the Li is substantially electrostatic in nature.[20] The stereochemistry about the bridging oxygen atoms varies; it is almost trigonal planar for the outer atoms O(1) and O(3) from mutually *trans*

Table 1. Selected bond lengths (Å) and angles (°) for $[\{Pt(C{\equiv}CtBu)(PPh_2O)_3Li_2(thf)(H_2O)\}_2]\cdot 1.75\,Et_2O$ (**3a**, molecule A).[a]

Pt(1)–C(1)	2.010 (12)	Pt(1)–P(2)	2.290 (3)	Pt(1)–P(1)	2.307 (3)
Pt(1)–P(3)	2.315 (3)	P(1)–O(1)	1.527 (8)	P(1)–C(13)	1.812 (12)
P(1)–C(7)	1.847 (13)	P(2)–O(2)	1.536 (7)	P(2)–C(19)	1.818 (12)
P(2)–C(25)	1.832 (11)	P(3)–O(3)	1.543 (8)	P(3)–C(37)	1.815 (12)
P(3)–C(31)	1.827 (12)	O(1)–Li(1)	1.92 (2)	O(1)–Li(2)	1.95 (2)
O(2)–Li(2)	1.95 2)	O(2)–Li(2′)	1.96 (2)	O(3)–Li(1′)	1.90 (2)
O(3)–Li(2′)	2.00 (2)	O(4)–Li(1)	1.99 (2)	O(5)–Li(1)	1.94 (2)
Li(1)–Li(2)	2.62 (3)	Li(2)–Li(2′)	2.57 (4)	C(1)–C(2)	1.21 (2)
C(2)–C(3)	1.49 (2)				
C(1)-Pt(1)-P(2)	175.0 (3)	O(3′)-Li(1)-O(4)	111.1 (11)	P(1)-O(1)-Li(2)	121.6 (7)
P(2)-Pt(1)-P(1)	89.51 (11)	O(5)-Li(1)-O(4)	99.0 (10)	P(2)-O(2)-Li(2)	110.0 (7)
P(2)-Pt(1)-P(3)	89.76 (10)	O(2)-Li(2)-O(2′)	97.9 (9)	Li(2)-O(2)-Li(2′)	82.1 (9)
C(13)-P(1)-C(7)	103.0 (6)	O(2)-Li(2)-O(3′)	126.5 (11)	P(3)-O(3)-Li(2′)	121.3 (7)
C(19)-P(2)-C(25)	96.9(5)	O(2′)-Li(2)-O(3′)	108.8(10)	O(3′)-Li(1)-O(1)	97.0(9)
C(37)-P(3)-C(31)	102.2 (6)	C(2)-C(1)-Pt(1)	174.9 (10)	O(1)-Li(1)-O(5)	104.7 (11)
P(1)-O(1)-Li(1)	148.9(8)	C(1)-Pt(1)-P(1)	90.9(3)	O(1)-Li(1)-O(4)	123.0(11)
Li(1)-O(1)-Li(2)	85.4(9)	C(1)-Pt(1)-P(3)	91.8(3)	O(2)-Li(2)-O(1)	110.2(10)
P(2)-O(2)-Li(2′)	109.2 (7)	P(1)-Pt(1)-P(3)	157.54 (10)	O(1)-Li(2)-O(2′)	123.3 (10)
P(3)-O(3)-Li(1′)	153.8(8)	O(1)-P(1)-Pt(1)	112.7(3)	O(1)-Li(2)-O(3′)	92.7(8)
Li(1′)-O(3)-Li(2′)	84.4(8)	O(2)-P(2)-Pt(1)	115.2(3)	Li(2′)-Li(2)-Li(1)	174.0(14)
O(3′)-Li(1)-O(5)	124.1 (12)	O(3)-P(3)-Pt(1)	110.9 (3)	C(1)-C(2)-C(3)	174.1 (13)

[a] Symmetry transformation used to generate equivalent primed atoms is $-x+2, -y+1, -z$.

PPh_2O^- ligands (the sums of angles are 356° and 359.5°, respectively) and clearly pyramidal at O(2) (sum of the angles 301.3°). The net result is that the six metal centers (Pt_2Li_4) and the phosphorus and oxygen atoms of the mutually *trans* phosphinite ligands [P(1), O(1) and P(3), O(3)] are essentially coplanar [max. deviation 0.165° for Pt(1)]. Finally, it should be noted that the simultaneous coordination of the three PPh_2O^- ligands to the Li_4 core produces a significant distortion in the platinum coordination; the angle P(1)−Pt(1)−P(3) (157.5°) is rather smaller than from the ideal value (180°) and considerably smaller than that observed in **2a** [170.95(5)°].

As is shown in Scheme 1 (path ii), addition of PPh_2H to an acetone/ethanol solution of $Li_2[Pt(C{\equiv}CPh)_4]$ generated a mixture from which, after 12 h of stirring under nitrogen, the complex *trans*-$[Pt(C{\equiv}CPh)_2(PPh_2H)_2]$ (**1b**) and mixed species **2′b**, which are analogous to **1a** and **2′a**, respectively, were obtained. Both complexes were isolated in very low yield (~11%) after adequate recrystallization ($CHCl_3$/hexane **1b** or THF/hexane **2′b**) of the corresponding first and second crude fractions (see Experimental Section), which also contained a considerable amount of a new mononuclear derivative $[Pt(C{\equiv}CPh)_2(PPh_2CHPhCH_2PPh_2)]$ (**4b**; characterized by ^{31}P NMR). We have observed that the formation of this latter complex **4b** is clearly favored by prolonged reaction times. Thus, by stirring the initial mixture for six days (even under not very rigorous anaerobic conditions, path iii), complex **4b** separates cleanly in very high yield (91%). An X-ray diffraction study (Figure 2, Table 2) confirms that **4b** is a square planar Pt^{II} complex formed by an unsymmetrical diphosphine ligand and two mutually *cis*-alkynide groups. The geometrical details are unexceptional for these types of ligands. Chemically equivalent both lengths Pt−P [2.258(3), 2.270(3) Å], Pt−C [1.997(12), 2.020(14) Å], and $C{\equiv}C$ [1.20(2) Å] are identical within experimental error, and the $Pt{-}C_\alpha{\equiv}C_\beta(Ph)$ fragments do not deviate significantly from linearity (angles at C_α/C_β 176.4(12)/174.6(14); 169.9(11)/174.8(16).

During our efforts to optimize the synthesis of the mononuclear complexes **1** as possible precursors to polynuclear species, we observed that the yields were dependent on the presence of air in the reaction system and on whether deoxygenated solvents were used. For instance, under anaerobic conditions the yield of **1a** was increased to about 40% or 88% by stirring for twelve hours or six days (path iv), respectively, while that of **2a** decreases to about 11% when isolated as a pure material and, under these conditions complex **3a** was not detected (see Experimental Section). Similarly, by stirring (24 h) $Li_2[Pt(C{\equiv}CPh)_4]$ with PPh_2H in an acetone/ethanol (1:1) mixture under aerobic conditions no trace of **1b** was detected, and **2′b** was isolated in 31% yield from the mixture after adequate workup (path v). All these facts clearly show that the formation of **2** and **3a**, containing phosphinite PPh_2O^- ligands, stems from the partial oxidation of the PPh_2H ligand to diphenylphosphine oxide $PPh_2(O)H$ during the course of the reactions. In fact, as is shown in Scheme 1 (path vi), treatment of tetraalkynylplatinate species $Li_2[Pt(C{\equiv}C\mathit{t}Bu)_4]$ with three equivalents of $PPh_2(O)H$ causes the slow precipitation (3 d) of a white solid identified by $^{31}P\{^1H\}$NMR as a mixture of **2′a** and **3′a** from which both complexes can be separated as a result of their different solubilities (see Experimental Section). In addition, the formation of **2′a** and **3′a** seems to be independent to the formation of the mononuclear derivative **1a**. Thus, an attempt to obtain **2a** by treatment of **1a** with a stoichiometric mixture of LiOH (2 equiv) and H_2O_2 (2 equiv) in acetone was not successful. After 15 hours of stirring at room temperature, no reaction was observed. However, we noted that under more

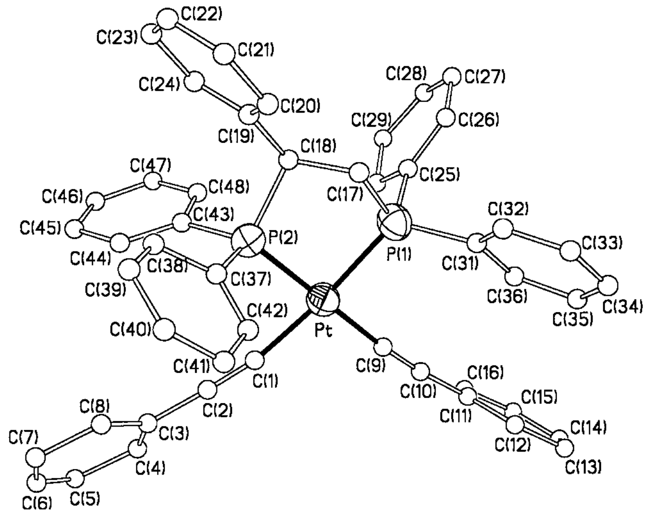


Figure 2. View of the molecular structure of $[Pt(C{\equiv}CPh)_2(PPh_2CHPhCH_2PPh_2)]$ **4b** with the atom numbering scheme.

Table 2. Selected bond lengths (Å) and angles (°) for $[Pt(C{\equiv}CPh)_2(PPh_2CHPhCH_2PPh_2)]$ **4b**.

Pt−C(1)	1.997 (12)	Pt−C(9)	2.020 (14)	Pt−P(2)	2.258 (3)
Pt−P(1)	2.270 (3)	P(1)−C(25)	1.786 (14)	P(1)−C(31)	1.809 (13)
P(1)−C(17)	1.833 (11)	P(2)−C(37)	1.78 (2)	P(2)−C(43)	1.817 (13)
P(2)−C(18)	1.859 (13)	C(1)−C(2)	1.20 (2)	C(2)−C(3)	1.41 (2)
C(9)−C(10)	1.20 (2)	C(10)−C(11)	1.44 (2)	C(17)−C(18)	1.50 (2)
C(18)−C(19)	1.51 (2)				
C(1)-Pt-C(9)	93.6 (5)	C(2)-C(1)-Pt	169.9 (11)	C(17)-P(1)-Pt	106.1 (4)
C(9)-Pt-P(1)	94.4 (3)	C(10)-C(9)-Pt	176.4 (12)	C(37)-P(2)-C(18)	106.2 (6)
C(25)-P(1)-C(31)	104.7 (6)	C(18)-C(17)-P(1)	108.0 (8)	C(37)-P(2)-Pt	116.1 (5)
C(31)-P(1)-C(17)	105.1 (6)	C(17)-C(18)-P(2)	108.5 (8)	C(18)-P(2)-Pt	106.7 (4)
C(31)-P(1)-Pt	119.9 (4)	C(1)-Pt-P(2)	85.8 (3)	C(1)-C(2)-C(3)	174.8 (16)
C(37)-P(2)-C(43)	108.5 (7)	P(2)-Pt-P(1)	86.26 (12)	C(9)-C(10)-C(11)	174.6 (14)
C(43)-P(2)-C(18)	106.1 (6)	C(25)-P(1)-C(17)	105.6 (6)	C(17)-C(18)-C(19)	113.2 (11)
C(43)-P(2)-Pt	112.5 (5)	C(25)-P(1)-Pt	114.3 (5)	C(19)-C(18)-P(2)	114.6 (9)

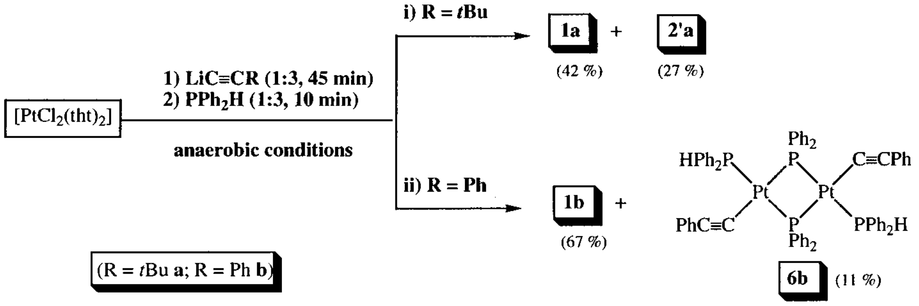
drastic conditions (excess of LiOH and H_2O_2) and a prolonged reaction time (6 d) complex **1a** disappears, giving a very complex mixture of unidentified platinum compounds containing phosphorus, in which no trace of **2′a** could be detected. Moreover, the formation of **3a** (**3′a**), which contains three diphenylphosphinito groups on each Pt center, seems to take place through the formation of **2a** (**2′a**) with only two PPh_2O^- ligands, as intermediate. This can be inferred from the observation that treatment of a suspension of **2a** in $CHCl_3$ with $PPh_2(O)H$ slowly produces the displacement of one *tert*-butylacetylide by one PPh_2O^- on each platinum center, transforming **2a** into complex **3a** (or **2′a** into **3′a**). The process is slow, with only ~50% conversion in two days [compound **2a** is still present in small amounts even with longer reaction times (~ 5 days)].

The mechanism of formation of **4b**, containing two mutually *cis*-alkynyl ligands and a new diphosphine 1-phenyl-1,2-bis(diphenylphosphino)ethane, is less clear. This complex can be seen as formed throgh the formal addition of $PhC{\equiv}CH$ to *cis*-$[Pt(C{\equiv}CPh)_2(PPh_2H)_2]$ (**5b**). The nearest example to be found in the literature is the base-induced addition of coordinated phosphines on $[M(CO)_4(PPh_2H)_2]$ (M = Cr, Mo) to acetylenes, yielding metal complexes of chelating diphosphine ligands.[8h–j] However our attempt to obtain **4b** starting from **5b** and $LiC{\equiv}CPh$ (3 equiv) was unsuccesful. The reaction yielded a complex reaction mixture in which no trace of **4b** was detected.

It should be mentioned that the yield of platinate lithium species can be diminished (see Scheme 2 path i for R = *t*Bu) or eliminated (R = Ph) by treating the initial suspension, formed with $[PtCl_2(tht)_2]$ (tht = tetrahydrothiophene), with a lesser excess of $LiC{\equiv}CR$ (1:3) [giving what is probably a mixture of species of the type $Pt(C{\equiv}CR)_{4-x}(tht)_xLi_{2-x}$ ($x = 0-2$)], with PPh_2H (Scheme 2, paths i and ii). In the case of R = Ph, the yield of **1b** can be increased to 67%; but surprisingly, under these conditions the unexpected new phosphido-bridged dinuclear compound $[\{Pt(C{\equiv}CPh)(\mu\text{-}PPh_2)(PPh_2H)\}_2]$ **6b** is also isolated in very low yield (11%) from the mother liquors.

All complexes **1**, **2**, **3a**, **4b**, and **6b** have been characterized by microanalysis, mass spectra (FAB), and IR and NMR spectroscopy (see Experimental Section). For the mononuclear complexes **1** the appearance in their IR spectra of absorptions assignable to ($C{\equiv}C$) (2106 cm^{-1} **1a**, 2110 cm^{-1} **1b**) and to (P–H)[12, 21] (2369 cm^{-1} **1a**, 2376 cm^{-1} **1b**) confirms the presence of terminal alkynyl[10] groups and PPh_2H ligands.[12, 21]

In addition, the presence of a singlet in their $^{31}P\{^1H\}$ NMR spectra (– 1.99 **1a**, –4.26 **1b**), which splits into the expected XX′ pattern ($N \sim 400$ Hz **1a**, 402.7 Hz **1b**) under off resonance conditions, and especially the magnitude of ^1J(Pt,P) [2616 Hz **1a**, 2547 Hz **1b**], indicates a *trans* configuration of the ligands about platinum.[22] In agreement with this, the P–H protons in the ^1H NMR spectra give rise to a pattern (centered at $\delta = 6.46$ for **1a** and at $\delta = 6.72$ for **1b**), corresponding to the AA′ part of an AA′XX′ system with characteristic values for the N parameter [^1J(P,H) + ^3J(P′,H)] (~400 Hz) and for the ^2J(Pt,H) coupling constant (26.2 Hz **1a**, 26.8 Hz **1b**). In the ^{13}C NMR spectra the acetylenic carbons (δ C_α/C_β 85.2/120.6 **1a**; 102.9/112.4 **1b**), which are easily identified owing to the significantly different coupling constants to ^{195}Pt nuclei [$^1J(Pt,C_\alpha) = 913$ Hz **1a**, 834 Hz **1b**; $^2J(Pt,C_\beta)$ 249 Hz **1a**, 259 Hz **1b**], are seen as triplets [$^2J(C_\alpha,P) = 15.9$ Hz **1a**, ~27 Hz **1b**; $^3J(C_\beta,P) = 2.6$ Hz **1a**] confirming unambiguously the *trans* disposition of the ligands.[22] The characterization of **2a** has been reported previously [14] (see also Experimental Section). As in complex **2a** (**2′a**), compounds **2′b** and **3a** (**3′a**) exhibit in their IR spectra broad ν(OH) bands (3374–3623 cm^{-1}), confirming the presence of water, and show absorptions in the P–O stretching region (997–1038 cm^{-1}), suggesting the presence of phosphinito bridging groups.[17] Moreover, while no ($C{\equiv}C$) vibration is observed in the typical region of alkynyl ligands for **3a**, a band at 2095 cm^{-1} is seen for **2′b.** As in complex **2a** (or **2′a**) compound **2′b** exhibits a singlet far downfield [$\delta = 68.07$, $^1J(Pt,P) = 2395$ Hz] in its $^{31}P\{^1H\}$ NMR spectrum, indicative of the phosphorus oxidation to P^V. In contrast, **3a** exhibits an A_2X pattern with ^{195}Pt satellites in the expected downfield region consisting of a doublet at $\delta_A = 73.14$ as a result of the two mutually *trans* phosphorus atoms and a triplet at $\delta_X = 58.70$ assigned to the phosphinite group *trans* to $C{\equiv}C$*t*Bu with a *cis* coupling constant $^2J(P_A,P_X)$ of 29.3 Hz. The considerable upfield shift of the phoshorous resonance of the latter phosphinite group suggests that the negative charge is more localized over the oxygen atom, in agreement with the pyramidal coordination found in the crystal structure (see above). The most remarkable features of the ^1H NMR spectrum of **3a** are the presence (in addition to Ph resonances) of a sharp singlet at $\delta = 0.49$ due to the equivalent *tert*-butyl groups and a broad signal at $\delta = 1.59$. This latter signal disappears upon addition of a drop of D_2O to the solution and, therefore, could be tentatively assigned to the H_2O molecules at the lithium centers. The low solubility of these heteronuclear complexes prevents ^{13}C NMR analysis. It is worth noting that although the ^{31}P and ^1H NMR spectra of these mixed species (**2**, **3a**) at room temperature are compatible with the solid structures (**2a**, **3a**), their ^7Li NMR does not show the expected two lithium environments. At room temperature the complexes show only one singlet signal ($\delta = 0.88$ **2a**, –0.62 **2′b** sharp; –1.03 **3a**,



Scheme 2. Reactions of $[PtCl_2(tht)_2]$ with PPh_2H.

