

Reactivity of Alkynyl Platinum Complexes towards PPh₂H and PPh₂(O)H: Unexpected Formation of Alkynyl Tetralithium Diplatinum Compounds Stabilized by μ_3 -(κ^3P,O,O -PPh₂O⁻) Ligands

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Abstract: The reactivity of Li₂-[Pt(C≡CR)₄] and *cis*-[Pt(C≡CR)₂COD] (R = *t*Bu **a**, Ph **b**) towards PPh₂H and PPh₂(O)H has been investigated. The course of the reaction of Li₂[Pt(C≡CR)₄] with PPh₂H strongly depends not only on the reaction conditions employed, but also on the alkyne substituent R. Thus, treatment of Li₂[Pt(C≡C*t*Bu)₄] with PPh₂H (1:3) in an acetone/ethanol mixture affords *trans*-[Pt(C≡C*t*Bu)₂(PPh₂H)₂] (**1a**) together with an unusual tetralithium diplatinum species [[Pt(C≡C*t*Bu)_{2-x}(PPh₂O)_{2+x}Li₂S_n]₂] (*x* = 0, S_n = (H₂O)₃, **2'a**; *x* = 1, S_n = (H₂O)₂, **3'a**) in low yield. Complexes [[Pt(C≡C*t*Bu)₂(PPh₂O)₂Li₂(μ -H₂O)-(Me₂CO)₂]₂] (**2a**) and [[Pt(C≡C*t*Bu)₂(PPh₂O)₃Li₂(H₂O)(thf)₂]₂] (**3a**) have been characterized by X-ray diffraction. On the other hand, treatment of Li₂[Pt(C≡CPh)₄] with PPh₂H (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≡CPh)₂(PPh₂CHPhCH₂PPh₂)] (**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≡CR)₂(PPh₂H)₂] **5** are easily prepared by displacement of the cyclooctadiene (COD) ligand from the precursor *cis*-[Pt(C≡CR)₂COD] at low temperature (-30 °C) by PPh₂H. The unexpected diplatinum complex [[Pt(C≡C*t*Bu)(μ -PPh₂)(PPh₂H)]₂] (**6a**), also character-

ized by X-ray diffraction, is also formed (2% yield) during the synthesis of complex **5a**. By contrast, *cis*-[Pt(C≡CR)₂COD] reacts with PPh₂(O)H in CH₂Cl₂ at low temperature (-40 °C), either in 1:2 or 1:3 molar ratio, to produce novel diphenylphosphinous acid/phosphinite complexes [[Pt(C≡CR)-{(PPh₂O)₂H}(PPh₂OH)] **7**, which are precursors of the related neutral compounds [Pt(C≡CR){(PPh₂O)₂H}L] (L = PEt₃, PPh₂H, CN*t*Bu **8–10**) and the ionic (NBu₄)[Pt(C≡CR)(CN)-{(PPh₂O)₂H}] (**11**), which are formed through simple PPh₂OH 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 (ER₃; E = P, As), diphosphines, and so forth. However, as far as we know, similar compounds containing secondary or primary phosphines (PR₂H or PRH₂) 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≡CR) or alkylidyne (M≡CR) bridging complexes.^[8a–e] P–C coupling reactions through the insertion of acetylenes, either at terminal or bridging PR₂ 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 (μ -PR₂⁻) and acetylide (μ -C≡CR⁻) bridges have been prepared through P–C(alkyne) bond cleavage reactions starting from phosphinoacetylene (PR₂C≡CR) and metal carbonyls.^[9]

Following our work on polynuclear alkynyl dibridged platinum complexes,^[10] we recently explored the reactivity of diphenylalkynylphosphine compounds *cis*-[PtX₂(PPh₂C≡CR')₂] (X = Cl^[11a] or C≡CR^[11b]; R, R' = Ph, *t*Bu) towards the labile neutral species *cis*-[Pt(C₆F₅)₂(thf)₂] (thf = tetrahydrofuran) as a possible synthetic route for obtaining hetero-bridged phosphido/acetylide compounds. However, the expected P–C(alkyne) bond cleavage process does not

take place and only homo-bridged (μ -X)₂ (X = Cl, C≡CR), or hetero-bridged (μ -PPh₂C≡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≡CR)₂L₂] platinum alkynyl complexes containing PR₂H 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 (PR₂⁻) 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.

We have previously prepared *trans*-substituted derivatives of the type *trans*-[Pt(C≡CR)₂(PPh₃)₂] by treatment of *cis*-[PtCl₂(PPh₃)₂] with classical alkynyl reagents such as LiC≡CSiMe₃^[10b] or (AgC≡CR)_n (R = Ph, *t*Bu),^[13] although *trans*-[Pt(C≡C*t*Bu)₂(PPh₃)₂] can also be obtained in high yield by partial displacement of the alkynyl groups (by PPh₃) from the reactive Li₂[Pt(C≡C*t*Bu)₄], prepared *in situ*.^[10b] After a few unsuccessful attempts to prepare related derivatives containing the secondary phosphine PPh₂H, by treatment of *cis*-[PtCl₂(PPh₂H)₂] with MC≡CR (M = Li, Ag) (the reactions yield very complex mixtures as deduced through ³¹P NMR spectroscopy), we finally decided to attempt their synthesis by treating Li₂[Pt(C≡CR)₄] with PPh₂H. Preliminary results^[14] revealed that treatment of Li₂[Pt(C≡C*t*Bu)₄] with PPh₂H (1:3 molar ratio) gives not only the expected *trans*-[Pt(C≡C*t*Bu)₂(PPh₂H)₂] (**1a**) in low yield (25%), but also a very unusual complex [[Pt(C≡C*t*Bu)₂(PPh₂O)₂Li₂(μ -H₂O)(Me₂CO)₂]₂] (**2a**; 40%), formed by two dianionic *trans*-OPPh₂[Pt(C≡C*t*Bu)₂]PPh₂O⁻ 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 Li₂[Pt(C≡CR)₄] (R = *t*Bu, Ph) with PPh₂H:

Complex *trans*-[Pt(C≡C*t*Bu)₂(PPh₂H)₂] (**1a**) was prepared in low yield (25%) in a way similar to that previously reported for *trans*-[Pt(C≡C*t*Bu)₂(PPh₃)₂],^[10b] by partial displacement with PPh₂H of the 3,3-dimethylbutynyl ligands of the reactive homoleptic species Li₂[Pt(C≡C*t*Bu)₄]. Complex **1a** slowly precipitates (~7 h) as a white solid after treatment of the colorless solution obtained by dissolving the species Li₂[Pt(C≡C*t*Bu)₄], generated *in situ*, in an acetone/ethanol mixture with an excess of PPh₂H (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≡C*t*Bu)₂(PPh₂O)₂Li₂(H₂O)₃]₂] and its solubility and spectroscopic data (IR, NMR, see below) are clearly different from those of the mononuclear complex **1a**. Recrystallization

Abstract in Spanish: Se han estudiado las reacciones de Li₂[Pt(C≡CR)₄] y *cis*-[Pt(C≡CR)₂COD] (R = *t*Bu **a**, Ph **b**) con PPh₂H y PPh₂(O)H. El transcurso de la reacción de Li₂[Pt(C≡CR)₄] con PPh₂H depende no solo de las condiciones de reacción usadas, sino también del sustituyente R del alquino. Así, el tratamiento de Li₂[Pt(C≡C*t*Bu)₄] con PPh₂H (1:3) en acetona/etanol da lugar a la formación de *trans*-[Pt(C≡C*t*Bu)₂(PPh₂H)₂] **1a** junto con las especies [[Pt(C≡C*t*Bu)_{2-x}(PPh₂O)_{2+x}Li₂S_n]₂] [x = 0, S_n = (H₂O)₃ **2'a**; x = 1, S_n = (H₂O)₂ **3'a**] que se obtienen en bajo rendimiento. [[Pt(C≡C*t*Bu)₂(PPh₂O)₂Li₂(μ -H₂O)(Me₂CO)₂]₂] **2a** y [[Pt(C≡C*t*Bu)(PPh₂O)₃Li₂(H₂O)(thf)]₂] **3a** han sido caracterizados por difracción de rayos X. Por otro lado, el tratamiento de Li₂[Pt(C≡CPh)₄] con PPh₂H (relación molar 1:3) permite preparar no solo los derivados análogos **1b** y **2'b**, sino también el compuesto mononuclear [Pt(C≡CPh)₂(PPh₂CHPhCH₂PPh₂)] **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≡CR)₂(PPh₂H)₂] **5** se preparan fácilmente a partir del correspondiente *cis*-[Pt(C≡CR)₂COD] por desplazamiento del ligando COD con PPh₂H a baja temperatura (-30°C). El complejo dinuclear [[Pt(C≡C*t*Bu)(μ -PPh₂)(PPh₂H)]₂] **6a**, caracterizado por difracción de rayos X, se forma también (2% rendimiento) en el proceso de síntesis de **5a**. *cis*-[Pt(C≡CR)₂COD] reacciona con PPh₂(O)H en CH₂Cl₂ (-40°C), tanto en relación molar 1:2 como 1:3, para formar el complejo [Pt(C≡CR){(PPh₂O)₂H}{(PPh₂OH)}] **7**, precursor de los derivados neutros [Pt(C≡CR){(PPh₂O)₂H}L] (L = PEt₃, PPh₂H, CN*t*Bu **8–10**) o aniónico [NBu₄][Pt(C≡CR)(CN){(PPh₂O)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**.

of **2'a** from hot acetone yields a crystalline solid identified by X-ray crystallography as the unexpected tetralithium diplatinum complex $[\text{Pt}(\text{C}\equiv\text{C}t\text{Bu})_2(\text{PPh}_2\text{O})_2\text{Li}_2(\mu\text{-H}_2\text{O})(\text{Me}_2\text{CO})_2]_2$ (**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*- $\text{OPPh}_2\{\text{Pt}(\text{C}\equiv\text{C}t\text{Bu})_2\}\text{PPh}_2\text{O}^-$) through bridging phosphinite groups, which display a novel μ_3 -($\kappa^3\text{P},\text{O},\text{O}$) bonding mode. The two inner lithium centers are connected by two ($\mu\text{-H}_2\text{O}$) 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 $[\{\text{Pt}(\text{C}\equiv\text{C}t\text{Bu})(\text{PPh}_2\text{O})_3\text{Li}_2(\text{H}_2\text{O})(\text{thf})\}_2]$ **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