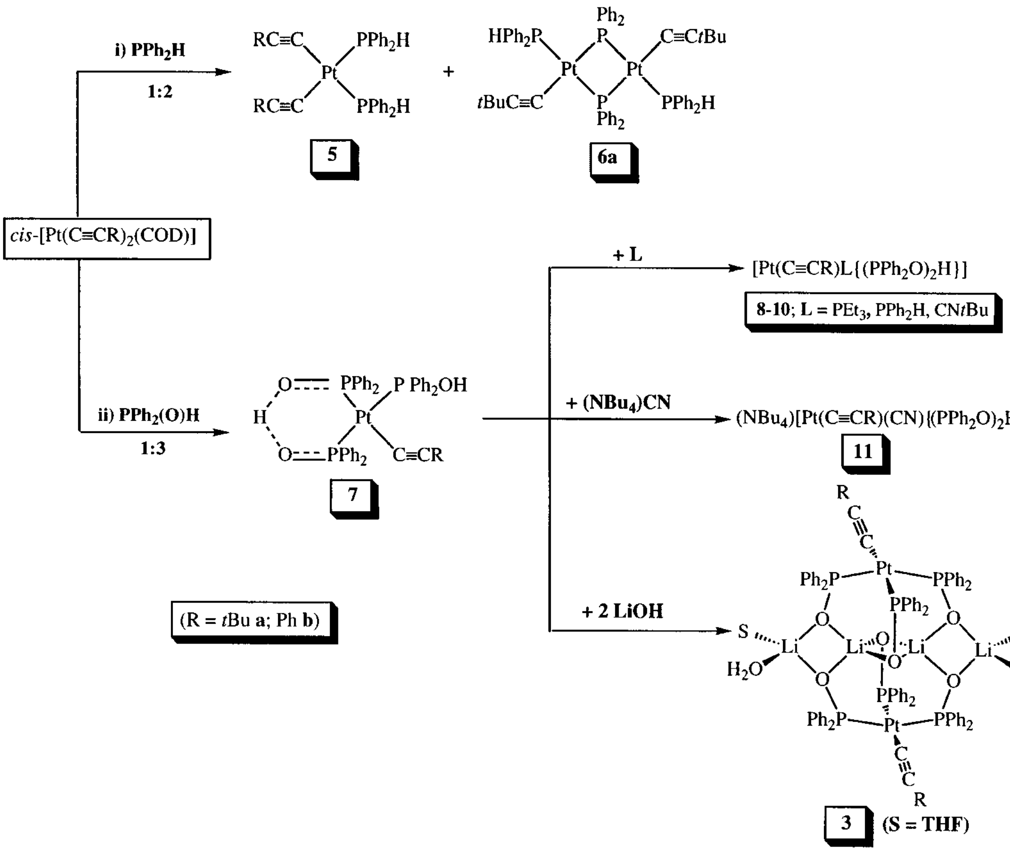
broad with $w_{1/2} = 129$ Hz), suggesting fast intermolecular lithium exchange (no P–Li splitting is observed),[23] most probably due to partial dissociation of Li^+ in solution, in agreement with the essentially electrostatic nature of the interactions. By lowering the temperature for complex **3a** the signal broadens (coalesces at ca. 1–3 °C) and is finally resolved into a pair of singlets of similar intensity (−20 °C, $\delta = -0.23, -1.97$).

The IR spectrum of **4b** confirms the presence of terminal alkynyl ligands [(C≡C) 2114 cm^{-1}] and its $^{31}P\{^1H\}$ NMR spectrum reveals two doublet [$^2J(P,P)_{cis} = 13.8$ Hz] resonances with ^{195}Pt satellites [$\delta/^1J(Pt,P)$ 49.24/2260 Hz; 21.53/2250 Hz], consistent with the presence of the unsymmetrical diphosphine. The most noteworthy features of its proton spectrum are the presence of two multiplets at $\delta = 3.83$ and 2.53 due to diasterotopic methylene protons (CH_2) and a doublet [$^2J(H,P) = 47$ Hz] of multiplets centered at $\delta = 3.19$ attributable to C*H*Ph.

The $^{31}P\{^1H\}$ spectrum of complex **6b** exhibits, as in complex **6a** (see below), two different [$\delta = 1.58$ for PPh_2H (AA′) and $\delta = -138.7$ for μ-PPh_2 (XX′)] and characteristic signals [AA′XX′ pattern; $N = {}^2J(P_A,\mu\text{-}P_{X trans}) + {}^2J(P_A\text{-}\mu,P_{X'cis}) = 321.4$, $^1J(Pt,P_A) = 2051$ Hz, $^1J(Pt,P_X,P_{X'}) = 1688$, 1766 Hz]. The ^1H NMR shows a signal at $\delta = 5.35$ (doublet of multiplets, dm) due to P–H. In addition, the IR spectrum of **6b** shows an absorption at 2104 cm^{-1}, which can be assigned to (C≡C). All these data are compatible with the formulation given and confirmed by X-ray crystallography on the analogous *tert*-butylacetylide derivative **6a**.

Reactions of *cis*-[Pt(C≡CR)$_2$COD] with PPh$_2$H and PPh$_2$(O)H: The results are shown in Scheme 3. As has already been mentioned, the P–H bonds are highly reactive and therefore, synthetic routes for generating [MPR_2H] complexes usually require only mild conditions.[21] A general synthetic strategy for preparing *cis*-[PtX_2L_2] (X = an anionic ligand such as alkynyl, alkyl, aryl, halide; L = PR_3) is based in the easy displacement of labile COD from appropiate precursors [PtX_2COD] by the incoming phosphine ligand.[10a, 11b] Therefore, the recently reported neutral platinum derivatives [Pt(C≡CR)$_2$COD] (R = *t*Bu,[10a] Ph[24]) were assumed to be the most suitable starting materials for the preparation of the corresponding geometrical isomers with the PPh_2H ligands mutually *cis*. As is shown in Scheme 3 (path i) treatment of the complex [Pt(C≡CR)$_2$COD] (R = *t*Bu, Ph) in CH_2Cl_2 at low temperature (−30 °C) with PPh_2H (1:2 molar ratio) results in the displacement of the cyclooctadiene ligand, yielding solutions from which the expected products *cis*-[Pt(C≡CR)$_2$(PPh$_2$H)$_2$] are obtained as white (R = *t*Bu **5a**) or yellow (R = Ph **5b**) solids in high yields (79% **5a**, 76% **5b**). Surprisingly, in the synthesis of the *tert*-butylacetylide derivative **5a**, cooling the resulting diethyl ether filtrate for a week results in the precipitation of a white solid (2% based on Pt), which after recrystallization from $CHCl_3$/hexane is identified as the phosphido-bridged dinuclear Pt^{II} complex [{Pt(C≡C*t*Bu)(μ-PPh$_2$)(PPh$_2$H)}$_2$] (**6a**).

Complexes **5**, which are stable enough to display their molecular peaks in FAB(+) mass spectra, are easily characterized by elemental analysis and spectroscopic means (see



Scheme 3. Reactions of *cis*-[Pt(C≡CR)$_2$(COD)].

Experimental Section). Thus, their IR spectra confirm the presence of P–H bonds [(P–H) 2354 cm^{-1} **5a**, 2342 cm^{-1} **5b**] and terminal alkynyl ligands [ν(C≡C) 2118 cm^{-1} **5a**, 2119 cm^{-1} **5b**]; their ^{1}H NMR spectra display the P–H resonances in the expected region ($\delta = 5.88$ **5a**, 6.08 **5b**) with a pattern (dm) corresponding to an AA′XX′ system (X = ^{31}P, $N = 378$ Hz **5a**, 390 Hz **5b**). The ^{31}P NMR spectra exhibit a doublet due to phosphorus–hydrogen coupling [^1J(P,H) $\sim N$] with ^{195}Pt satellites, which is reduced to the expected singlet (δ –5.49 **5a**, –7.07 **5b**) by ^{1}H decoupling. Similar to previous findings,[21] the observed large value for ^1J(P,H) coupling compared with free PPh$_2$H (214 Hz) is consistent with the change in the hybridization of P to sp^3, leading to more s character in the P–H bond upon coordination.[25] The platinum coupling constants ^1J(Pt,P) are significantly lower (2156 Hz **5a**, 2169 Hz **5b**) than those observed in the *trans* derivative **1** (2616 Hz **1a**, 2547 Hz **1b**), suggesting that the PPh$_2$H ligand in these mononuclear complexes exerts a weaker *trans* influence than the terminal alkynyl ligands. Finally, in accordance with the proposed *cis* formulation[26] for these isomers the acetylene carbon resonances C$_\alpha$ and C$_\beta$ appear in the ^{13}C{^{1}H} NMR spectra (δ C$_\alpha$/C$_\beta$ = 84.3/118.8 **5a**; 99.9/110.6 **5b**) as a first-order doublet of doublets (dd) [^2J(C$_\alpha$,P*trans*)/^2J(C$_\alpha$,P*cis*) 153.0 Hz/21.2 Hz **5a**, 148.8 Hz/21.4 Hz **5b**] and as a typical A part of a second-order AXX′ system [^3J(C$_\beta$,P*trans*) + ^3J(C$_\beta$,P*cis*) ~ 36.3 Hz **5a**, 36.4 Hz **5b**], respectively. Comparison of the one-bond Pt–C$_\alpha$ coupling constants (Hz) with those observed for the corresponding *trans* isomers again confirms a higher influence for the C≡CR ligands (1122.4 **5a**, 1114.6 **5b** vs. 913 **1a**, 834 **1b**).

The identity of the complex [{Pt(C≡C*t*Bu)(μ-PPh$_2$)(PPh$_2$H)}$_2$] **6a** has been determined not only by elemental analysis and spectroscopic techniques, but also by a single-crystal X-ray diffraction study. The IR spectrum of **6a** exhibits a strong absorption at 2352 cm^{-1} assignable to the (P–H) stretching vibration, but no absorption is observed in the typical $\tilde{\nu}$(C≡C) region. The presence of alkynyl C≡C*t*Bu ligands is better revealed by the ^{1}H NMR spectrum which shows, in addition to a doublet of multiplets centered at 5.25 [J(P,H) = 368 Hz], as a result of P–H protons, a singlet signal at $\delta = 0.86$ attributable to equivalent *t*Bu groups. In agreement with the formulation, two well-separated signals were observed in the ^{31}P{^{1}H} NMR spectrum at $\delta = 1.36$ and –145.4 whose central lines, due to the Pt–Pt isotopomer (43.8%), show the expected AA′XX′ pattern (see Experimental Section for numbering) with a value of 328.4 Hz for the N parameter [$^2J(\mathrm{P_A,P_x}) + {}^2J(\mathrm{P_A,P_{x'}}) = {}^2J(\mathrm{P,P}_{trans}) + {}^2J(\mathrm{P,P}_{cis})$] and are comparable with those observed in related systems, for example, [{PtCl(μ-PPh$_2$)L}$_2$] (L = PEt$_3$ 378.8 Hz, L = PPh$_2$H 394.4 Hz),[27a] [{PtCl(μ-PHMes)(PH$_2$Mes)}$_2$] (360 Hz).[27d] The values of the K [$K = {}^4J(\mathrm{P_A,P_{A'}}) + {}^2J(\mathrm{P_X,P_{X'}}) = 136.4$ Hz] and L [$L = {}^2J(\mathrm{P_A,P_X}) - {}^2J(\mathrm{P_A,P_{X'}}) = 362$ Hz] parameters, which allow the determination of the coupling constants $^2J(\mathrm{P_A},\mu\text{-}\mathrm{P}_{\mathrm{X}trans})$ [345.2 Hz] and $^2J(\mathrm{P_A},\mu\text{-}\mathrm{P}_{\mathrm{X'}cis})$ [16.8 Hz], are directly obtained from the analysis of the spectrum. Comparison of the N and L values ($|N| < |L|$) proves that their signs are opposite and, probably, that $^2J(\mathrm{P_A},\mu\text{-}\mathrm{P}_{\mathrm{X'}cis})$ is negative, since coupling constants between phosphorus atoms in mutually *trans* positions, such as $^2J(\mathrm{P_A},\mu\text{-}\mathrm{P_X})$ are known to be large and positive.[27] If $^4J(\mathrm{P_A,P_{A'}})$ is assumed to be ~0, this leads a value of 136 Hz for $|{}^2J(\mathrm{P_X,P_{X'}})|$, comparable with those reported for related systems.[27] The low-field resonance ($\delta = 1.36$) is assigned to the equivalent PPh$_2$H ligands, while the strongly shielded signal (at δ –145.4) is in accordance with the high-field shifts found in related phosphido-bridged dimers in which no significant metal–metal interaction is observed,[25, 27, 28] and is consistent with the platinum–platinum separation [3.649(1) Å] found in the crystal structure. Each signal is flanked by satellites due to the isotopomer ^{195}Pt–Pt (AA′XX′M spin system, 44.8%), which permits the determination of the platinum–phosphorus coupling constants. In agreement with the formulation, the downfield resonance ($\delta = 1.36$) only exhibits one set of short ^{195}Pt satellites [$^1J(\mathrm{Pt,P_A}) = 2035$ Hz, $^3J(\mathrm{Pt,P_{A'}}) \sim 0$ Hz], while the upfield signal shows two different sets of ^{195}Pt satellites [$^1J(\mathrm{Pt,P_X, P_{X'}}) = 1689, 1792$ Hz), unambiguously confirming the bridging nature of these phosphorus atoms (μ-PPh$_2$). In keeping with earlier observations[27] the one-bond Pt–P$_\mathrm{A}$ coupling constant for the terminal phosphine is larger than for the phosphido bridge (346 and 243 Hz, respectively), consistent not only with the observation of a shorter Pt–P distance in the X-ray structure [2.2944(11) Å terminal vs. 2.3376(10), 2.3169(11) Å bridging], but also with previous suggestions of a lower phosphorus s-orbital contribution to the P$_\mu$–Pt bond due to ring strain effects.[12b] If as in complexes **1** and **5** (and also in **9**) the PPh$_2$H ligand exerts a lower *trans* influence than does C≡CR, then the $^1J(\mathrm{Pt,P_{X'}})$ [1792 Hz] could be assigned to the P$_{\mathrm{X'}}$ atom *trans* to PPh$_2$H, although this assignment is not unequivocal. The X-ray structural data for **6a** reveal (Table 3, Figure 3) that the Pt–P (bridging) bond *trans* to PPh$_2$H [2.3376(10) Å] is slightly longer than the Pt–P(bridging) bond *trans* to C≡C*t*Bu [2.3169 (11) Å], suggesting the opposite assignement. Clearly more structural and spectroscopic studies including other secondary phosphines and other types of platinum complexes will be

Table 3. Selected bond lengths (Å) and angles (°) for [{Pt(C≡C*t*Bu)(μ-PPh$_2$)(PPh$_2$H)}$_2$] **6a**.[a]

Pt–C(1)	2.003 (4)	Pt–P(1)	2.2944 (11)	Pt–P(2)	2.3196 (11)
Pt–P(2′)	2.3376 (10)	P(1)–C(7)	1.814 (4)	P(1)–C(13)	1.815 (4)
P(2)–C(25)	1.821 (4)	P(2)–C(19)	1.847 (3)	C(1)–C(2)	1.212 (5)
Pt···Pt	3.649 (1)				
C(1)-Pt-P(1)	90.38 (11)	C(25)-P(2)-Pt′	114.77 (12)	C(7)-P(1)-Pt	118.47 (12)
P(1)-Pt-P(2)	98.31 (4)	Pt-P(2)-Pt′	103.17 (4)	C(25)-P(2)-C(19)	103.3 (2)
P(1)-Pt-P(2′)	173.23 (3)	C(1)-C(2)-C(3)	177.2 (4)	C(19)-P(2)-Pt	111.35 (12)
C(7)-P(1)-C(13)	103.5 (2)	C(1)-Pt-P(2)	169.98 (10)	C(19)-P(2)-Pt′	109.40 (12)
C(13)-P(1)-Pt	117.15 (13)	C(1)-Pt-P(2′)	94.90 (10)	C(2)-C(1)-Pt	174.8 (3)
C(25)-P(2)-Pt	114.99 (13)	P(2)-Pt-P(2′)	76.83 (4)		

[a] Symmetry transformation used to generate equivalent primed atoms is $-x, -y, -z$.

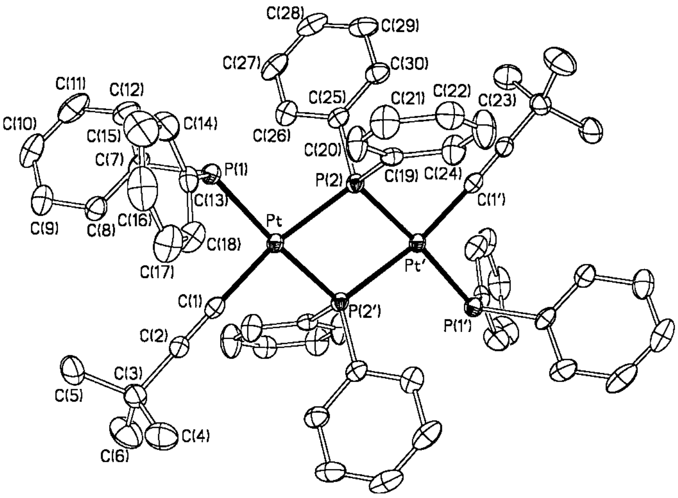


Figure 3. View of the molecular structure of $[\{Pt(C\equiv C\mathit{t}Bu)(\mu\text{-}PPh_2)(PPh_2H)\}_2]$ **6a** with the atom numbering scheme.

required to obtain more conclusive results relevant to the *trans* influence of the PR_2H and $C\equiv CR$ ligands. Complex **6a**, which is the first structurally characterized platinum compound simultaneously stabilized by alkynyl, phosphide, and PPh_2H ligands, crystallizes as the more symmetrical *anti* isomer, as observed previously for other μ-phosphido dimers.[27a, 29] The central Pt_2P_2 core is roughly planar and exhibits angles at the Pt center $[P(2){-}Pt{-}P(2') = 76.83(4)^\circ]$ and the phosphorus atoms $[Pt{-}P(2){-}Pt' = 103.17(4)^\circ]$ comparable with those found in other phosphide-bridged platinum(II) dimers without metal–metal bonds (P–Pt–P 74.6–77.2°; P–P–Pt 102.8–105.4°).[12e, 27c,d, 29] The angles and Pt ··· Pt separation [3.649(1) Å] in **6a** can be compared with those observed in $[\{PtCl(\mu\text{-}PPh_2)(PPh_2H)\}_2]$ (angles at P/Pt 102.8°/77.20°; Pt–Pt 3.585(1) Å].[29] As expected, the terminal Pt–P(1) bond [2.2944(11) Å] is shorter than the bridging Pt–P bonds [2.3376(10) Å and 2.3169(11) Å]. The Pt–C [2.003(4) Å] and C–C [1.212(5) Å] separations and the angles at C_α [174.8(3)°] and C_β [177.2(4)°] of the terminal $C\equiv C\mathit{t}Bu$ group are unexceptional and merit no further comment.

For comparative purposes, the reactivity of *cis*-$[Pt(C\equiv CR)_2COD]$ towards diphenylphosphine oxide [diphenylphosphinous acid $PPh_2(O)H$] has also been explored. The coordination chemistry of these ditopic ligands, $R_2P(O)H$, (soft P and hard O donors) and that of their monoanionic phosphinite counterparts, $R_2(O)P^-$, has been thoroughly investigated,[17] and special mention is due the chelating mixed system $R_2PO\cdots{-}OPR_2$ that is easily formed when a phosphinite ligand, R_2PO^-, and a hydroxyphosphine $PR_2(O)H$ group are in a cisoidal disposition about a metal center.[17h, 30] Interest in this system, formed through strong intramolecular hydrogen bonds[31] (O ··· H ··· O), as well as the recent implication of several complexes of the type $[MH\{(PR_2O)_2H\}L]$ (M = Pt, Pd) in catalytic processes such as hydrogenation or hydroformylation of alkenes[32] and hydrophosphinylation or hydrophosphorylation of alkynes,[6] gives renewed importance to the search for new complexes stabilized by these ligands.

It was not surprising that treatment of *cis*-$[Pt(C\equiv CR)_2COD]$ in CH_2Cl_2, at low temperature (−40 °C) with $PPh_2(O)H$ in either 1:2 or 1:3 molar ratio led to the formation of the respective neutral phosphinito/hydroxyphosphine containing derivatives $[Pt(C\equiv CR)\{(PPh_2O)_2H\}(PPh_2OH)]$ (**7a** R = *t*Bu; **7b** R = Ph; Scheme 3, path ii). In the reaction with R = *t*Bu, a small amount of $[Pt\{(PPh_2O)_2H\}_2]$ is also detected in the mixture by ^{31}P NMR spectroscopy. The quantity increases considerably with the temperature of the reaction; at room temperature the reaction of *cis*-$[Pt(C\equiv C\mathit{t}Bu)_2COD]$ with two equivalents of $PPh_2(O)H$ gives $[Pt\{(PPh_2O)_2H\}_2]$[30e] [$\delta = 72.33$, $^1J(Pt,P) = 2454$ Hz] in 36% yield, and only small amounts of **7a** are detected in the reaction mixture. The formation of the bis(phosphinite) bis(hydroxyphosphine) derivative under these mild conditions contrasts with the more drastic conditions previously reported for its preparation ($[PtX\{(PPh_2O)_2H\}_2PPh_2OH]$ and $[AgPPh_2O]_n$, 18 h, RT[30e]).

Complexes **7** are air-stable white solids, slightly soluble in $CHCl_3$ or CH_2Cl_2 and very insoluble[33] in other common solvents such as acetone or THF, and which display spectral properties (see Experimental Section) consistent with their formulation. Thus, both complexes show in their FAB(+) mass spectra the expected peak corresponding to the molecular ion and in their IR spectra absorptions in the ν(P–O) region (900–1028 cm^{-1}). As has been previously noted,[30a,d–f] the lack of (O–H) bands in the usual spectral region is consistent with the presence of symmetrical hydrogen-bonding interactions of type O ··· H ··· O, because the vibrations ascribed to this system occur below 2000 cm^{-1}.[34] On the basis of deuteration experiments, only an absorption at 1260 cm^{-1} in **7a** and at 1221 cm^{-1} in **7b**, which disappears in the IR spectra of the deuterated derivatives, could be assigned tentatively to such an O ··· H ··· O system. Both compounds also exhibit a broad band at about 1650 cm^{-1}, which is weakened upon deuteration, and which could also result from the O–H stretch. The (OH) modes of strong hydrogen bonds are typically broad, intense bands in this region.[31] Although the presence of alkynyl ligands is only observed in the IR spectrum of **7b** (2120 cm^{-1}), the ^1H NMR spectrum of **7a** exhibits the expected singlet due to $C\equiv C\mathit{t}Bu$ at $\delta = 0.8$ with the correct integration ratio. In spite of their poor solubility, which limits the sensitivity of the solution NMR measurements, both derivatives exhibit a broad downfield signal ($\delta =$ 16.9 **7a**, $\delta = 16.5$ **7b**) in their low temperature (−50 °C) ^1H spectra, confirming the presence of strong O ··· H ··· O hydrogen bonds.[30c,d, 31] Furthermore, at −50 °C they display the expected ABX pattern with ^{195}Pt satellites in their ^{31}P NMR spectra. The most deshielded signals [δ $P_A/P_X = 81.75/75.56$ **7a**; 84.91/75.66 **7b**; $^2J(P_A,P_{B\mathit{trans}})/^2J(P_A,P_{X\mathit{cis}})$ 405.4 Hz/20.4 Hz **7a**; 405.3 Hz/~24 Hz **7b**] are assigned (tentatively for P_A) to the inequivalent phosphorus atoms of the $PPh_2O\cdots H\cdots OPPh_2$ system and the highfield resonance [δ $P_B/^2J(P_B,P_X)$ 70.29/26.3 Hz **7a**; 70.35/~24 Hz **7b**] to the hydroxydiphenylphosphine PPh_2OH. The magnitudes of the one-bond platinum–phosphorus coupling constants $^1J(Pt,P_X) > {}^1J(Pt,P_B) > {}^1J(Pt,P_A)$ provide information about the *trans* influence of these groups ($C\equiv CR < PPh_2O^- < PPh_2OH$). It should be noted that due to the insolubility of the related $[PtX\{(PPh_2O)_2H\}(PPh_2OH)]$ (X = H or halide)[30e, 32b] derivatives no structural data were reported for them. In complexes

7a and **7b** the $^{31}P\{^1H\}$ NMR spectra are temperature dependent (see Figure 4 for complex **7a**). When the temperature is increased, the mutually *trans* phosphorus resonances P_A and P_B broaden, and disappear into the baseline at $\sim$25 °C [no merging was observed at the high temperature limit of the experiment ($\sim$50 °C)], while the central signal (P_X) due to PPh_2O^- *trans* to C≡C*t*Bu is seen as a sharp triplet [$J(P_X,P_{A,B}) \sim 23$ Hz] through the whole range of temperatures. These spectra clearly indicate that at high temperature P_A and P_B become magnetically equivalent without phosphine dissociation, imputing a fast migration of the acidic protons H_a and H_b between the forms **7A** and **7A′** depicted in Scheme 4. The motion of a proton between donor and acceptor atoms is one of the simplest chemical reactions, and has been thoroughly studied.[35] In complexes **7** the transformation of **7A** to **7A′** may occur intramolecularly through the concerted motion of the two hydrogens via an intermediate as such as **7B**, or by two successive motions through the *trans*-alkynyl, bis(hydroxyphosphine)phosphinite platinum intermediate **7C**. However, although an intramolecular pathway seems reasonable, isomerization pathways involving intermolecular interaction through hydrogen bonding cannot be excluded.

Reactivity studies on [Pt(C≡CR){(PPh₂O)₂H}(PPh₂OH)] (7): It has been previously reported that one of the diphenylphosphinous acid molecules in $[PtH(PPh_2OHOPPh_2)(PPh_2OH)]$ is easily displaced by other functionalized phosphines or phosphinites (alkenyl or alkynyl), yielding related $[PtH(PPh_2OHOPPh_2)L]$ compounds.[32b] We have also examined the reactivity of complexes **7** towards a variety of different ligands. These complexes remain intact after stirring with PPh_3 or prolonged bubbling with CO. However, they react immediately in CH_2Cl_2 with stoichiometric amounts of PEt_3, PPh_2H, CN*t*Bu, or $(NBu_4)CN$, affording colorless solutions from which the related neutral $[Pt(C{\equiv}CR)\{(PPh_2O)_2H\}L]$ **8**–**10** or anionic $(NBu_4)[Pt(C{\equiv}CR)(CN)\{(PPh_2O)_2H\}]$ **11** derivatives are isolated as white microcrystalline solids in moderate (**8a**, **9**, **11b**) or high yield (**8b**, **10**, **11a**). The characterization of these complexes by microanalysis and spectroscopic means (mass spectra, IR and NMR spectroscopy) is straightforward (see Experimental Section for data). Particularly clear are the ^{13}C NMR spectra that show, in addition to the expected aromatic carbon resonances for two nonequivalent PPh_2O moieties of the $PPh_2OHOPPh_2$ fragment and signals due to the ligand L, resonances attributed to the acetylenic fragment (C_α and C_β) with the expected splitting pattern. Thus, whereas the C_α and C_β resonances are seen as a doublet of doublets in complexes **10** (L = CN*t*Bu) and **11** ($L = CN^-$) [for complexes **10** the C_β appears only as a doublet], compounds **8** ($L = PEt_3$) and **9a** (only C_α; C_β not observed) exhibit a ddd coupling pattern due to the three inequivalent phosphorus nuclei. Complex **9b** shows a dm at $\delta = 105.4$ [$^2J(C_\alpha,P_{trans}) \sim 120$ Hz] and a doublet at $\delta = 117.07$ [$^3J(C_\beta,P_{trans}) = 32$ Hz] for C_α and C_β in the expected region. The ^{31}P NMR data provide additional information about the *trans* influence of these groups in these very similar species. Complexes **8** ($L = PEt_3$) and **9** ($L = PPh_2H$) display in their ^{31}P NMR the three expected mutually coupled (AMX system) set

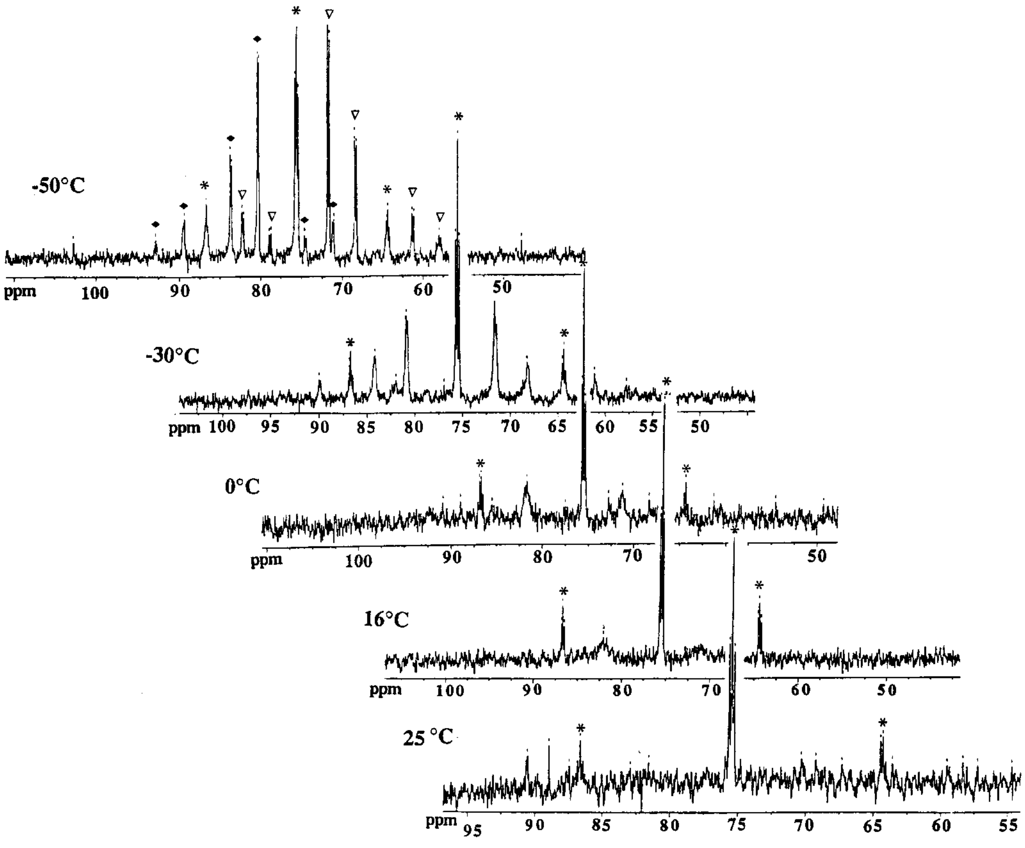
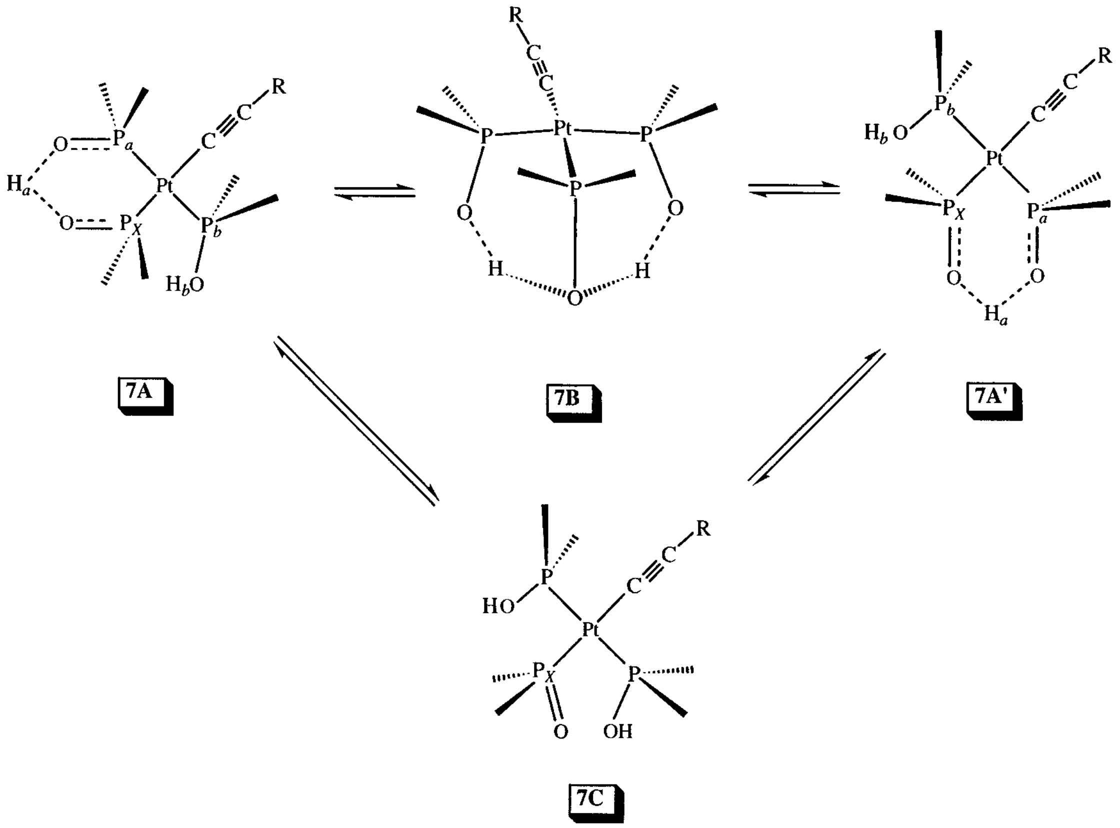


Figure 4. $^{31}P\{^1H\}$ NMR spectra ($CDCl_3$) of complex $[Pt(C{\equiv}C\mathit{t}Bu)\{(PPh_2O)_2H\}(PPh_2OH)]$ **7a** at different temperatures. At +50 °C the spectrum observed is identical to that at 25 °C. ABX system: * X; ▽◆ AB (for assignment see Experimental Section).