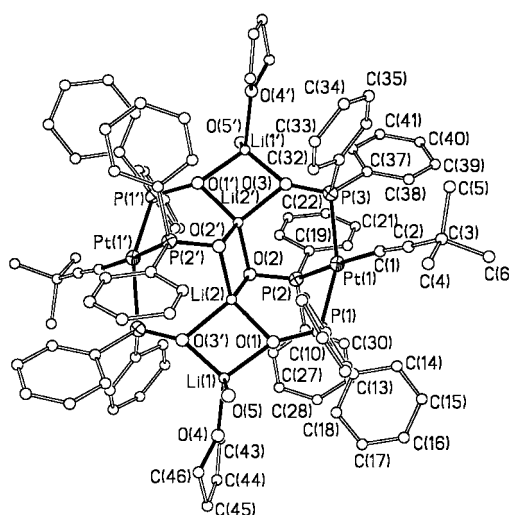
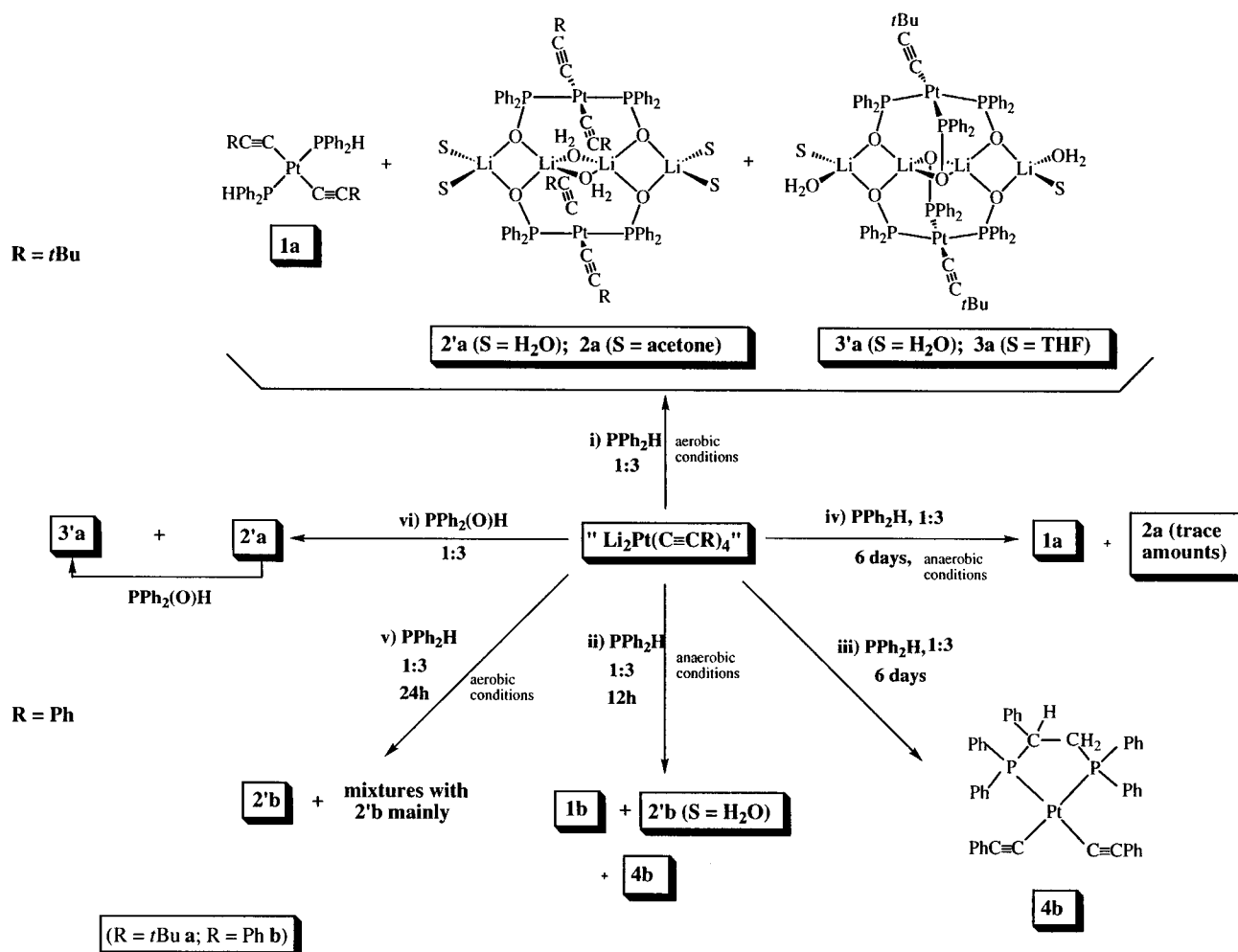
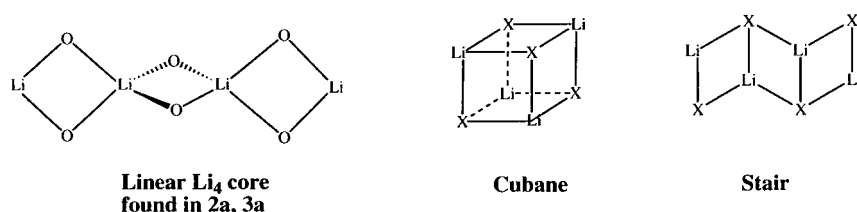


Figure 1. View of the molecular structure of $[\{\text{Pt}(\text{C}\equiv\text{C}t\text{Bu})(\text{PPh}_2\text{O})_3\text{Li}_2(\text{thf})(\text{H}_2\text{O})\}_2]$ **3a** with the atom numbering scheme.

chemistry,^[15] this simple linear Li_4 core resulting from the perpendicular disposition of the three four-membered Li_2O_2 planar rings (apex sharing) is remarkable and contrasts with the more usual cubane (two stacked rings) or stair-shaped



Scheme 1. Reactions of $\text{Li}_2\text{Pt}(\text{C}=\text{CR})_4$ with PPh_2H .