Scheme 4. Migration of protons in **7**.

of resonances. The most deshielded P_X resonance ($\delta = 75.68-79.41$), due to the phosphorus atom *trans* to the C≡CR group, occurs as a triplet due to similar *cis*-P_X–$P_{M,A}$ (21.5–27.4 Hz) coupling, and the remaining P_M ($\delta = 69.19-72.49$ $PPh_2O\cdots H$) and P_A [$\delta = (-3.61)-5.14$, L] signals due to mutually *trans* phosphorus atoms exhibit the expected dd splitting pattern with a large two-bond *trans* P_A,P_M coupling (380.1–404.7 Hz). Comparison of the value of the ^1J(Pt,P) coupling constants (see Experimental Section) suggests the *trans* influence order of $PEt_3 \sim C\equiv CR > PPh_2H$

As was expected, compounds **10** and **11** display only two sets of coupled signals [$J(P,P_{cis})$ 24.4–25.4 Hz] in the phosphinite region. Consistent with what is observed for **8** and **9**, in **10** and **11**, the downfield resonance ($\delta = 69.85-70.93$) is tentatively assigned to the PPh_2O^- unit *trans* to C≡CR, and the low-frequency signal ($\delta = 60.95-66.11$) is then assigned to the phosphorus atom *trans* to CN*t*Bu in **10** or CN^- in **11**. The larger coupling to platinum observed for this latter signal (2816–3071 Hz) suggests, that the *trans* influence of alkynyl ligands is slightly stronger than that of the isoelectronic CN*t*Bu or CN^- groups.

On the other hand, the similarity between these alkynylphosphinite/bis(hydroxyphosphine) di(acidic) species **7a** and **7b** and the observed deprotonated skeleton in each of the alkynyltris(phosphinite)platinum *ate* units of the dimeric Pt_2Li_4 complex **3a** led us to investigate their reactivity towards lithium hydroxide. As was expected, treatment of complex **7a** with a slight excess of LiOH (1:2.2) in tetrahydrofuran at room temperature induces the self-assembly of the resulting *tert*-butylalkynyltris(diphenylphosphinite)platinate fragments with the lithium counter ions, yielding the sandwiched Pt_2Li_4 complex **3′a** in very high yield. Using this alternative strategy, we can also prepare the corresponding phenylacetylide derivative **3b** in a similar reaction of **7b** with 2.2 equivalents of LiOH. The similarity of the spectroscopic data for **3′a** and **3b** suggest the same geometry for both species. Thus, complex **3b** displays in its ^{31}P NMR spectrum two sets of signals whose multiplicities, chemical shifts (a doublet at $\delta = 73.20$ and a triplet at $\delta = 58.8$), and ^1J(Pt,P) coupling constants are analogous to those observed for **3′a**. Its ^7Li NMR spectrum exhibits a broad signal at room temperature ($\delta = -0.89$, $w_{1/2} = 86$ Hz) which splits at 0 °C into two signals ($\delta = -0.1$, -1.8; coalescence ca. 3–4 °C), confirming the presence of inequivalent lithium environments. Finally, further support of this formulation for **3b** comes from its mass spectrum in which a peak with $m/z = 1826$, corresponding to the central hexanuclear $[Pt_2(C\equiv CPh)_2(PPh_2O)_6Li_4]$ fragment, is also observed.

Conclusion

It is well known that the development of a selective chemistry in many circumstances is strongly conditioned by the possibility of access to adequate precursors. With this in mind we have concentrated on the reactivity of the homoleptic tetraalkynyl platinate species $Li_2[Pt(C\equiv CR)_4]$ (R = *t*Bu, Ph) and *cis*-$[Pt(C\equiv CR)_2COD]$ towards PPh_2H and $PPh_2(O)H$ and the identification of the products obtained. This study has enabled us to prepare five different new types of alkynyl platinum compounds, which may will be inaccessible by other synthetic routes: i) the mononuclear bis(alkynyl) complexes stabilized by PPh_2H ligands $[PtC{\equiv}CR)_2(PPh_2H)_2]$ (*trans*-**1** or *cis*-**2**); ii) the unexpected mononuclear diphosphine derivative $[Pt(C{\equiv}CR)_2(PPh_2CHPhCH_2PPh_2)]$ (**4b**); iii) the phosphide-bridged diplatinum complexes $[\{Pt(C{\equiv}CR)(\mu\text{-}PPh_2)(PPh_2H)\}_2]$ (**6**), also containing alkynyl and PPh_2H as coligands; iv) the novel mononuclear alkynyl derivatives $[Pt(C{\equiv}CR)\{(PPh_2O)_2H\}(PPh_2OH)]$ (**7**), stabilized by one diphenylphosphinito anion and two diphenylphosphonious acid molecules; v) and finally the very unusual tetralithium diplatinum species formed by a linear chain of four lithium ions sandwiched by two square-planar dianionic platinate units: $[\{Pt(C{\equiv}CR)_2(PPh_2O)_2Li_2(\mu\text{-}H_2O)(Me_2CO)_2\}_2]$ (**2**) and $[\{Pt(C{\equiv}CR)(PPh_2O)_3Li_2(thf)(H_2O)\}_2]$ (**3**).

Complexes **1** and **5**, which are the first reported alkynyl derivatives incorporating only secondary phosphines, are notably stable, remaining unaltered after several hours of refluxing in acetone. The absence of halide coligands avoids the very common dehydrohalogenation reaction[27b, 36] leading to phosphido bridging; moreover they seem not to be reactive enough to add the P–H bond either oxidatively to the metal[12] or through the C≡C triple bond of the alkynyl fragments.[7a] However, the formation of the diplatinum complexes **6** under the reaction conditions used for the synthesis of the mononuclear complexes **5a** or **1b**, respectively, is surprising and the mechanism of their formation remains obscure. Alternatively, both complexes **6a** and **6b** can be obtained, although in very low yield, by treating **5** with an excess of acetic acid (see Experimental Section) suggesting that these diplatinum complexes are formed by formal elimination of acetylene from **5** (probably initiated by protonation of the alkynyl function) followed by a subsequent dimerization through a double-diphenylphosphido-bridging system. On this basis, their formation in the synthesis of **5a** or **1b** could be tentatively attributed to the presence of an excess of PPh_2H. However, we have also observed that the treatment of complexes **5** with one equivalent of PPh_2H slowly produces their isomerization to the corresponding *trans*-isomers **1** (see Experimental Section), but in the case of **5a** the dimer **6a** is also generated (final ratio **1a**/**6a** 3.7:1). The structure of **6a** demonstrates that the PPh_2^- groups have a stronger preference to act as bridges than do the alkynyl ligands. The μ-phosphido ligand is very common in coordination chemistry, and has been found to stabilize both early and late transition metal dinuclear systems.[28, 37] However, although there are many examples of homo- and heterodinuclear di-μ-phosphido-bridged complexes of the type $[L_mM(\mu\text{-}PPh_2)_2M'L'_n]$, to our knowledge complex **6a** is only the second example reported that also possesses terminal alkynyl ligands.[38] In contrast, it should be noted that there are many homo- and heterodinuclear compounds stabilized by mixed $(\mu\text{-}PR_2)(\mu\text{-}C{\equiv}CR)$-bridging systems.[9, 28, 39]

The availability of all these alkynyl platinum complexes offers us an excellent opportunity for further investigation. We have conducted a preliminary exploration of the potential of one of the new complexes. Thus, treatment of $[Pt(C{\equiv}CR)\{(PPh_2O)_2H\}(PPh_2OH)]$ (**7**), which formally contains two $PPh_2(O)H$ ligands, with Lewis bases such as PEt_3, PPh_2H, CNR, or CN^-, produces simple displacement of one of the molecules of diphenylphosphinous acid, leading to the mononuclear complexes (**8**–**11**). However, the promising deprotonation-induced chemistry of these new complexes is partially demonstrated by the aggregation of **7** into **3** following treatment with the deprotonation agent LiOH (see Scheme 3).

In light of the fact that all these new mononuclear complexes contain alkynyl groups and acidic molecules (PPh_2H **1**, **5**, **6**, **9** or PPh_2OH **7**) in mutually *cis* positions, we are currently studying their reactivity towards a variety of deprotonating metal complexes with the aim to obtain homo- and heterometallic, heterobridged $(\mu\text{-}C_2R)/(\mu\text{-}PPh_2)$ or $(\mu\text{-}C_2R)/\mu\text{-}PPh_2O^-)$ species.

Experimental Section

General considerations: Unless noted otherwise, all reactions and manipulations were carried out under nitrogen atmosphere with Schlenk techniques, and with distilled solvents purified by known procedures. IR spectra were recorded on Perkin–Elmer 883 and Perkin–Elmer FT-IR 1000 spectrometers from Nujol mulls between polyethylene sheets unless otherwise noted. NMR spectra were recorded on a Bruker ARX300 spectrometer, and chemical shifts are reported relative to external standards ($SiMe_4$, $CFCl_3$, 85% H_3PO_4, and LiCl in H_2O). Elemental analyses were carried out with a Perkin–Elmer 2400 CHNS/O microanalyzer; the electrospray mass spectra on a HP5989B with interphase API-ES HP59987A (in the negative ion mode with methanol as mobile phase), and the mass spectra (FAB+) on a VG Autospec spectrometer. The starting complexes $[PtCl_2(tht)_2]$[40] and *cis*-$[Pt(C{\equiv}CR)_2COD]$ (R = Ph,[24] *t*Bu[10a]) were prepared by published methods. PPh_2H and $PPh_2(O)H$ were purchased from commercial suppliers.

Reaction of $Li_2[Pt(C{\equiv}CtBu)_4]$ with PPh_2H. Preparation of *trans*-$[Pt(C{\equiv}CtBu)_2(PPh_2H)_2]$ (1a), $[\{Pt(C{\equiv}CtBu)_2(PPh_2O)_2Li_2(\mu\text{-}H_2O)(Me_2CO)_2\}_2]$ (2a) and $[\{Pt(C{\equiv}CtBu)(PPh_2O)_3Li_2(thf)(H_2O)\}_2]$ (3a): $[PtCl_2(tht)_2]$ (0.400 g, 0.904 mmol) was added to a fresh solution of $LiC{\equiv}CtBu$ (4.972 mmol) in diethyl ether/hexane (~25 mL) at low temperature (−20 °C). The mixture was allowed to warm to room temperature and the solvent was then removed in vacuum. The solid residue containing $Li_2Pt(C{\equiv}CtBu)_4$ was treated with 25 mL of an acetone/EtOH mixture (1:4; not deoxygenated). The resulting colourless solution was treated with PPh_2H (0.5 mL, 2.745 mmol), and the mixture stirred. After 2 h of stirring a white solid began to precipitate. The mixture was stirred for another 5 h and then the resulting solid (0.122 g) was filtered and washed with cold EtOH. This solid was identified as *trans*-$[Pt(C{\equiv}CtBu)_2(PPh_2H)_2]$ (**1a**). Concentration of the mother liquor (to ca. 15 mL) yielded an additional fraction of complex **1a** (0.043 g; total yield 25%). The ethanolic filtrate was again stirred in air for 7 hours, causing the precipitation of **2′a**, which was filtered and washed with ether. The analysis of **2′a** gives $[Pt(C{\equiv}CtBu)_2(PPh_2O)_2Li_2(H_2O)_n]$ (*n* = 3). $C_{36}H_{44}Li_2O_5P_2Pt$ (827.7): calcd C 52.24, H 5.36; found C 52.12, H 4.85. However, recrystallization of this solid from hot acetone yields $[\{Pt(C{\equiv}CtBu)_2(PPh_2O)_2Li_2(\mu\text{-}H_2O)(Me_2CO)_2\}_2]$ (**2a**) as a microcrystalline solid (40% yield). This solid has a tendency to exchange acetone molecules for H_2O. In fact, all samples analysed give analyses in agreement either with **2′a** or with a composition between **2a** and **2′a**. This notwithstanding, the IR of **2a** and **2′a** are essentially identical and the NMR spectra (^1H and ^{31}P) are identical. Finally, prolonged stirring of the last ethanolic filtrate for 1 day slowly produced a new white solid (**3′a**), which was filtered and washed with ethanol. The analysis of compound **3′a** gives $[Pt(C{\equiv}CtBu)(PPh_2O)_3Li_2(H_2O)_n]$ (*n* = 2). $C_{42}H_{43}Li_2O_5P_3Pt$ (929.7): calcd: C 54.26, H 4.66; found: C 54.28, H 4.71. Recrystallization of **3′a** from a mixture of THF/diethyl-ether gives $[\{Pt(C{\equiv}CtBu)(PPh_2O)_3Li_2(H_2O)(thf)\}_2]$ **3a** as colorless microcrystalline prisms (4% yield). Different samples of **3a** give analyses corresponding to **3′a** or between **3′a** and **3a**. If the reaction is carried out under anaerobic conditions **1a** and **2a** are obtained in yields of

40% and 11%, respectively. **3a** is not detected under these conditions. Longer periods of stirring (6 days) under the same conditions improved the yield of **1a** (88%).

*Data for **1a***: ^{1}H NMR ($CDCl_3$): $\delta = 7.96$ (br, 8H), 7.37 (br, 8H; Ph), 6.46 (AA′ part of an AA′XX′ system (X = P); $N = {}^1J(P,H) + {}^3J(P',H) = 400$ Hz, $^2J(Pt,H) = 26.2$ Hz, P*H*), 1.05 (s, 18H; *t*Bu); $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = -1.99$ ($^1J(Pt,P) = 2616$ Hz); ^{31}P NMR ($CDCl_3$): $\delta = -1.97$, (XX′ part of an AA′XX′ system (A = H); $^1J(P,H) = 399.9$ Hz, $^2J(P,P') = 484$ Hz, $^3J(P,H') = 3.6$ Hz, $J(H,H') \sim 0$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 134.2$ (t, $J(C,P) = 6.2$ Hz, $^3J(Pt,C) = 24.5$ Hz; *o*-C, PPh_2H), 130.1 (s; *p*-C, PPh_2H), 128.7 (t, $J(C,P) = 28.3$ Hz; *i*-C, PPh_2H), 128.0 (t, $J(C,P) = 5.4$ Hz; *m*-C, PPh_2H), 120.6 (t, $^3J(C_\beta,P) = 2.6$ Hz, $^2J(Pt,C_\beta) = 249$ Hz; C_β, $-C_\alpha{\equiv}C_\beta{-}t$Bu), 85.2 (t, $^2J(C_\alpha,P) = 15.9$ Hz, $^1J(Pt,C_\alpha) = 913$ Hz; C_α, $C_\alpha{\equiv}C_\beta{-}t$Bu), 32.0 (s; $C(CH_3)_3$), 29.0 (s, $^3J(Pt,C) = 17.9$ Hz; $-CMe_3$]; IR: $\tilde{\nu} = 2369$ (vs; P−H), 2106 cm^{-1} (m; C≡C); MS: *m/z* (%): 1294 (9) $[\{Pt(PPh_2H)(C{\equiv}CtBu)(\mu\text{-}PPh_2)\}_2]^+ = [A]^+$, 1212 (9) $[A - C{\equiv}CtBu - H]^+$, 1027 (6) $[A - C{\equiv}CtBu - PPh_2H]^+$, 729 (31) $[M^+]$, 647 (33) $[M - C{\equiv}CtBu - H]^+$, 565 (68) $[Pt(PPh_2)_2]^+$, 379 (70) $[PtPPh_2 - H]^+$; $C_{36}H_{40}P_2Pt$ (729.7): calcd C 59.25, H 5.52; found: C 59.12, H 5.54.

*Data for **2a***: ^{1}H NMR (CD_3COCD_3): $\delta = 7.18$ (m), 7.82 (m) Ph, 0.46 (s; *t*Bu); $^{31}P\{^1H\}$NMR (CD_3COCD_3): $\delta = 67.37$ ($J(Pt,P) = 2510$ Hz); $^7Li\{^1H\}$ NMR (CD_3COCD_3): $\delta = 0.88$ (s); IR: $\tilde{\nu} = 3646$ (w), 3402 (m; $O{-}H)_s$, 1611 (w; $O{-}H)_b$, 2092 (w; C≡C), 1030 (m), 1006 (m), 996 cm^{-1} (m; P−O); MS: *m/z* (%): 1294 (53) $[\{Pt(PPh_2H)(C{\equiv}CtBu)(\mu\text{-}PPh_2H)\}_2]^+ = [A]^+$, 1213 (59) $[A - C{\equiv}CtBu]^+$, 1108 (27) $[A - PPh_2H]^+$, 1026 (32) $[A - C{\equiv}CtBu - PPh_2H]^+$, 767 (30) $[Pt(C{\equiv}CtBu)_2(PPh_2O)_2Li{+}H]^+$, 679 (46) $[Pt(C{\equiv}CtBu)(PPh_2O)_2{+}H]^+$, 604 (100) $[Pt(PPh_2O)_2Li]^+$, 402 (87) $[Pt(PPh_2O)Li]^+$.

*Data for **3a***: ^{1}H NMR ($CDCl_3$): $\delta = 7.94$ (m), 7.51 (t), 7.30 (m), 7.13 (t), 6.69 (t), 6.40 (t) (Ph), 1.59 (br; H_2O), 0.49 (s; *t*Bu); $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 73.14$ (d, $^1J(Pt,P_A) = 2723$ Hz, 2P), 58.70 (t, $^1J(Pt,P_X) = 2673$ Hz, 1P), $^2J(P_A,P_X) = 29.3$ Hz; $^7Li\{^1H\}$ NMR ($CDCl_3$): at 20 °C, $\delta = -1.03$ (br s); at 3 °C, $\delta = -1.3$ (br); at 0 °C, $\delta = -0.22$ (br), −1.75 (br); at −20 °C, $\delta = -0.23$ (s), −1.97 (s); IR: $\tilde{\nu} = 3623$ (br), 3374 (br; OH), 1036 (s), 1024 (m), 998 cm^{-1} (w; P−O); MS: *m/z* (%): 1705 (10) $[Pt_2(C{\equiv}CtBu)(PPh_2O)_6Li_4]^+$; 882 (100) $[Pt(C{\equiv}CtBu)(PPh_2O)_3{+}3H]^+$, 806 (27) $[Pt(PPh_2O)_3Li]^+$, 604 (80) $[Pt(PPh_2O)_2Li]^+$, 396 (54) $[Pt(PPh_2O)]^+$.

Reaction of $Li_2[Pt(C{\equiv}CtBu)_4]$ with $PPh_2(O)H$: A fresh solution of $Li_2Pt(C{\equiv}CtBu)_4$ (0.452 mmol) in an acetone/EtOH mixture (25 mL) prepared as described above was treated with $PPh_2(O)H$ (0.283 g, 1.356 mmol) and the mixture stirred for 3 days. The resulting white precipitate was filtered, washed with EtOH, and identified by ^{31}P NMR as a mixture of **2′a** and **3′a**. Upon stirring of this solid with $CHCl_3$ (ca. 10 mL), complex **3′a** dissolved and **2′a**, which is insoluble in $CHCl_3$, was separated by filtration (0.083 g, 20% yield based on Pt in $[PtCl_2(tht)_2]$). Removal of the solvent from the filtrate and addition of diethyl ether (5 mL) gave **3′a** (0.168 g, 37% yield).

Reaction of $[\{Pt(C{\equiv}CtBu)_2(PPh_2O)_2Li_2(\mu\text{-}H_2O)(Me_2CO)_2\}_2]$ (2a) with $PPh_2(O)H$: A white suspension of **2a** (0.050 g, 0.027 mmol) in $CHCl_3$ (30 mL), was treated with $PPh_2(O)H$ (0.011 g, 0.054 mmol), and the mixture stirred for 2 d at room temperature. The remaining white solid was filtered off and identified ($^{31}P\{^1H\}$ NMR in CD_3COCD_3) as **2a** (40% yield with respect to the initial quantity). Evaporation of the filtrate to dryness and treatment with diethyl ether (10 mL) gave a white solid, which was a mixture (^{31}P NMR) of **3a** and free $PPh_2(O)H$. When the reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy at 20 °C for longer periods (5 days), it was observed that complex **2a** was always present in the reaction mixture, since the formation of **3a** was not complete.

Reaction of *trans*-$[Pt(C{\equiv}CtBu)_2(PPh_2H)_2]$ (1a) with LiOH and H_2O_2: H_2O_2 (27.7 µl, 0.274 mmol) and LiOH (0.011 g, 0.274 mmol) were added to a solution of **1a** (0.100 g, 0.137 mmol; 2:2:1 molar ratio) in acetone (20 mL), and the mixture was stirred for 15 h at room temperature. The $^{31}P\{^1H\}$ NMR of this solution shows only the presence of starting material. When an excess of LiOH and H_2O_2 (4:4:1 molar ratio) and longer periods of stirring (6 d) are employed, a complex mixture of unidentified platinum complexes is observed by $^{31}P\{^1H\}$ NMR.

Preparation of *trans*-$[Pt(C{\equiv}CPh)_2(PPh_2H)_2]$ (1b), $[\{Pt(C{\equiv}CPh)_2(PPh_2O)_2Li_2(\mu\text{-}H_2O)S_2\}_2]$ (S = H_2O 2′b), $[Pt(C{\equiv}CPh)_2(PPh_2CHPhCH_2PPh_2)]$ (4b), and $[\{Pt(C{\equiv}CPh)(\mu\text{-}PPh_2)(PPh_2H)\}_2]$ (6b)

a) Reaction of $Li_2[Pt(C{\equiv}CPh)_4]$ with PPh_2H: A white suspension of $Li_2[Pt(C{\equiv}CPh)_4]$, prepared from $[PtCl_2(tht)_2]$ (0.300 g, 0.678 mmol) and LiC≡CPh, (3.73 mmol; 1:5. molar ratio) in diethyl ether/hexane was concentrated in vacuo, dissolved in a deoxygenated acetone/EtOH mixture (20 mL), and finally treated with PPh_2H (0.352 mL, 2.035 mmol). After stirring the mixture for 12 hours, the solution was concentrated giving a beige solid (mixture of **1b** and **4b** ∼1:1 as shown by ^{31}P NMR). Slow crystallization of this solid from $CHCl_3$/hexane in air afforded **1b** as pale-yellow crystals (0.06 g, 11% yield). Concentration of the mother liquor (ca. 5 mL) caused the precipitation of a second beige solid (mixture of **2b** and **4b**), which was recrystallized from THF/hexane, yielding **2′b** as a microcrystalline solid (0.06 g, 11% yield). If the reaction is carried out under aerobic conditions and for longer periods of stirring (24 h), only **2′b** was obtained in the first fraction (0.57 g, 31% yield). Upon stirring the ethanolic filtrate for 3 days a white solid separates, which is a complex mixture of products ($^{31}P\{^1H\}$ NMR) containing mainly **2′b**. However, when a solution of $Li_2[Pt(C{\equiv}CPh)_4]$ (2.261 mmol) dissolved in an acetone/ethanol mixture (5 mL/15 mL) was treated directly with PPh_2H (1.17 mL, 6.78 mmol) and stirred for 6 days under aerobic conditions, a new white solid precipitated (1.8 g, 91% yield). This solid was identified as **4b**.

*b) Preparation of **1b** and **6b***: Treatment of $[PtCl_2(tht)_2]$ (0.600 g, 1.356 mmol) at low temperature (−20 °C) with a lesser excess of LiC≡CPh (4.069 mmol, 1:3 molar ratio) slowly (∼45 min) yields a suspension [probably mixtures of species of the type $Pt(C{\equiv}CPh)_{4-x}(tht)_xLi_{2-x}$, ($x = 0{-}2$)]. Addition of PPh_2H (0.7 mL, 4.069 mmol, 1:3 molar ratio) to this mixture at room temperature, immediately produces a yellow suspension. After 10 minutes of stirring, the mixture was evaporated to dryness, treated with CH_2Cl_2 (50 mL), filtered through celite, and the resulting filtrate evaporated to small volume (∼5 mL). Addition of *n*-hexane (15 mL) gave a beige solid, which was recrystallized from $CHCl_3$/hexane, yielding **1b** (0.7 g, 67%) as a yellow microcrystalline solid. The mother liquor (CH_2Cl_2/hexane) was evaporated to dryness, treated with ethanol (20 mL), and stirred for three days. The resulting white solid, which was filtered off and washed with diethyl ether, was identified as **6b** (0.10 g, 11% yield). If the reaction is carried out in a 1:2 molar ratio (Pt:PPh_2H), identical products are observed in yields of 48% (for **1b**) and 3% (for **6b**). Complex **6b** is also obtained by treatment of **5b** with CH_3COOH: Acetic acid (0.5 mL) was added to a solution of **5b** (0.100 g, 0.1299 mmol) in CH_2Cl_2 (10 mL), and the mixture was stirred for 6 days. The brown solution was evaporated to dryness, and the residue was treated with a mixture of diethyl ether/hexane (1:2). The resulting beige solid containing **6b** with other unidentified products (**9b** is also observed) was recrystallized twice from $CHCl_3$/hexane yielding **6b** in very low yield (∼15%).

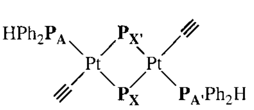
*Data for **1b***: ^{1}H NMR ($CDCl_3$): $\delta = 7.96$, 7.41, 7.11 (m, Ph), ∼6.72 (AA′ part of an AA′XX′ system (X = P), due to overlapping with Ph resonances only $^2J(Pt,H) = 26.8$ Hz can be calculated; P*H*); $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = -4.26$ ($^1J(Pt,P) = 2547$ Hz); ^{31}P NMR ($CDCl_3$): $\delta = -4.25$, (XX′ part of an AA′XX′ system (A = H); $N = 402.7$ Hz, $^1J(P,H) = 397.5$ Hz, $^2J(P,P') = 459.5$ Hz, $^3J(P,H') = 5.2$ Hz, $J(H,H') \sim 0$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): at 20 °C, $\delta = 134.4$ (*o*-C, PPh_2H), 131.2 ($^4J(Pt,C) = 8.7$ Hz; *o*-C, C≡CPh), 130.5 (*p*-C, PPh_2H), 128.63 (*m*-C, PPh_2H), 127.9 (*i*-C, C≡CPh), 127.7 (*m*-C, C≡CPh), 125.8 (*p*-C, C≡CPh), 112.4 ($^2J(Pt,C_\beta) = 259$ Hz; C_β, $-C_\alpha{\equiv}C_\beta{-}Ph$), 102.9 ($^1J(Pt,C_\alpha) = 834$ Hz; C_α, $C_\alpha{\equiv}C_\beta{-}Ph$; at −50 °C, $^2J(P,C_\alpha) \sim 27$ Hz is observed); IR: $\tilde{\nu} = 2376$ (m; P−H), 2110 cm^{-1} (vs; C≡C); MS: *m/z* (%): 770 (100) $[M{+}H]^+$, 666 (97) $[Pt(C{\equiv}CPh)(PPh_2)_2]^+$, 565 (62) $[Pt(PPh_2)_2]^+$, 378 (47) $[PtPPh_2 - 2H]^+$; $C_{40}H_{32}P_2Pt$ (769.7): calcd C 62.42, H 4.19; found C 62.45, H 4.12.

*Data for **2′b***: ^{1}H NMR ($CDCl_3$): $\delta = 7.78$, 7.14, 6.76, 6.19 (Ph, PPh_2, C≡CPh), 3.53 (br s, H_2O), signals due to THF are also observed 3.73 (m), 1.84 (m); $^{31}P\{^1H\}$NMR ($CDCl_3$): $\delta = 68.07$ (s, $^1J(Pt,P) = 2395$ Hz); $^7Li\{^1H\}$ NMR ($CDCl_3$): at 20 °C, $\delta = -0.62$ (s), at −20 °C, $\delta = -0.32$ (br s); IR: $\tilde{\nu} = 3565$ (vs), 3398 (vs; $O{-}H)_s$, 2095 (s; C≡C), 1038 (vs), 1024 (vs), 997 cm^{-1} (w; P−O); ES-MS (−): *m/z* (%): 800.6 (100) $[Pt(C{\equiv}CPh)_2(PPh_2O)_2{+}H]^-$, 498.4 (14) $[Pt(C{\equiv}CPh)(PPh_2OH)]^-$; $[Pt(C{\equiv}CPh)_2(PPh_2O)_2Li_2(H_2O)_3]$, $C_{40}H_{36}Li_2O_5P_2Pt$ (867.6): calcd C 55.37, H 4.18; $[Pt(C{\equiv}CPh)_2(PPh_2O)_2Li_2(H_2O)_2(thf)]$, $C_{44}H_{42}Li_2O_5P_2Pt$ (921.7): calcd C 57.34, H 4.59; found: C 48.67, H 3.98, poor analyses with low C content are found systematically.

*Data for **4b***: ^{1}H NMR ($CDCl_3$): $\delta = 8.19$ (m, 2H), 7.99 (m, 2H), 7.70–6.90 (m, 29H), 6.66 (d, 2H) (Ph), 3.83 (m, 1H; CH_2), 3.19 (dm, $^2J(H,P) = 47$ Hz, $^3J(Pt,H) \sim 25$ Hz; CH), 2.53 (m, 1H, CH_2); $^1H\{^{31}P\}$ NMR ($CDCl_3$): Decoupling the $\delta = 21.4$ phosphorus resonance: 8.19 (d, $J(H,H) = 6$ Hz), 7.99 (d, $J(H,H) = 6.3$ Hz), 7.59–6.90 (m), 6.66 (d, $J(H,H) = 7.5$ Hz) (Ph), 3.83 (tm, $^2J(H_a,H_b) \sim {}^3J(P,H_a) = 9.3$ Hz; H_a, CH_aH_b), 3.21 (ddd,

^{2}J(P,H$_{c}$) = 47 Hz, ^{3}J(H$_{c}$,H$_{b}$) = 14.4 Hz, ^{3}J(H$_{c}$,H$_{a}$) = 3.3 Hz, ^{3}J(Pt,H$_{c}$) ~ 25 Hz), 2.53 (td, ^{2}J(H$_{b}$,H$_{a}$) = 9.3 Hz, ^{3}J(H$_{b}$,H$_{c}$) ~ ^{3}J(H$_{b}$,P) = 14.4 Hz; H$_{b}$, CH$_{a}$H$_{b}$). By decoupling the signal at $\delta = 49.24$ under similar conditions the modification of the proton spectrum was negligible. ^{31}P{^{1}H} NMR (CDCl$_{3}$): $\delta = 49.24$ (d, ^{1}J(Pt,P) = 2260 Hz), 21.53 (d, ^{1}J(Pt,P) = 2250 Hz, ^{3}J(P,P) = 13.8 Hz); the ^{13}C NMR spectrum could not be recorded due to the low solubility of the complex; IR: $\tilde{\nu} = 2114$ cm^{-1} (s; C≡C); ES-MS(+): *m/z* (%): 871 (44) [*M*]$^{+}$, 771 (47) [*M* – C$_{2}$Ph+H]$^{+}$, 668 (58) [*M* – 2C$_{2}$Ph – H]$^{+}$, 565 (100) [Pt(PPh$_{2}$)$_{2}$]$^{+}$, 487 (90) [PtPPh$_{2}$PPh – H]$^{+}$, 379 (95) [PtPPh$_{2}$ – H]$^{+}$; C$_{48}$H$_{38}$P$_{2}$Pt (871.9): calcd C 66.12, H 4.39; found C 65.87, H 3.97.

Data for ***6b***: ^{1}H NMR (CDCl$_{3}$): $\delta = 7.63$, 7.28, 7.06, 6.71 (m, Ph), 5.35 (dm, *J*(P,H) = 372 Hz, 2H; P*H*); ^{31}P{^{1}H} NMR (CDCl$_{3}$): AA′XX′ + AA′XX′M (M = Pt) spin systems δP$_{AA'}$ = 1.58 (PPh$_{2}$H), δP$_{XX'}$ = – 138.7 (μ-PPh$_{2}^{-}$), [$N = {}^{2}J$(P$_{A}$,P$_{X}$) + ^{2}J(P$_{A}$,P$_{X'}$) = 321.4 Hz, $K = {}^{4}J$(P$_{A}$,P$_{A'}$) + ^{2}J(P$_{X}$,P$_{X'}$) = 132.6 Hz, $L = {}^{2}J$(P$_{A}$,P$_{X}$) – ^{2}J(P$_{A}$,P$_{X'}$) = 351.9 Hz, |^{2}J(P$_{A}$,P$_{X}$)| = 336.7 Hz, |^{2}J(P$_{A}$,P$_{X'}$)| = 15.3 Hz, ^{1}J(Pt,P$_{X}$) = 1688 Hz, ^{1}J(Pt,P$_{X'}$) = 1766 Hz, ^{1}J(Pt,P$_{A}$) = 2051 Hz]; IR: $\tilde{\nu} = 2357$ (w; P–H), 2104 cm^{-1} (s; C≡C); ES-MS (apci +): *m/z* (%): 666.5 (98) [Pt(C≡CPh)(PPh$_{2}$)$_{2}$]$^{+}$, 667.5 (100) [Pt(C≡CPh)(PPh$_{2}$)(PPh$_{2}$H)]$^{+}$, 566 (15) [Pt(PPh$_{2}$)(PPh$_{2}$H)]$^{+}$; C$_{64}$H$_{52}$P$_{4}$Pt$_{2}$ (1335.2): calcd C 57.57, H 3.92; found C 57.73, H 4.42.



Preparation of *cis*-[Pt(C≡C*t*Bu)$_{2}$(PPh$_{2}$H)$_{2}$] (5a) and [{Pt(C≡C*t*Bu)(μ-PPh$_{2}$)(PPh$_{2}$H)}$_{2}$] (**6a**): A solution of *cis*-[Pt(C≡C*t*Bu)$_{2}$(COD)] (1.114 g, 2.393 mmol) in CH$_{2}$Cl$_{2}$ (10 mL) was treated at – 30 °C with PPh$_{2}$H (0.87 mL, 4.770 mmol), and the resulting mixture was stirred for 15 min at low temperature. Then the solvent was removed in vacuum and the addition of diethyl ether (5 mL) caused the precipitation of *cis*-[Pt(C≡C*t*Bu)$_{2}$(PPh$_{2}$H)$_{2}$] **5a** as a white solid (1.383 g, 79% yield). On cooling the filtrate to – 30 °C for a week, a beige solid separated, which was recrystallised from CH$_{2}$Cl$_{2}$/hexane and identified as **6a** 0.031 g, 2% yield). The complex **6a** is also obtained by treatment of **5a** with CH$_{3}$COOH: **5a** (0.100 g, 0.1379 mmol) in CH$_{2}$Cl$_{2}$ (10 mL) was treated with glacial acetic acid (1 mL). After 7 d of stirring, the solution was evaporated to dryness and the residue treated with *n*-hexane, affording a beige solid identified by ^{31}P NMR spectroscopy as impure **6a**. Recrystallization from CHCl$_{3}$/hexane gives pure **6a**, but in very low yield (~25%).