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 LiO₄ units.^[15–16] While in **2a** the outer Li₂O₂ rings possess bridging H₂O, in **3a** these rings

(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 Li₄[(MeGa)₆(μ₃-O)₂(tBuPO₃)₆]·(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-H₂O 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 Pt₂Li₄ molecule is made up by two identical and staggered (180°) dianionic platinate Pt(C≡CtBu)(PPh₂O)₃²⁻ 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 PPh₂O⁻ ligands (two from each platinum fragment), while the peripheral lithium centers [Li(1), Li(1')] interact with only two oxygen atoms of two different PPh₂O⁻ ligands (one from each Pt unit) and complete their coordination spheres with two different solvent molecules each (THF and H₂O). However, in spite of this structural difference, the Li–O bond distances [range 1.95(2)–2.00(2) Å for Li(2) and

are bound by the oxygen atoms [O(2), O(2')] of the PPh₂O⁻ groups *trans* to C≡CtBu 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 Li₂O₂ 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 μ₃-(κ³P,O,O') bonding mode. Although a variety of metal coordination modes have been observed^[17] for PR₂O⁻ 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 PPh₂O⁻ 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–μ₃-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 [[Me₃Si₂N]Cd{(mes)₂P=O}–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 {μ₂-P(mes)₂O}, and only slightly larger than those seen in Ph₃P=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≡CtBu)(PPh₂O)₃Li₂(thf)(H₂O)]₂]·1.75 Et₂O (**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** [$170.95(5)^\circ$].

As is shown in Scheme 1 (path ii), addition of PPh_2H to an acetone/ethanol solution of $\text{Li}_2[\text{Pt}(\text{C}\equiv\text{CPh})_4]$ generated a mixture from which, after 12 h of stirring under nitrogen, the complex *trans*- $[\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{PPh}_2\text{H})_2]$ (**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 ($\sim 11\%$) after adequate recrystallization ($\text{CHCl}_3/\text{hexane}$ **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 $[\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{PPh}_2\text{CHPhCH}_2\text{PPh}_2)]$ (**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=C [1.20(2) Å] are identical within experimental error, and the Pt–C $_{\alpha}$ –C $_{\beta}$ (Ph) fragments do not deviate significantly from linearity (angles at C $_{\alpha}$ /C $_{\beta}$ 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%

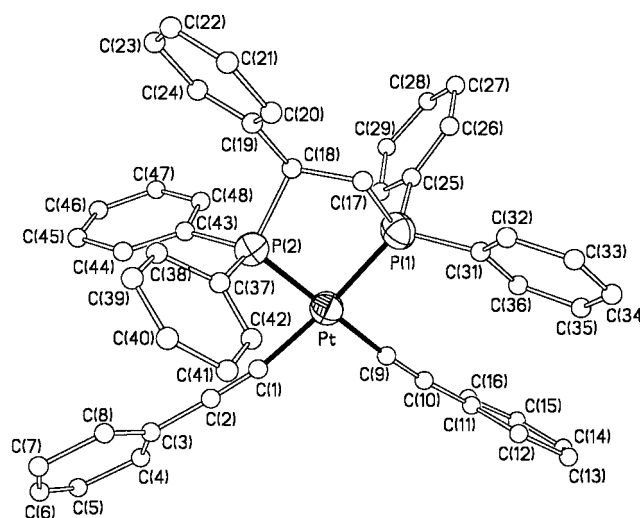


Figure 2. View of the molecular structure of $[\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{PPh}_2\text{CHPhCH}_2\text{PPh}_2)]$ **4b** with the atom numbering scheme.

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) $\text{Li}_2[\text{Pt}(\text{C}\equiv\text{CPh})_4]$ 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 $\text{PPh}_2(\text{O})\text{H}$ during the course of the reactions. In fact, as is shown in Scheme 1 (path vi), treatment of tetraalkynylplatinate species $\text{Li}_2[\text{Pt}(\text{C}\equiv\text{C}t\text{Bu})_4]$ with three equivalents of $\text{PPh}_2(\text{O})\text{H}$ causes the slow precipitation (3 d) of a white solid identified by $^{31}\text{P}\{^1\text{H}\}$ 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

Table 2. Selected bond lengths (Å) and angles ($^\circ$) for $[\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{PPh}_2\text{CHPhCH}_2\text{PPh}_2)]$ **4b**.