Data for ***5a***: ^{1}H NMR (CDCl$_{3}$): $\delta = 7.65$ (m, 8H), 7.33 (m, 12H) (Ph), 5.88 (dm, $N = {}^{1}J$(P,H) + ^{3}J(P′,H) = 378 Hz; 2H, P*H*), 1.02 (s, 18H, *t*Bu); ^{31}P{^{1}H} NMR (CDCl$_{3}$): $\delta = -5.49$ (s, ^{1}J(Pt,P) = 2156 Hz); ^{31}P NMR (CDCl$_{3}$): $\delta = -5.49$ (d, *J*(P,H) = 377 Hz); ^{13}C{^{1}H} NMR (CDCl$_{3}$): at 20 °C, $\delta = 134.0$ (t, *J*(C,P) = 5.3 Hz, *J*(Pt,C) = 20.2 Hz; *o*-C, PPh$_{2}$H), 130.3 (s, *p*-C, PPh$_{2}$H), 128.1 (t, *J*(C,P) = 5.4 Hz; *m*-C, PPh$_{2}$H), 127.4 (AXX′, ^{1}J(C,P) + ^{3}J(C,P′) = 57.5 Hz; *i*-C), 118.8 (AXX′, ^{3}J(C$_{\beta}$,P*trans*) + ^{3}J(C$_{\beta}$,P*cis*) ~ 36.3 Hz, ^{2}J(Pt,C$_{\beta}$) = 306.4 Hz; C$_{\beta}$, –C$_{\alpha}$≡C$_{\beta}$*t*Bu), 84.3 (dd, ^{2}J(C$_{\alpha}$,P*trans*) = 153.0 Hz, ^{2}J(C$_{\alpha}$,P*cis*) = 21.2 Hz, ^{1}J(Pt,C$_{\alpha}$) = 1122.4 Hz; Cα, –C$_{\alpha}$≡C$_{\beta}$*t*Bu) 31.6 (s, ^{4}J(Pt,C) = 8.0 Hz; C(*C*H$_{3}$)$_{3}$), 28.7 (s, ^{3}J(Pt,C) = 20.9 Hz; – *C*Me$_{3}$); IR: $\tilde{\nu} = 2354$ (m; P–H), 2118 cm^{-1} (w; C≡C); MS: *m/z* (%): 1214 (8) [Pt$_{2}$(C≡C*t*Bu)(μ-PPh$_{2}$)$_{2}$(PPh$_{2}$H)$_{2}$]$^{+}$, 730 (76) [*M*+H]$^{+}$, 647 (33) [*M* – C≡C*t*Bu – H]$^{+}$, 566 (100) [Pt(PPh$_{2}$H)(PPh$_{2}$)]$^{+}$, 379 (42) ([PtPPh$_{2}$ – H]$^{+}$; C$_{36}$H$_{40}$P$_{2}$Pt (729.8): calcd C 59.25, H 5.52; found C 58.99, H 5.65.

Data for ***6a***: ^{1}H NMR (CDCl$_{3}$): $\delta = 7.61$ (m,16H), 7.27 (m), 7.07 (m) (24H) (Ph), 5.25 (dm, *J* = 368 Hz; 2H, P*H*), 0.86 (s, 18H, *t*Bu); ^{31}P{^{1}H} NMR (CDCl$_{3}$): AA′XX′ spin system δP$_{AA'}$ = 1.36 (PPh$_{2}$H), δP$_{XX'}$ = – 145.4 (μ-PPh$_{2}^{-}$), [$N = {}^{2}J$(P$_{A}$,P$_{X}$) + ^{2}J(P$_{A}$,P$_{X'}$) = 328.4 Hz, $K = {}^{4}J$(P$_{A}$,P$_{A'}$) + ^{2}J(P$_{X}$,P$_{X'}$) = 136.4 Hz, $L = {}^{2}J$(P$_{A}$,P$_{X}$) – ^{2}J(P$_{A}$,P$_{X'}$) = 362 Hz, |^{2}J(P$_{A}$,P$_{X}$)| = 345.2 Hz, |^{2}J(P$_{A}$,P$_{X'}$)| = 16.8 Hz, ^{1}J(Pt,P$_{X}$) = 1689 Hz, ^{1}J(Pt,P$_{X'}$) = 1792 Hz, ^{1}J(Pt,P$_{A}$) = 2035 Hz]; IR: $\tilde{\nu} = 2352$ cm^{-1} (s; P–H); MS: *m/z* (%): 1294 (60) [*A*]$^{+}$, 1213 (100) [*A* – C≡C*t*Bu]$^{+}$, 1108 (31) [*A* – PPh$_{2}$H – H]$^{+}$, 1027 (53) [*A* – C≡C*t*Bu – PPh$_{2}$H]$^{+}$; C$_{60}$H$_{60}$P$_{4}$Pt$_{2}$ (1295.2): calcd C 55.64, H 4.67; found C 55.49, H 4.76.

Preparation of *cis*-[Pt(C≡CPh)$_{2}$(PPh$_{2}$H)$_{2}$] (5b): A yellow solution of *cis*-[Pt(C≡CPh)$_{2}$(COD)] (1.004 g, 1.986 mmol) in CH$_{2}$Cl$_{2}$ (10 mL) was treated at low temperature (– 30 °C) with PPh$_{2}$H (0.72 mL, 3.973 mmol) and the mixture stirred for 5 min. The solvent was removed in vacuum, and the residue was treated with diethyl ether (5 mL) to give **5b** as a yellow solid, which was washed with diethylether and dried under vacuum (1.169 g, 76% yield). ^{1}H NMR (CDCl$_{3}$): $\delta = 7.67$ (m), 7.38 (m), 7.08 (m), (30H; Ph), 6.08 (dm, $N = {}^{1}J$(P,H) + ^{3}J(P′,H) = 390 Hz, 2H; P*H*); ^{31}P{^{1}H} NMR (CDCl$_{3}$): $\delta = -7.07$ (s, ^{1}J(Pt,P) = 2169 Hz); ^{31}P NMR (CDCl$_{3}$): $\delta = -7.07$ (d, *J*(P,H) = 383 Hz); ^{13}C{^{1}H} NMR (CDCl$_{3}$): at – 50 °C, $\delta = 134.2$ (t, *J*(C,P) = 5.2 Hz; *o*-C, PPh$_{2}$H), 131.4 (in this signal, the *o*-C of the –C≡CPh groups and *p*-C of the ligands PPh$_{2}$H probably overlap), 131.1 (s; Ph), 128.6 (t, *J*(C,P) = 5.0 Hz; *m*-C, PPh$_{2}$H), 127.5 (s; *m*-C, Ph, –C≡CPh), 127.3 (s; *i*-C, Ph, –C≡CPh), 126.2 (AXX′, ^{1}J(C,P) + ^{3}J(C,P′) = 59.4 Hz, *i*-C, PPh$_{2}$H), 125.5 (s; *p*-C, Ph, –C≡CPh), 110.6 (AXX′, ^{3}J(C$_{\beta}$,P*trans*) + ^{3}J(C$_{\beta}$,P*cis*) = 36.4 Hz, ^{2}J(Pt,C$_{\beta}$) = 308.4 Hz; C$_{\beta}$, –C$_{\alpha}$≡C$_{\beta}$Ph), 99.9 (dd, ^{2}J(C$_{\alpha}$,P*trans*) = 148.8 Hz, ^{2}J(C$_{\alpha}$,P*cis*) = 21.4 Hz, ^{1}J(Pt,C$_{\alpha}$) = 1114.6 Hz; C$_{\alpha}$, –C$_{\alpha}$≡C$_{\beta}$Ph); IR: $\tilde{\nu} = 2342$ (m; P–H), 2119 cm^{-1} (m; C≡C); MS: *m/z* (%): 1334 (10) [{Pt(C≡CPh)(μ-PPh$_{2}$)(PPh$_{2}$H)}$_{2}$]$^{+}$ = [*B*]$^{+}$, 1233 (14) [*B* – C≡CPh]$^{+}$, 1133 (11) [*B* – 2C≡CPh+H]$^{+}$, 1047 (6) [*B* – C≡CPh – PPh$_{2}$H]$^{+}$, 769 (51) [*M*]$^{+}$, 667 (35) [*M* – C≡CPh – H]$^{+}$, 566 (100) [Pt(PPh$_{2}$H)(PPh$_{2}$)]$^{+}$, 379 (39) [PtPPh$_{2}$ – H]$^{+}$; C$_{40}$H$_{32}$P$_{2}$Pt (769.7): calcd C 62.42, H 4.19; found C 62.05, H 4.06.

Reactions of *cis*-[Pt(C≡CR)$_{2}$(PPh$_{2}$H)$_{2}$] with PPh$_{2}$H: For R = *t*Bu; PPh$_{2}$H (28.9 µL, 0.167 mmol) was added to a stirred solution of **5a** (0.122 g, 0.167 mmol) in deoxygenated CH$_{2}$Cl$_{2}$ (5 mL). After 24 h stirring, the solution was evaporated to dryness and the residue treated with deoxygenated diethyl ether (5 mL) to give a solid (0.09 g), identified as a mixture of *trans*-[Pt(C≡C*t*Bu)$_{2}$(PPh$_{2}$H)$_{2}$] **1a** and [{Pt(C≡C*t*Bu)(μ-PPh$_{2}$)(PPh$_{2}$H)}$_{2}$] **6a** (3.7:1 ratio). If the initial mixture is stirred for 3 days under aerobic conditions, oxidation of PPh$_{2}$H takes place and PPh$_{2}$(O)H is generated. The ^{31}P NMR spectrum of the final mixture shows the complete transformation of **6a** to [Pt(C≡C*t*Bu){(PPh$_{2}$O)$_{2}$H}(PPh$_{2}$H)] (**9a**). Similar results were obtained starting from **5b** (0.120 g, 0.156 mmol) and 1 equiv of PPh$_{2}$H (26.98 µL, 0.156 mmol). In this case after 48 hours under anaerobic conditions, the solid obtained (0.08 g) is identified as *trans*-[Pt(C≡CPh)$_{2}$(PPh$_{2}$H)$_{2}$] **1b** with a small amount of PPh$_{2}$(O)H as impurity.

Preparation of [Pt(C≡CR){(PPh$_{2}$O)$_{2}$H}(PPh$_{2}$OH)] (R = *t*Bu 7a; R = Ph 7b): A suspension of *cis*-[Pt(C≡C*t*Bu)$_{2}$(COD)] (0.150 g, 0.322 mmol) in CH$_{2}$Cl$_{2}$ (20 mL) was treated at – 40 °C with PPh$_{2}$(O)H (97%; 0.201 g, 0.996 mmol) and the mixture stirred for 15 min at low temperature. The solution was evaporated to dryness and the residue treated with acetone (5 mL) to give **7a** as a white solid (0.213 g, 75% yield). Complex **7b** was prepared similarly starting from *cis*-[Pt(C≡CPh)$_{2}$(COD)] (0.200 g, 0.396 mmol) and PPh$_{2}$(O)H (0.247 g, 1.188 mmol), but in this case the reaction time was 4 h and the final solid was recrystallized from CHCl$_{3}$/hexane yielding **7b** as a white solid (0.215g, 60%). Similar results were obtained using a Pt/PPh$_{2}$(O)H ratio of 1:2 at – 20 °C (yield: 45% **7a**, 43% **7b**). If *cis*-[Pt(C≡C*t*Bu)$_{2}$(COD)] (0.250 g, 0.537 mmol) is treated with two molar equiv of PPh$_{2}$(O)H (0.224 g, 1.074 mmol) in CHCl$_{3}$ (20 mL) at room temperature, and the resulting solution evaporated to dryness after 15 min. of stirring, a white solid is obtained (0.192 g, 36% yield based on Pt) by treating with diethyl ether (10 mL), and is identified as [Pt{(PPh$_{2}$O)$_{2}$H}$_{2}$]:[30e] ^{31}P{^{1}H} NMR (CDCl$_{3}$): $\delta = 72.33$ (*J*(Pt–P) = 2454 Hz).

Data for ***7a***: ^{1}H NMR (CDCl$_{3}$): at 20 °C, $\delta = 7.55–7.03$ (m; Ph), 0.80 (s; *t*Bu); at – 50 °C, a broad signal is seen at 16.92, which can tentatively be assigned to O···*H*···O; ^{31}P{^{1}H} NMR (CDCl$_{3}$): at – 50 °C, ABX pattern δP$_{A}$ = 81.75 (PPh$_{2}$O^{-}), δP$_{B}$ = 70.29 (PPh$_{2}$OH), δP$_{X}$ = 75.56 (P *trans* to C≡C*t*Bu), ^{2}J(P$_{A}$,P$_{B\mathit{trans}}$) = 405.4 Hz, ^{2}J(P$_{A}$,P$_{X\mathit{cis}}$) = 20.4 Hz, ^{2}J(P$_{B}$,P$_{X\mathit{cis}}$) = 26.3 Hz, ^{1}J(Pt,P$_{A}$) = 2223 Hz, ^{1}J(Pt,P$_{B}$) = 2537 Hz, ^{1}J(Pt,P$_{X}$) = 2713 Hz; at 25 °C, 75.45 (t, ^{2}J(P$_{X}$,P$_{\mathit{cis}}$) = 23.2 Hz, ^{1}J(Pt,P$_{X}$) = 2696 Hz). Coalescence of δ_{A} and δ_{B} is observed at about 50 °C ($\Delta G^{\ddagger} \sim 53.8$ kJ mol^{-1}); IR (KBr)$\tilde{\nu}$ = 960 (s), 932 (vs), 900 (sh), bands at 1027 (w) and 1000 cm^{-1} (w) are also observed (P–O); MS: *m/z* (%): 881 (100) [*M*]$^{+}$, 800 (16) [*M* – C≡C*t*Bu]$^{+}$, 598 (50) [Pt(PPh$_{2}$O)$_{2}$H]$^{+}$, 395 (47) [PtPPh$_{2}$O – H]$^{+}$; C$_{42}$H$_{41}$O$_{3}$P$_{3}$Pt (881.8): calcd C 57.21, H 4.69; found C 57.27, H 4.05.

Data for ***7b***: ^{1}H NMR (CDCl$_{3}$): at – 50 °C, $\delta = 16.53$ (br; O···*H*···O), 7.76, 7.25, 6.62 (m; Ph); at 25 °C, 7.60, 7.32, 7.08, 6.65 (m, Ph); ^{31}P{^{1}H} NMR (CDCl$_{3}$): at – 50 °C, ABX pattern, δP$_{A}$ = 84.91 (PPh$_{2}$O^{-}), δP$_{B}$ = 70.35 (PPh$_{2}$OH), δP$_{X}$ = 75.66 (P *trans* to C≡CPh), ^{2}J(P$_{A}$,P$_{B\mathit{trans}}$) = 405.3 Hz, ^{1}J(Pt,P$_{A}$) = 2246 Hz, ^{1}J(Pt,P$_{B}$) = 2512 Hz, ^{1}J(Pt,P$_{X}$) = 2670 Hz); at 25 °C, $\delta = 74.81$ (t, ^{2}J(P$_{X}$,P$_{\mathit{cis}}$) = 23.7 Hz, ^{1}J(Pt,P$_{X}$) = 2737 Hz). A similar pattern was seen at 45 °C; IR: $\tilde{\nu} = 2120$ (w; C≡C) , 964 (vs), 919 (vs), 900 (sh), bands at 1028 (w) and 1000 cm^{-1} (w) are also observed (P–O); MS: *m/z* (%): 901 (100) [*M*]$^{+}$, 797 (20) [Pt(PPh$_{2}$O)$_{3}$ – H]$^{+}$, 699 (22) [*M* – PPh$_{2}$OH]$^{+}$, 599 (37) [Pt(PPh$_{2}$O)$_{2}$H+H]$^{+}$, 395 (52) [PtPPh$_{2}$O – H]$^{+}$; C$_{44}$H$_{37}$O$_{3}$P$_{3}$Pt (901.8): calcd C 58.61, H 4.14; found C 58.31, H 3.86.

Preparation of [Pt(C≡CR){(PPh$_2$O)$_2$H}L] 8–10: These complexes were prepared using a common procedure. A typical preparation (R = *t*Bu, L = PEt$_3$ **8a**) was as follows: A suspension of **7a** (0.15 g, 0.17 mmol) in CH$_2$Cl$_2$ (~10 mL) was treated with a stoichiometric amount of PEt$_3$ (23 μL, 0.17 mmol). The initial white suspension dissolved almost instantaneously. After stirring for about 5 min the solvent was removed in vacuum and the residue treated with several portions of diethyl ether, yielding **8a** as a white microcrystalline solid (0.06 g, 45% yield). Complexes **8b** and **10** were obtained in a similar way starting from the corresponding complex **7** and the appropiate donor ligand. The following amounts were used: For **8b** (R = Ph, PEt$_3$) **7b** (0.200 g, 0.222 mmol) and PEt$_3$ (3.01 µL, 0.222 mmol), yield 78%; **10a** (R = *t*Bu, L = CN*t*Bu) **7a** (0.200 g, 0.227 mmol) and CN*t*Bu (25.6 µL, 0.222 mmol), yield 88%; **10b** (R = Ph, L = CN*t*Bu) **7b** (0.200 g, 0.222 mmol) and (CN*t*Bu 25.1 µL, 0.222 mmol), yield 76%. For complex **9a** the final residue was treated with isopropanol and for complex **9b** (L = PPh$_2$H) the reaction was carried out at ~ −30 to −40 °C and the reaction mixture was stirred at low temperature for 45 min. The starting precursors used were: **7a** (0.200 g, 0.227 mmol) with PPh$_2$H (39.5 µL, 0.227 mmol) for complex **9a** (yield 56%) and **7b** (0.128 g, 0.142 mmol) with PPh$_2$H (24.7 µL, 0.142 mmol) for **9b** (yield 64%), respectively.