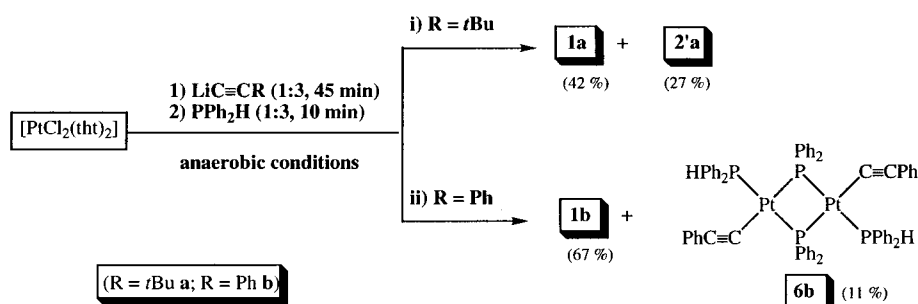
Pt–C(1)	1.997 (12)	Pt–C(9)	2.020 (14)	Pt–P(2)	2.258 (3)
Pt–P(1)	2.270 (3)	P(1)–C(25)	1.786 (14)	P(1)–C(31)	1.809 (13)
P(1)–C(17)	1.833 (11)	P(2)–C(37)	1.78 (2)	P(2)–C(43)	1.817 (13)
P(2)–C(18)	1.859 (13)	C(1)–C(2)	1.20 (2)	C(2)–C(3)	1.41 (2)
C(9)–C(10)	1.20 (2)	C(10)–C(11)	1.44 (2)	C(17)–C(18)	1.50 (2)
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 H₂O₂) 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 PPh₂O⁻ ligands, as intermediate. This can be inferred from the observation that treatment of a suspension of **2a** in CHCl₃ with PPh₂(O)H slowly produces the displacement of one *tert*-butylacetylide by one PPh₂O⁻ 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 through the formal addition of PhC≡CH to *cis*-[Pt(C≡CPh)₂(PPh₂H)₂] (**5b**). The nearest example to be found in the literature is the base-induced addition of coordinated phosphines on [M(CO)₄(PPh₂H)₂] (M=Cr, Mo) to acetylenes, yielding metal complexes of chelating diphosphine ligands.^[8b–j] However our attempt to obtain **4b** starting from **5b** and LiC≡CPh (3 equiv) was unsuccessful. 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 [PtCl₂(tht)₂] (tht = tetrahydrothiophene), with a lesser excess of LiC≡CR (1:3) [giving what is probably a mixture of species of the type Pt(C≡CR)_{4-x}(tht)_xLi_{2-x} (x = 0–2)], with PPh₂H (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≡CPh)(μ-PPh₂)(PPh₂H)]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≡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 PPh₂H ligands.^[12, 21]



Scheme 2. Reactions of [PtCl₂(tht)₂] with PPh₂H.

In addition, the presence of a singlet in their ³¹P{¹H} NMR spectra (–1.99 **1a**, –4.26 **1b**), which splits into the expected XX' pattern (*N* ~ 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 δ = 6.46 for **1a** and at δ = 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 ¹³C 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 ¹⁹⁵Pt nuclei [¹J(Pt,C_α) = 913 Hz **1a**, 834 Hz **1b**; ²J(Pt,C_β) 249 Hz **1a**, 259 Hz **1b**], are seen as triplets [²J(C_α,P) = 15.9 Hz **1a**, ~27 Hz **1b**; ³J(C_β,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 **2b** 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≡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 [δ = 68.07, ¹J(Pt,P) = 2395 Hz] in its ³¹P{¹H} NMR spectrum, indicative of the phosphorus oxidation to P^V. In contrast, **3a** exhibits an A₂X pattern with ¹⁹⁵Pt satellites in the expected downfield region consisting of a doublet at δ_A = 73.14 as a result of the two mutually *trans* phosphorus atoms and a triplet at δ_X = 58.70 assigned to the phosphinite group *trans* to C≡C*t*Bu with a *cis* coupling constant ²J(P_A,P_X) of 29.3 Hz. The considerable upfield shift of the phosphorous 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 δ = 0.49 due to the equivalent *tert*-butyl groups and a broad signal at δ = 1.59. This latter signal disappears upon addition of a drop of D₂O to the solution and, therefore, could be tentatively assigned to the H₂O molecules at the lithium centers. The low solubility of these heteronuclear complexes prevents

¹³C NMR analysis. It is worth noting that although the ³¹P 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 (δ = 0.88 **2a**, –0.62 **2'b** sharp; –1.03 **3a**,

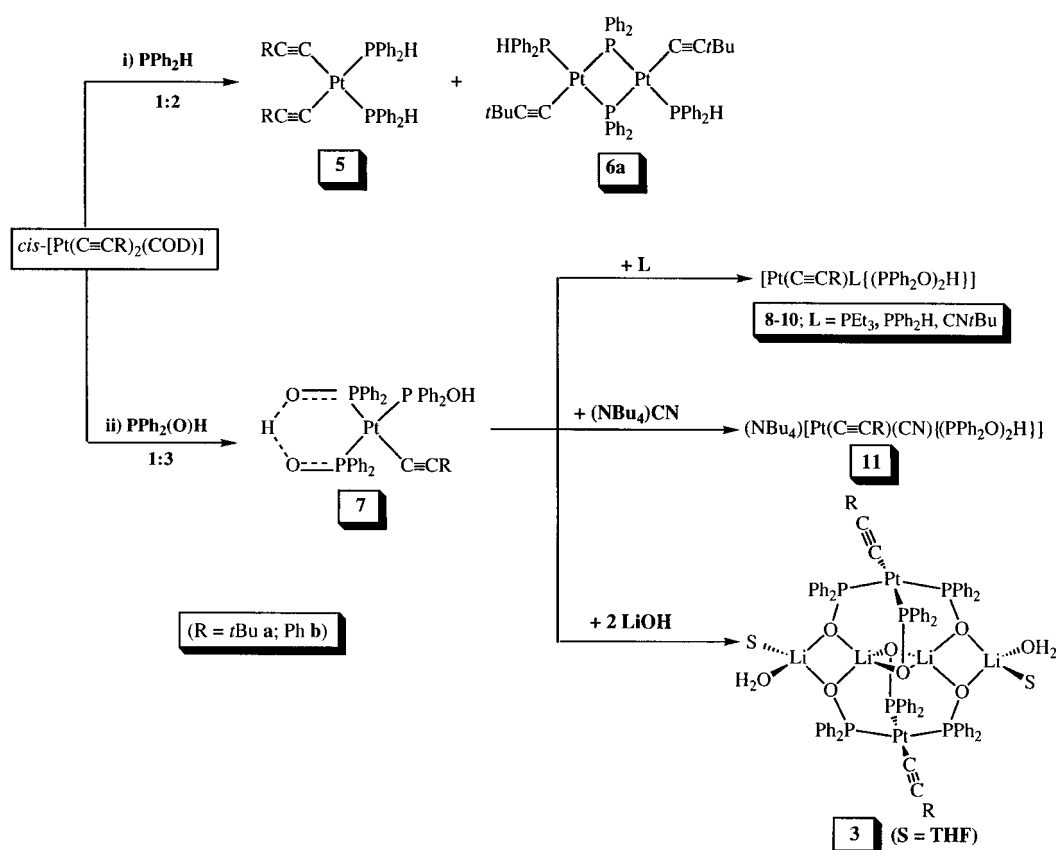
broad with $w_{1/2} = 129$ Hz), suggesting fast intermolecular lithium exchange (no P–Li splitting is observed),^[23] most probably due to partial dissociation of Li^+ in solution, in agreement with the essentially electrostatic nature of the interactions. By lowering the temperature for complex **3a** the signal broadens (coalesces at ca. $1\text{--}3^\circ\text{C}$) 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 [$\text{C}\equiv\text{C}$ 2114 cm^{-1}] and its $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum reveals two doublet [$^2J(\text{P,P})_{\text{cis}} = 13.8\text{ Hz}$] resonances with ^{195}Pt satellites [$\delta/{}^1J(\text{Pt,P})$ $49.24/2260\text{ Hz}$; $21.53/2250\text{ Hz}$], 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 diastereotopic methylene protons (CH_2) and a doublet [$^2J(\text{H,P}) = 47\text{ Hz}$] of multiplets centered at $\delta = 3.19$ attributable to CHPh .

The $^{31}\text{P}\{^1\text{H}\}$ 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 $\mu\text{-PPh}_2$ (XX')] and characteristic signals [$\text{AA}'\text{XX}'$ pattern; $N = {}^2J(\text{P}_{\text{A}},\mu\text{-P}_{\text{Xtrans}}) + {}^2J(\text{P}_{\text{A}},\mu\text{-P}_{\text{Xcis}}) = 321.4$, ${}^1J(\text{Pt,P}_{\text{A}}) = 2051\text{ Hz}$, ${}^1J(\text{Pt,P}_{\text{X}},\text{P}_{\text{X}}) = 1688, 1766\text{ Hz}$]. 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 $\text{C}\equiv\text{C}$. 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)₂COD] with PPh₂H and PPh₂(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 [MPR₂H] complexes usually require only mild conditions.^[21] A general synthetic strategy for preparing *cis*-[PtX₂L₂] (X = an anionic ligand such as alkynyl, alkyl, aryl, halide; L = PR₃) is based in the easy displacement of labile COD from appropriate precursors [PtX₂COD] by the incoming phosphine ligand.^[10a, 11b] Therefore, the recently reported neutral platinum derivatives [Pt(C≡CR)₂COD] (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 PPh₂H ligands mutually *cis*. As is shown in Scheme 3 (path i) treatment of the complex [Pt(C≡CR)₂COD] (R = *t*Bu, Ph) in CH_2Cl_2 at low temperature (-30°C) with PPh₂H (1:2 molar ratio) results in the displacement of the cyclooctadiene ligand, yielding solutions from which the expected products *cis*-[Pt(C≡CR)₂(PPh₂H)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)($\mu\text{-PPh}_2$)(PPh₂H)]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 [$\nu(\text{C}\equiv\text{C})$ 2118 cm⁻¹ **5a**, 2119 cm⁻¹ **5b**]; their ¹H 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 ($X = {}^{31}\text{P}$, $N = 378$ Hz **5a**, 390 Hz **5b**). The ³¹P NMR spectra exhibit a doublet due to phosphorus–hydrogen coupling [${}^1J(\text{P},\text{H}) \sim N$] with ¹⁹⁵Pt satellites, which is reduced to the expected singlet ($\delta = 5.49$ **5a**, -7.07 **5b**) by ¹H decoupling. Similar to previous findings,^[21] the observed large value for ${}^1J(\text{P},\text{H})$ coupling compared with free PPh₂H (214 Hz) is consistent with the change in the hybridization of P to sp³, leading to more s character in the P–H bond upon coordination.^[25] The platinum coupling constants ${}^1J(\text{Pt},\text{P})$ 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 PPh₂H 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_α and C_β appear in the ¹³C{¹H} NMR spectra (δ C_α/C_β = 84.3/118.8 **5a**; 99.9/110.6 **5b**) as a first-order doublet of doublets (dd) [${}^2J(\text{C}_\alpha,\text{P}_{\text{trans}})/{}^2J(\text{C}_\alpha,\text{P}_{\text{cis}})$ 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 [${}^3J(\text{C}_\beta,\text{P}_{\text{trans}}) + {}^3J(\text{C}_\beta,\text{P}_{\text{cis}}) \sim 36.3$ Hz **5a**, 36.4 Hz **5b**], respectively. Comparison of the one-bond Pt–C_α 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 $[\{\text{Pt}(\text{C}\equiv\text{C}t\text{Bu})(\mu\text{-PPh}_2)(\text{PPh}_2\text{H})\}_2]$ **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 $\bar{\nu}(\text{C}\equiv\text{C})$ region. The presence of alkynyl C≡CtBu ligands is better revealed by the ¹H NMR spectrum which shows, in addition to a doublet of multiplets centered at 5.25 [${}^1J(\text{P},\text{H}) = 368$ 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 ³¹P{¹H} 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 [${}^2J(\text{P}_A,\text{P}_X) + {}^2J(\text{P}_A,\text{P}_{X'}) = {}^2J(\text{P},\text{P}_{\text{trans}}) + {}^2J(\text{P},\text{P}_{\text{cis}})$] and