*Data for **8a***: ^{1}H NMR (CDCl$_3$): δ = 7.89, 7.68, 7.33 (Ph), 1.55 (m; CH$_2$, PEt$_3$), 0.85 (dt, ^{3}J(P,H) = 16 Hz, ^{2}J(H,H) = 7.5 Hz; CH$_3$, PEt$_3$), 0.85 (s; *t*Bu, C≡C*t*Bu); ^{31}P{^{1}H} NMR (CDCl$_3$): AMX spin system, δ = 79.41 (t, ^{2}J(P$_X$,P$_{Mcis}$) = 27.4 ~ ^{2}J(P$_X$,P$_{Acis}$) = 21.5 Hz, ^{1}J(Pt,P$_X$) = 2699 Hz; P$_X$, P$_{trans}$ to C≡C*t*Bu), 72.49 (dd, ^{2}J(P$_A$,P$_{Mtrans}$) = 389.9 Hz, ^{1}J(Pt,P$_M$) = 2639.3 Hz; P$_M$, P$_{trans}$ to PEt$_3$), 5.14 (dd, ^{1}J(Pt,P$_A$) = 1968.2 Hz; P$_A$, PEt$_3$); ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 140.0 (d, ^{1}J(C,P) = 62.5 Hz, ^{2}J(Pt,C) ~ 47 Hz), 139.99 (dd, ^{1}J(C,P) = 69.5 Hz, ^{3}J(C,P) = 6.9 Hz, ^{2}J(Pt,C) ~ 31 Hz; *i*-C, PPh$_2$O$^-$), 132.5 (m; *o*-C, PPh$_2$O$^-$), 130.39 (d, ^{4}J(C,P) = 1.7 Hz), 129.29 (d, ^{4}J(C,P) = 2.3 Hz; *p*-C, PPh$_2$O$^-$), 127.86 (d, ^{3}J(C,P) = 10.5 Hz), 127.12 (d, ^{3}J(C,P) = 11.3 Hz; *m*-C, PPh$_2$O$^-$), 121.04 (dd, ^{3}J(C$_\beta$,P$_{trans}$) = 30.5 Hz, ^{3}J(C$_\beta$,P$_{cis}$) = 1.9 Hz, ^{2}J(Pt,C$_\beta$) ~ 235 Hz; C$_\beta$, C$_\alpha$≡C$_\beta$*t*Bu), 90.92 (ddd, ^{2}J(C$_\alpha$,P$_{trans}$) = 129.1 Hz, ^{2}J(C$_\alpha$,P$_{cis}$) = 20.6, 16.8 Hz, ^{1}J(Pt,C$_\alpha$) ~ 980 Hz; C$_\alpha$, C$_\alpha$≡C$_\beta$*t*Bu), 31.01 (s; C(*C*H$_3$)$_3$, *t*Bu), 29.04 (*C*Me$_3$, *t*Bu), 15.43 (d, ^{1}J(C,P) = 31.2 Hz, ^{2}J(Pt,C) = 27 Hz; CH$_2$, PEt$_3$), 8.18 (br, ^{3}J(Pt,C) = 19 Hz; CH$_3$, PEt$_3$); IR: $\tilde{\nu}$ = 1031 (s), 1008 (vs), 997 cm^{-1} (sh; P–O); MS: *m/z* (%): 798 (70) [*M*+H]$^+$, 717 (30) [*M* − C≡C*t*Bu+H]$^+$, 598 (25) [Pt(PPh$_2$O)$_2$H]$^+$; C$_{36}$H$_{45}$O$_2$P$_3$Pt (797.8): calcd C 54.20, H 5.68; found C 53.83, H 5.64.

*Data for **8b***: ^{1}H NMR (CDCl$_3$): δ ~15.0 (br; H⋯O⋯H), 7.92, 7.73, 7.35, 7.10, 6.80 (m; Ph), 1.63 (m; CH$_2$, PEt$_3$), 0.91 (dt, ^{3}J(H,P) = 16.6 Hz, ^{2}J(H,H) = 7.2 Hz; CH$_3$, PEt$_3$); ^{31}P{^{1}H} NMR (CDCl$_3$): AMX spin system, δ = 78.36 (t, ^{2}J(P$_X$,P$_{Acis}$) = 21.5 ~ ^{2}J(P$_X$,P$_{Mcis}$) = 27.1 Hz, ^{1}J(Pt,P$_X$) = 2717 Hz; P$_X$, P$_{trans}$ to C≡CPh), 71.52 (dd, ^{2}J(P$_M$,P$_{Atrans}$) = 380.1 Hz, ^{1}J(Pt,P$_M$) = 2591 Hz; P$_M$, P$_{trans}$ to PEt$_3$), 5.61 (dd, ^{1}J(Pt,P$_A$) = 1950 Hz; P$_A$, PEt$_3$); ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 139.78 (dd, ^{1}J(C,P) = 70.0 Hz, ^{3}J(C,P) = 7.1 Hz, ^{2}J(Pt,C) = 61.6 Hz; *i*-C, PPh$_2$O$^-$ *trans* to C≡C*t*Bu), 139.61 (dd, ^{1}J(C,P) = 63.2 Hz, ^{3}J(C,P) = 1.3 Hz, ^{2}J(Pt,C) = 48.5 Hz; *i*-C, PPh$_2$O$^-$ *trans* to PEt$_3$), 132.4 (d, ^{2}J(C,P) = 13 Hz, ^{3}J(Pt,C) = 13.1 Hz), 132.1 (dd, ^{2}J(C,P) = 10.7 Hz, ^{4}J(C,P) = 0.6 Hz; *o*-C, PPh$_2$O$^-$), 130.50 (d, *J*(C,P) = 2 Hz), 130.47 (d, *J* = 1.2 Hz), 129.47 (d, *J*(C,P) = 2.5 Hz; *p*-C, PPh$_2$O$^-$ and *o*-C, Ph, C≡CPh), 127.96 (d, ^{3}J(C,P) = 10.7 Hz), 127.39 (d, ^{3}J(C,P) = 11.2 Hz; *m*-C, PPh$_2$O$^-$), 127.46 (s; *m*-C, Ph, C≡CPh), 125.66 (s; *p*-C, Ph, C≡CPh), 112.66 (ddd, ^{3}J(C$_\beta$,P$_{trans}$) = 30.8 Hz, ^{3}J(C$_\beta$,P$_{cis}$) = 2.9, 1.1 Hz, ^{2}J(Pt,C$_\beta$) = 320.7 Hz; C$_\beta$, C$_\alpha$≡C$_\beta$Ph), 108.4 (ddd, ^{2}J(C$_\alpha$,P$_{trans}$) = 129.7 Hz, ^{2}J(C$_\alpha$,P$_{cis}$) = 20.5, 17.0 Hz, ^{1}J(Pt,C$_\alpha$) ~ 1010 Hz; C$_\alpha$, C$_\alpha$≡C$_\beta$Ph), 15.57 (dt, ^{1}J(C,P) = 31.1 Hz, ^{2}J(Pt,C) = 26 Hz; CH$_2$, PEt$_3$), 8.2 (t, ^{2+4}J(C,P) = 3.8 Hz; CH$_3$, PEt$_3$); IR: $\tilde{\nu}$ = 2121 (m; C≡C), 1027 (s), 1007 cm^{-1} (vs; P–O); ES-MS(+): *m/z* (%): 819 (60) [*M*+2]$^+$, 716 (95) [*M* − C≡CPh]$^+$, 598 (100) [Pt(PPh$_2$O)$_2$H]$^+$; C$_{38}$H$_{41}$O$_2$P$_3$Pt (817.8): calcd C 55.81, H 5.05; found C 55.88, H 4.84.

*Data for **9a***: ^{1}H NMR (CDCl$_3$): δ = 7.99, 7.52, 7.29, (Ph), 5.38 (ddd, ^{1}J(H,P) = 364.9 Hz, ^{3}J(H,P$_{trans}$) = 14.4 Hz, ^{3}J(H,P$_{cis}$) = 7.3 Hz; PPh$_2$*H*), 0.73 (s; *t*Bu); ^{31}P{^{1}H} NMR (CDCl$_3$): AMX spin system, δ = 76.86 (t, ^{2}J(P$_X$,P$_{Mcis}$) ~ 25.5 Hz, ^{2}J(P$_X$,P$_{Acis}$) = 21.9 Hz, ^{1}J(Pt,P$_X$) = 2521 Hz; P$_X$, P$_{trans}$ to C≡C*t*Bu), 69.39 (dd, ^{2}J(P$_M$,P$_{Atrans}$) = 404.7 Hz, ^{1}J(Pt,P$_M$) = 2887 Hz; P$_M$, P$_{trans}$ to PPh$_2$H), −3.67 (dd, ^{1}J(Pt,P$_A$) = 1982 Hz; P$_A$, PPh$_2$H); ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 138.82 (dd, ^{1}J(C,P) = 70.5 Hz, ^{3}J(C,P) = 7.4 Hz, ^{2}J(Pt,C) ~ 65 Hz; *i*-C, PPh$_2$O$^-$ *trans* to C≡C*t*Bu), 137.81 (dd, ^{1}J(C,P) = 66.2 Hz, ^{3}J(C,P) = 1.8 Hz, ^{2}J(Pt,C) = 42 Hz; *i*-C, PPh$_2$O$^-$ *trans* to PPh$_2$H), 134.00 (d, ^{2}J(C,P) = 9.2 Hz), 132.24 (d, ^{2}J(C,P) = 11.5 Hz), 132.02 (d, ^{2}J(C,P) = 12.5 Hz; *o*-C), 130.62, 130.54, 129.8 (*p*-C), 128.12 (d, ^{3}J(C,P) = 10.6 Hz), 127.31 (d, ^{3}J(C,P) = 11.3 Hz; *m*-C), C$_\beta$ not observed, 87.27 (ddd, ^{2}J(C$_\alpha$,P*trans*) = 124.3 Hz, ^{2}J(C$_\alpha$,P*cis*) = 21.16 Hz; C$_\alpha$, C$_\alpha$≡C$_\beta$*t*Bu), 30.81 (s; C(*C*H$_3$)$_3$), 28.96 (s; *C*Me$_3$); IR: $\tilde{\nu}$ = 2357 (m; P–H), 1029 (s), 1011(vs), 997 cm^{-1} (sh; P–O); ES-MS (+): *m/z* (%): 866 (100) [*M*+H]$^+$; C$_{42}$H$_{41}$O$_2$P$_3$Pt (865.8): calcd C 58.27, H 4.77; found C 58.17, H 4.85.

*Data for **9b***: ^{1}H NMR (CDCl$_3$): δ = 7.96, 7.56, 7.47, 7.28, 7.03, 6.62 (Ph), 5.44 (ddd, ^{1}J(H,P) = 368.2 Hz, ^{3}J(H,P$_{trans}$) = 13.8 Hz, ^{3}J(H,P$_{cis}$) = 6.5 Hz, ^{2}J(Pt,H) ~ 50 Hz; PPh$_2$*H*); ^{31}P{^{1}H} NMR (CDCl$_3$): AMX spin system, δ = 75.68 (t, ^{2}J(P$_X$,P$_{Mcis}$) = 24.7 Hz ~ ^{2}J(P$_X$,P$_{Acis}$) = 21.9 Hz, ^{1}J(Pt,P$_X$) = 2536 Hz; P$_X$, P$_{trans}$ to C≡CPh), 69.19 (dd, ^{2}J(P$_M$,P$_{Atrans}$) = 394.5 Hz, ^{1}J(Pt,P$_M$) = 2843 Hz; P$_M$, P$_{trans}$ to PPh$_2$H), −2.92 (dd, ^{1}J(Pt,P$_A$) = 1960 Hz; P$_A$, PPh$_2$H); ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 138.8 (m; overlapping of *i*-C, PPh$_2$O$^-$, PPh$_2$H), 134.18 (d, ^{2}J(C,P) = 10.1 Hz), 132.23 (d, ^{2}J(C,P) = 8.2 Hz), 132.07 (d, ^{2}J(C,P) = 8.8 Hz; *o*-C, PPh$_2$O$^-$, PPh$_2$H), 130.84, 129.94 (*p*-C, PPh$_2$O$^-$), 130.57 (s; *o*-C, Ph, C≡CPh), 128.47 (d, ^{3}J(C,P) = 11.8 Hz), 128.09 (d, ^{3}J(C,P) = 10.8 Hz), 127.59 (d, ^{3}J(C,P) = 11.3 Hz; *m*-C, PPh$_2$O$^-$, PPh$_2$H), 127.57 (s; *m*-C, Ph, C≡CPh), 126.42 (*i*-C, Ph, C≡CPh), 125.68 (s; Ph, C≡CPh), 117.07 (d, ^{3}J(C$_\beta$,P$_{trans}$) = 32 Hz; C$_\beta$, C$_\alpha$≡C$_\beta$Ph), ~105.4 (poorly resolved signal as dm, ^{2}J(C$_\alpha$,P*trans*) ~ 120 Hz; C$_\alpha$); IR: $\tilde{\nu}$ = 2351 (w; P–H), 2118 (m; C≡C), 1030 (s), 1014 (vs), 997 cm^{-1} (m; P–O); ES-MS (+): *m/z* (%): 887 (100) [*M*+H]$^+$; C$_{44}$H$_{37}$O$_2$P$_3$Pt (885.8): calcd C 59.66, H 4.21; found C 59.38, H 4.14.

*Data for **10a***: ^{1}H NMR (CDCl$_3$): δ = 7.91, 7.60, 7.35, (m; Ph), 1.24 (s; *t*Bu, CN*t*Bu), 1.01 (s; *t*Bu, C≡C*t*Bu); ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 70.93 (d, ^{2}J(P,P$_{cis}$) = 25.4 Hz, ^{1}J(Pt,P) = 2474 Hz; P$_{trans}$ to C≡C*t*Bu), 60.95 (d, ^{1}J(Pt,P) = 3071 Hz; P$_{trans}$ to CN*t*Bu); ^{13}C{^{1}H} NMR (CDCl$_3$): signal due to CN$^-$ not observed, δ = 140.44 (d, ^{1}J(C,P) = 66.1 Hz, ^{2}J(Pt,C) = 41.8 Hz; *i*-C, PPh$_2$O$^-$ *trans* to C≡C*t*Bu), 138.5 (d, ^{1}J(C,P) = 75.2 Hz, ^{2}J(Pt,C) = 64.4 Hz; *i*-C, PPh$_2$O$^-$ *trans* to CN*t*Bu), 132.31 (d, ^{2}J(C,P) = 11.5 Hz, ^{3}J(Pt,C) = 16.4 Hz), 131.64 (d, ^{2}J(C,P) = 12.5 Hz, ^{3}J(Pt,C) = 13.9 Hz) (*o*-C, PPh$_2$O$^-$), 130.32 (d, ^{4}J(C,P) = 2.04 Hz), 129.00 (d, ^{4}J(C,P) = 2.49 Hz; *p*-C, PPh$_2$O$^-$), 127.90 (d, ^{3}J(C,P) = 10.9 Hz), 127.54 (d, ^{3}J(C,P) = 11.6 Hz; *m*-C, PPh$_2$O$^-$), 121.83 (d, ^{3}J(C$_\beta$,P$_{trans}$) = 29.7 Hz; C$_\beta$, C$_\alpha$≡C$_\beta$*t*Bu), 85.38 (dd, ^{2}J(C$_\alpha$,P$_{trans}$) = 127.9 Hz, ^{2}J(C$_\alpha$,P$_{cis}$) = 16.7 Hz; C$_\alpha$, C$_\alpha$≡C$_\beta$*t*Bu), 58.04 (s; *C*Me$_3$, CN*t*Bu), 31.7 (s; C(*C*H$_3$)$_3$, C≡C*t*Bu), 29.29 (s; C(*C*H$_3$)$_3$, CN*t*Bu), 28.99 (s; *C*Me$_3$, C≡C*t*Bu); IR: $\tilde{\nu}$ = 2216 (s) (C≡N), ((C≡C) not observed), 1019 (s), 998 (sh), 978 cm^{-1} (sh; P–O); ES-MS (+): *m/z* (%): 764 (100) [*M*+H]$^+$; C$_{35}$H$_{39}$NO$_2$P$_2$Pt (762.7): calcd N 1.84, C 55.12, H 5.15; found N 1.87, C 54.85, H 5.35.

*Data for **10b***: ^{1}H NMR (CDCl$_3$): δ = 7.92, 7.66, 7.37, 7.12, 6.98 (m; Ph), 1.23 (s; *t*Bu, CN*t*Bu); ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 69.85 (d, ^{2}J(P,P$_{cis}$) = 24.8 Hz, ^{1}J(Pt,P) = 2491.5 Hz; P$_{trans}$ to C≡CPh), 61.1 (d, ^{1}J(Pt,P) = 3045 Hz; P$_{trans}$ to CN*t*Bu); ^{13}C{^{1}H} NMR (CDCl$_3$): CN$^-$ not observed, δ = 139.97 (d, ^{1}J(C,P) = 67 Hz, ^{2}J(Pt,C) = 42 Hz; *i*-C, PPh$_2$O$^-$ *trans* to C≡CPh), 138.26 (d, ^{1}J(C,P) = 75.9 Hz, ^{2}J(Pt,C) = 62.6 Hz; *i*-C, PPh$_2$O$^-$ *trans* to CN*t*Bu), 132.19 (d, ^{2}J(C,P) = 11.7 Hz, ^{3}J(Pt,C) = 16.3 Hz), 131.35 (d, ^{2}J(C,P) = 12.5 Hz, ^{3}J(Pt,C) = 13.0 Hz; *o*-C, Ph, PPh$_2$), 131.07 (s; *o*-C, PPh$_2$O$^-$, C≡CPh), 130.49 (d, ^{4}J(C,P) = 1.9 Hz), 130.18 (d, ^{4}J(C,P) = 2.26 Hz; *p*-C, Ph, PPh$_2$O$^-$), 128.01 (d, ^{3}J(C,P) = 11 Hz), 127.70 (d, ^{3}J(C,P) = 11.6 Hz; *m*-C, Ph, PPh$_2$O$^-$), 127.67 (s; *m*-C, C≡CPh), 126.72 (d, ^{4}J(C,P) ~ 2.34, ^{3}J(Pt,C) ~ 23 Hz; *i*-C, Ph, C≡CPh), 125.97 (s; *p*-C, Ph, C≡CPh), 112.43 (d, ^{3}J(C$_\beta$,P$_{trans}$) = 30.6 Hz, ^{2}J(Pt,C$_\beta$) = 260 Hz; C$_\beta$, C$_\alpha$≡C$_\beta$Ph), 102.6 (dd, ^{2}J(C$_\alpha$,P$_{trans}$) = 128.5 Hz, ^{2}J(C$_\alpha$,P$_{cis}$) = 16.6 Hz; C$_\alpha$, C$_\alpha$≡C$_\beta$Ph), 58.34 (s; *C*Me$_3$, CN*t*Bu), 29.27 (s; C(*C*H$_3$)$_3$, CN*t*Bu); IR: $\tilde{\nu}$ = 2215 (vs) (C≡N), 2122 (w) (C≡C) , 1029 (s), 1015 (vs), 997 cm^{-1} (s; P–O); MS : *m/z* (%): 783 (40) [*M*+H]$^+$, 681 (38) [*M* − C≡CPh]$^+$, 598 (100) [Pt(PPh$_2$O)$_2$H]$^+$, 396 (65) [Pt(PPh$_2$O)]$^+$; C$_{37}$H$_{35}$NO$_2$P$_2$Pt (782.7): calcd N 1.79, C 56.78, H 4.51; found N 1.82, C 56.18, H 4.54.