are comparable with those observed in related systems, for example, $[\{\text{PtCl}(\mu\text{-PPh}_2)\text{L}\}_2]$ (L = PEt₃ 378.8 Hz, L = PPh₂H 394.4 Hz),^[27a] $[\{\text{PtCl}(\mu\text{-PHMes})(\text{PH}_2\text{Mes})\}_2]$ (360 Hz).^[27d] The values of the K [$K = {}^4J(\text{P}_A,\text{P}_{A'}) + {}^2J(\text{P}_X,\text{P}_{X'}) = 136.4$ Hz] and L [$L = {}^2J(\text{P}_A,\text{P}_X) - {}^2J(\text{P}_A,\text{P}_{X'}) = 362$ Hz] parameters, which allow the determination of the coupling constants ${}^2J(\text{P}_A,\mu\text{-P}_{X\text{trans}})$ [345.2 Hz] and ${}^2J(\text{P}_A,\mu\text{-P}_{X\text{cis}})$ [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 ${}^2J(\text{P}_A,\mu\text{-P}_{X\text{cis}})$ is negative, since coupling constants between phosphorus atoms in mutually *trans* positions, such as ${}^2J(\text{P}_A,\mu\text{-P}_X)$ are known to be large and positive.^[27] If ${}^4J(\text{P}_A,\text{P}_{A'})$ is assumed to be ~ 0 , this leads a value of 136 Hz for $|{}^2J(\text{P}_X,\text{P}_{X'})|$, comparable with those reported for related systems.^[27] The low-field resonance ($\delta = 1.36$) is assigned to the equivalent PPh₂H ligands, while the strongly shielded signal (at $\delta = 145.4$) 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 ¹⁹⁵Pt–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 ¹⁹⁵Pt satellites [${}^1J(\text{Pt},\text{P}_A) = 2035$ Hz, ${}^3J(\text{Pt},\text{P}_A) \sim 0$ Hz], while the upfield signal shows two different sets of ¹⁹⁵Pt satellites [${}^1J(\text{Pt},\text{P}_X, \text{P}_{X'}) = 1689, 1792$ Hz], unambiguously confirming the bridging nature of these phosphorus atoms ($\mu\text{-PPh}_2$). In keeping with earlier observations^[27] the one-bond Pt–P_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_μ–Pt bond due to ring strain effects.^[12b] If as in complexes **1** and **5** (and also in **9**) the PPh₂H ligand exerts a lower *trans* influence than does C≡CR, then the ${}^1J(\text{Pt},\text{P}_{X'})$ [1792 Hz] could be assigned to the P_{X'} atom *trans* to PPh₂H, 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 PPh₂H [2.3376(10) Å] is slightly longer than the Pt–P (bridging) bond *trans* to C≡CtBu [2.3169(11) Å], suggesting the opposite assignment. 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 $[\{\text{Pt}(\text{C}\equiv\text{C}t\text{Bu})(\mu\text{-PPh}_2)(\text{PPh}_2\text{H})\}_2]$ **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 $-x, -y, -z$.

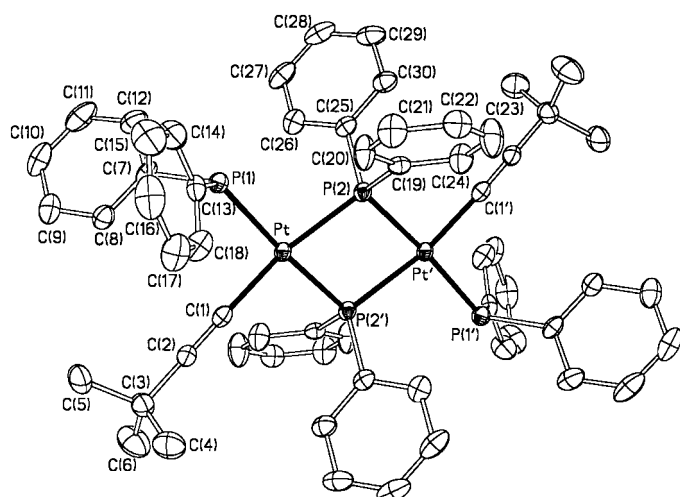


Figure 3. View of the molecular structure of $[[Pt(C\equiv C\text{tBu})(\mu\text{-PPh}_2)(PPh_2H)_2]_2$ **6a** with the atom numbering scheme.

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 $[[PtCl(\mu\text{-PPh}_2)(PPh_2H)_2]_2$ (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 $C\equiv C\text{tBu}$ 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] ($O\cdots H\cdots O$), 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 ($-40^\circ C$)