Preparation of (NBu$_4$)[Pt(C≡CR)(CN){(PPh$_2$O)$_2$H}] (R = *t*Bu 11a, R = Ph, 11b): (NBu$_4$)CN (0.063 g, 0.227 mmol) was added to a suspension of **7a** (0.200 g, 0.227 mmol) in CH$_2$Cl$_2$ (10 mL), immediately giving a colourless solution. The mixture was stirred for 2 min and then the solvent was removed under vacuum, yielding an oily residue, which was treated with diethyl ether. The resulting white solid (**11a**) was filtered and washed with several portions of diethyl ether (86.5% yield). Complex **11b** was prepared in a similar way, starting from **7b** (0.25 g, 0.277 mmol) and (NBu$_4$)CN (0.078 g, 0.277 mmol), yield 76%.

*Data for **11a***: ^{1}H NMR (CDCl$_3$): δ = 17.2 (br; O⋯H⋯O), 7.97, 7.88, 7.26, (m; Ph), 2.92 (m; N–CH$_2$, NBu$_4$), 1.26 (m; CH$_2$, NBu$_4$), 1.44 (m; CH$_2$), 0.90 (s; *t*Bu), 0.80 (t; –CH$_3$, NBu$_4$); ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 70.88 (d,

$^{2}J(\mathrm{P,P}_{cis}) = 24.7$ Hz, $^{1}J(\mathrm{Pt,P}) = 2506$ Hz; P_{trans} to $\mathrm{C{\equiv}C}t\mathrm{Bu}$), 66.11 (d, $^{1}J(\mathrm{Pt,P}) = 2844.2$ Hz; P_{trans} to CN); $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): $\delta = 141.7$ (d, $^{1}J(\mathrm{C,P}) = 62.5$ Hz, $^{2}J(\mathrm{Pt,C}) = 45$ Hz), 140.7 (d, $^{1}J(\mathrm{C,P}) = 68.2$ Hz, $^{2}J(\mathrm{Pt,C}) \sim 57$ Hz; *i*-C, $\mathrm{PPh_2O^-}$), 132.36 (d, $^{2}J(\mathrm{C,P}) = 11.5$ Hz), 131.78 [d, $^{2}J(\mathrm{C,P}) = 12$ Hz; *o*-C, $\mathrm{PPh_2O^-}$), 128.95 (s; *p*-C, $\mathrm{PPh_2O^-}$), 127.07 (d, $^{3}J(\mathrm{C,P}) = 10.6$ Hz), 126.76 (d, $^{3}J(\mathrm{C,P}) = 10.9$ Hz; *m*-C, $\mathrm{PPh_2O^-}$), 118.67 (dd, $^{3}J(\mathrm{C}_\beta,\mathrm{P}_{trans}) = 32.3$ Hz, $^{3}J(\mathrm{C}_\beta,\mathrm{P}_{cis}) = 1.7$ Hz, $^{2}J(\mathrm{Pt,C}_\beta) = 269$ Hz; C_β, $\mathrm{C}_\alpha{\equiv}\mathrm{C}_\beta t\mathrm{Bu}$), 89.5 (dd, $^{2}J(\mathrm{C}_\alpha,\mathrm{P}_{trans}) = 139.6$ Hz, $^{2}J(\mathrm{C}_\alpha,\mathrm{P}_{cis}) = 16.9$ Hz, $^{1}J(\mathrm{Pt,C}_\alpha) \sim 1000$ Hz; C_α, $\mathrm{C}_\alpha{\equiv}\mathrm{C}_\beta t\mathrm{Bu}$), 57.72 ($\mathrm{N{-}CH_2}$, *n*Bu), 31.6 ($\mathrm{C(}C\mathrm{H_3)_3}$, *t*Bu), 23.39 ($\mathrm{-CH_2}$, *n*Bu), 19.15 ($\mathrm{CH_2}$, *n*Bu), 28.6 (m; $C\mathrm{Me_3}$, *t*Bu), 13.39 ($\mathrm{CH_3}$, *n*Bu); IR (KBr): $\tilde{\nu} = 2127$ (s; $\mathrm{C{\equiv}C}$ or $\mathrm{C{\equiv}N}$), 1029.5 (s), 1006 (s), 993 $\mathrm{cm^{-1}}$ (s; P–O); ES-MS (–): *m/z* (%): 705 (100) $[\mathrm{Pt(C{\equiv}C}t\mathrm{Bu)(CN)\{PPh_2O)_2H\}}]^- = [M]^-$, 623 (13) $[M - (\mathrm{C{\equiv}C}t\mathrm{Bu})]^-$; $\mathrm{C_{47}H_{66}N_2O_2P_2Pt}$ (948.1): calcd N 2.95, C 59.54, H 7.02; found N 3.10, C 59.16, H 7.18.

*Data for **11b***: ^{1}H NMR ($\mathrm{CDCl_3}$): $\delta = 17.28$ (br; $\mathrm{O \cdots H \cdots O}$), 7.91, 7.27, 7.06, 6.94 (m; Ph), 2.94 (m; $\mathrm{N{-}CH_2}$, $\mathrm{NBu_4}$), 1.23 (m; $\mathrm{CH_2}$, $\mathrm{NBu_4}$), 1.12 (m; $\mathrm{CH_2}$), 0.78 (m; $\mathrm{-CH_3}$, $\mathrm{NBu_4}$); $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): $\delta = 70.20$ (d, $^{2}J(\mathrm{P,P}_{cis}) = 24.43$ Hz, $^{1}J(\mathrm{Pt,P}) = 2540$ Hz; P_{trans} to $\mathrm{C{\equiv}CPh}$), 64.81 (d, $^{1}J(\mathrm{Pt,P}) = 2816$ Hz; P_{trans} to CN); $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): $\delta = 141.36$ (d, $^{1}J(\mathrm{C,P}) = 64.08$ Hz), 140.86 (d, $^{1}J(\mathrm{C,P}) = 68.6$ Hz; *i*-C, $\mathrm{PPh_2O^-}$), 132.2 (d, $^{2}J(\mathrm{C,P}) = 11.5$ Hz), 131.9 (d, $^{2}J(\mathrm{C,P}) = 12$ Hz; *o*-C, $\mathrm{PPh_2O^-}$), 130.6 (s; *o*-C, Ph, $\mathrm{C{\equiv}CPh}$), 129.31 (d), 129.2 (d, $^{4}J(\mathrm{C,P}) = 1.9$ Hz, *p*-C, $\mathrm{PPh_2O^-}$), 127.5 (d, $^{3}J(\mathrm{C,P}) = 17$ Hz), 127.15 (d, $^{3}J(\mathrm{C,P}) = 16.6$ Hz; *m*-C, $\mathrm{PPh_2O^-}$), 127.16 (s; *m*-C, Ph, $\mathrm{C{\equiv}CPh}$), 125.08 (s; *p*-C, Ph, $\mathrm{C{\equiv}CPh}$), 110.6 (dd, $^{3}J(\mathrm{C}_\beta,\mathrm{P}_{trans}) = 33$ Hz, $^{3}J(\mathrm{C}_\beta,\mathrm{P}_{cis}) = 1.4$ Hz; C_β, $\mathrm{C}_\alpha{\equiv}\mathrm{C}_\beta\mathrm{Ph}$), 109.28 (dd, $^{2}J(\mathrm{C}_\alpha,\mathrm{P}_{trans}) = 139.6$ Hz, $^{2}J(\mathrm{C}_\alpha,\mathrm{P}_{cis}) = 16.7$ Hz; C_α, $\mathrm{C}_\alpha{\equiv}\mathrm{C}_\beta\mathrm{Ph}$), 57.9 ($\mathrm{N{-}CH_2}$, *n*Bu), 23.4 ($\mathrm{-CH_2}$, *n*Bu), 19.3 ($\mathrm{CH_2}$, *n*Bu), 13.50 ($\mathrm{CH_3}$, *n*Bu); IR (KBr): $\tilde{\nu} = 2127$ (m), 2109 (s; $\mathrm{C{\equiv}C}$, $\mathrm{C{\equiv}N}$), 1028.5 (s), 1006 (vs), 993 $\mathrm{cm^{-1}}$ (vs; P–O); ES-MS (–): *m/z* (%): 725 (100) $[M]^-$; $\mathrm{C_{49}H_{62}N_2O_2P_2Pt}$ (968.1): calcd N 2.89, C 60.80, H 6.45; found N 2.90, C 60.76, H 6.45.

Reactions of 7a and 7b with LiOH: preparation of $[\{\mathrm{Pt(C{\equiv}CR)(PPh_2O)_3Li_2(thf)(H_2O)}\}_2]$ (R = *t*Bu 3a; R = Ph 3b): $\mathrm{LiOH \cdot H_2O}$ (0.013 g, 0.305 mmol) was added to a white suspension of complex **7b** (0.125 g, 0.139 mmol) in THF (20 mL). The initial suspension dissolved slowly and after 90 min the resulting yellow solution was filtered over Celite and evaporated to small volume. After addition of *n*-hexane (10 mL), the complex **3b** precipitated as a yellow solid (0.105 g, 75 % yield). Compound **3a** was obtained similarly by this second method, using the complex **7a** and with four hours of stirring (70 % yield).

*$[\{\mathrm{Pt(C{\equiv}CPh)(PPh_2O)_3Li_2(thf)(H_2O)}\}_2]$ (**3b**)*: ^{1}H NMR ($\mathrm{CDCl_3}$): $\delta = 7.96$, 7.52, 7.21, 6.88, 6.69, 6.41 (m; Ph); $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): $\delta = 73.20$ (d, $^{1}J(\mathrm{Pt,P}) = 2679$ Hz, 2P), 58.8 (t, $^{1}J(\mathrm{Pt,P}) = 2704$ Hz, $^{2}J(\mathrm{P,P}_{cis}) = 29.02$ Hz, 1P); $^{7}\mathrm{Li}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): at 20 °C, $\delta = -0.89$ (s); at 0 °C, $\delta = -0.1$ (br s), -1.8 (br s); at -20 °C, $\delta = -0.23$ (br s), -1.96 (s); IR: $\tilde{\nu} = 3615$ (br), 3362 (br; OH), 2109 (m; $\mathrm{C{\equiv}C}$), 1037 (s), 1025 (m), 998 $\mathrm{cm^{-1}}$ (w; P–O); MS: *m/z* (%): 1826 (10) $[\mathrm{Pt_2(C{\equiv}CPh)_2(PPh_2O)_6Li_4}]^+$, 1726 (5) $[\mathrm{Pt_2(C{\equiv}CPh)(PPh_2O)_6Li_4}]^+$, 907 (40) $[\mathrm{Pt(C{\equiv}CPh)(PPh_2O)_3Li}]^+$, 806 (10) $[\mathrm{Pt(PPh_2O)_3Li}]^+$, 604 (58) $[\mathrm{Pt(PPh_2O)_2Li}]^+$, 401 (35) $[\mathrm{Pt(PPh_2O)Li - 2H}]^+$; $\mathrm{C_{96}H_{90}Li_4O_{10}P_6Pt_2}$ (2007.6): calcd C 57.44, H 4.52; found C 57.22, H 4.62.

X-ray crystal structure determinations: Details of the crystal structure determinations are collected in Table 4. Suitable crystals of **3a** · $1.75\,\mathrm{Et_2O}$ were grown by slow diffusion of diethyl ether into a THF solution of **3a**. Suitable crystals of **4b** were grown by slow diffusion of *n*-hexane into a tetrahydrofuran solution of **4b**. Suitable crystals of **6a** were grown by slow diffusion of *n*-hexane into a chloroform solution of **6a**. All diffraction measurements were made on an Enraf-Nonius CAD4 diffractometer. Lorentz and polarization corrections were applied. The structures were solved by Patterson and Fourier methods. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were constrained to idealised geometries and assigned isotropic displacement parameters of 1.2 times the U_{iso} values of their respective parent atoms. For the structure of **3a** · $1.75\,\mathrm{Et_2O}$, the methyl groups of one of the *tert*-butyl acetylide ligands [C(4), C(5), and C(6)] were disordered over two

Table 4. Details of the crystal structure determinations of the complexes $[\{\mathrm{Pt(C{\equiv}C}t\mathrm{Bu)(PPh_2O)_3Li_2(thf)(H_2O)}\}_2] \cdot 1.75\,\mathrm{Et_2O}$ (**3a** · $1.75\,\mathrm{Et_2O}$), $[\mathrm{Pt(C{\equiv}CPh)_2\{Ph_2P(CHPh)(CH_2)PPh_2\}}]$ (**4b**), and $[\mathrm{Pt_2(}\mu\mathrm{\text{-}PPh_2)_2(C{\equiv}C}t\mathrm{Bu)_2(PPh_2H)_2}]$ (**6a**).

	3a · $1.75\,\mathrm{Et_2O}$	**4b**	**6a**
formula	$\mathrm{C_{92}H_{98}Li_4O_{10}P_6Pt_2 \cdot 1.75\,Et_2O}$	$\mathrm{C_{48}H_{38}P_2Pt}$	$\mathrm{C_{60}H_{60}P_4Pt_2}$
crystal size [mm]	0.27 × 0.20 × 0.10	0.30 × 0.20 × 0.20	0.35 × 0.32 × 0.12
crystal system	triclinic	trigonal	triclinic
space group	$P\bar{1}$	$R\bar{3}$	$P\bar{1}$
a [Å]	16.1646(13)	40.727(6)	9.122(2)
b [Å]	17.1032(10)	40.727(6)	12.419(3)
c [Å]	19.0177(12)	12.6234(15)	13.059(3)
α [°]	90.441(9)	90	108.13(2)
β [°]	102.621(9)	90	95.30(3)
γ [°]	98.044(9)	120	111.16(2)
V [Å^3]	5076.2(6)	18133(4)	1275.7(5)
Z	2	18	1
M_{R}	2097.17	871.81	1295.14
ρ_{calcd} [g cm^{-3}]	1.372	1.437	1.686
μ ($\mathrm{Mo_{K\alpha}}$) [mm^{-1}]	2.902	3.593	5.641
λ [Å]	$\mathrm{Mo_{K\alpha}}$, graphite monochromated, 0.71073		
T [K]	150(1)	293(2)	150(1)
$2\theta_{\mathrm{max}}$ [°]	50	50	50
scan method	ω/θ	ω	ω
hkl range	0/19, –20/20, –22/22	0/41, 0/41, –14/14	–10/10, –14/14, –15/15
measured reflections	18596	7479	9583
unique reflections	17815 [R(int) = 0.0565]	7082 [R(int) = 0.0516]	4484 [R(int) = 0.0225]
observed reflections [$I > 2\sigma(I)$]	11753	3939	4153
absorption correction	Ψ scans	Ψ scans	Ψ scans
transmission factors	1.000, 0.547	0.594, 0.527	0.988, 0.445
parameters refined	1120	418	301
GoF	1.045	1.044	1.054
R (observed reflections only)	0.0576	0.0608	0.0203
wR2 (all reflections)	0.1704	0.1745	0.0509
residual density max/hole (e Å^3)	1.43/ –0.91	1.24/ –0.54	1.12/ –0.55
($w = [\sigma^2(F_o^2) + (\mathrm{AP})^2 + \mathrm{BP}]^{-1}$)			
A, B	0.0723, 7.43	0.0655, 48.61	0.0317, 0
P	$[\max\{F_o^2, 0\} + 2\,F_c^2]/3$		

sets of positions and refined with partial occupancy of 0.50 each. The thermal parameters of the opposite methyl groups of each set were constrained to be the same. In the final phases of the refinement the presence of several diethyl ether molecules, one of the solvents used in the obtention of the crystals, was discovered. One of these [O(11) to C(96)] was refined with full occupancy and no constraints. However, the other two sites were very disordered and, of the several models tested, the one that gave the best results was as follows: One molecule [O(12) to C(100)] was refined with occupancy 0.50, the distances and angles were restrained to sensible geometries, and the thermal parameters of all the carbon atoms were constrained to be the same. The final molecule [O(13) to C(103)] was found to lie near an inversion center, and thus only partial occupancy was appropiate. These atoms were refined with a partial occupancy of 0.25, the distances and angles were restrained to sensible geometries, and the thermal parameters of all of the carbon atoms were constrained to be the same. No hydrogen atoms were included for this molecule, nor for the water molecules present in the complex. For the structure of **4b**, the geometry of the phenyl ring C(3) to C(8) was constrained to be a hexagon, and all its carbon atoms were refined with a common set of anistropic thermal parameters. The hydrogen atoms of this phenyl group were not included in the final model. Full-matrix least-squares refinement of these models against F^2 converged to the final residual indices given in Table 4. All calculations were carried out using the program SHELXL-93.[41] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-102057 (**3a**), 102058 (**4b**), and 102059 (**6a**). 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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