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** $R = tBu$; **7b** $R = Ph$; Scheme 3, path ii). In the reaction with $R = tBu$, 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*- $[Pt(C\equiv C\text{tBu})_2COD]$ 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 $\nu(P-O)$ region ($900-1028\text{ cm}^{-1}$). 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 $O\cdots H\cdots O$, 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 $O\cdots H\cdots O$ 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 $C\equiv C\text{tBu}$ 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 ($-50^\circ C$) 1H spectra, confirming the presence of strong $O\cdots H\cdots O$ hydrogen bonds.^[30c,d, 31] Furthermore, at $-50^\circ C$ they display the expected ABX pattern with ^{195}Pt satellites in their ^{31}P NMR spectra. The most deshielded signals [$\delta P_A/P_X = 81.75/75.56$ **7a**; $84.91/75.66$ **7b**; $^2J(P_A, P_{Btrans})/^2J(P_A, P_{Xcis})$ 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 [$\delta P_B/2J(P_B, P_X)$ 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 $^{31}\text{P}\{^1\text{H}\}$ 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 $\sim 25^\circ\text{C}$ [no merging was observed at the high temperature limit of the experiment ($\sim 50^\circ\text{C}$)], while the central signal (P_X) due to PPh_2O^- *trans* to $\text{C}\equiv\text{CtBu}$ is seen as a sharp triplet [$J(\text{P}_\text{X}, \text{P}_{\text{A,B}}) \sim 23\text{ Hz}$] 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 $[\text{Pt}(\text{C}\equiv\text{CR})\{(\text{PPh}_2\text{O})_2\text{H}\}(\text{PPh}_2\text{OH})]$ (7**):** It has been previously reported that one of the diphenylphosphinous acid molecules in $[\text{PtH}(\text{PPh}_2\text{OHOPPh}_2)(\text{PPh}_2\text{OH})]$ is easily displaced by other functionalized phosphines or phosphinites (alkenyl or alkynyl), yielding related $[\text{PtH}(\text{PPh}_2\text{OHOPPh}_2)\text{L}]$ compounds.^[32b] We have also exam-

ined 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 , CNtBu , or $(\text{NBu}_4)\text{CN}$, affording colorless solutions from which the related neutral $[\text{Pt}(\text{C}\equiv\text{CR})\{(\text{PPh}_2\text{O})_2\text{H}\}\text{L}]$ **8–10** or anionic $(\text{NBu}_4)[\text{Pt}(\text{C}\equiv\text{CR})(\text{CN})\{(\text{PPh}_2\text{O})_2\text{H}\}]$ **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 $\text{PPh}_2\text{OHOPPh}_2$ 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** ($\text{L} = \text{CNtBu}$) and **11** ($\text{L} = \text{CN}^-$) [for complexes **10** the C_β appears only as a doublet], compounds **8** ($\text{L} = \text{PEt}_3$) 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 $\delta = 105.4$ [$^2J(\text{C}_\alpha, \text{P}_{\text{trans}}) \sim 120\text{ Hz}$] and a doublet at $\delta = 117.07$ [$^3J(\text{C}_\beta, \text{P}_{\text{trans}}) = 32\text{ Hz}$] 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** ($\text{L} = \text{PEt}_3$) and **9** ($\text{L} = \text{PPh}_2\text{H}$) display in their ^{31}P NMR the three expected mutually coupled (AMX system) set

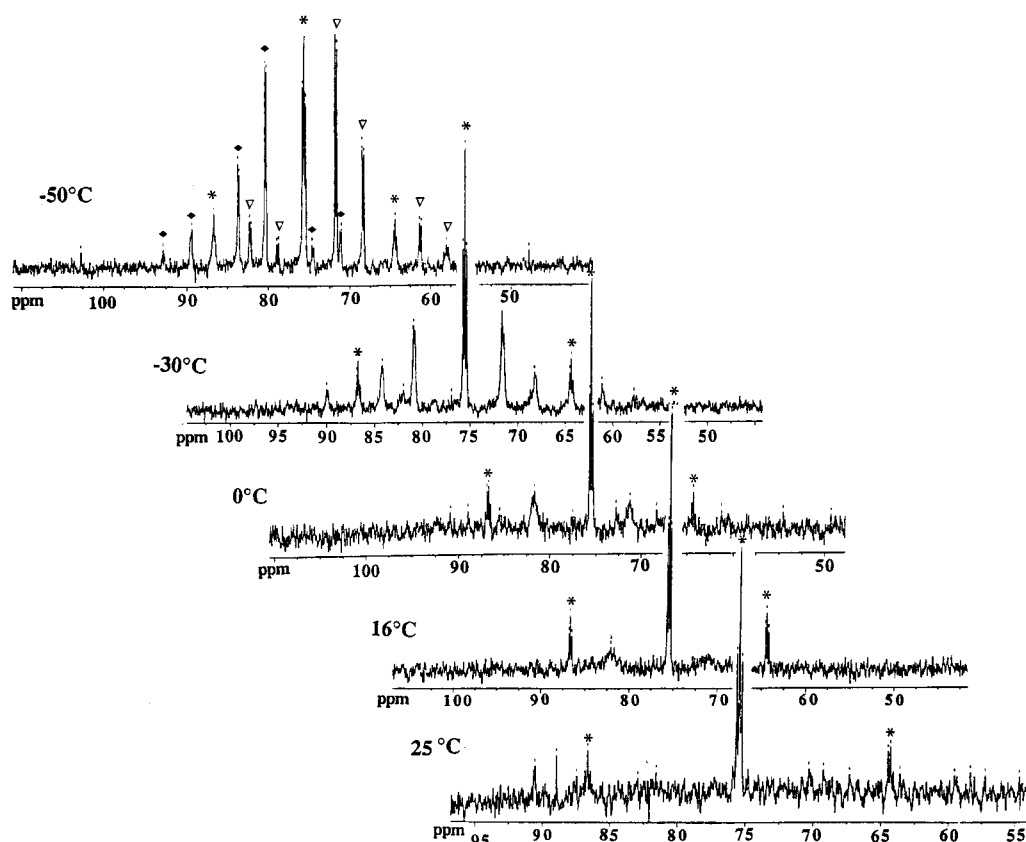
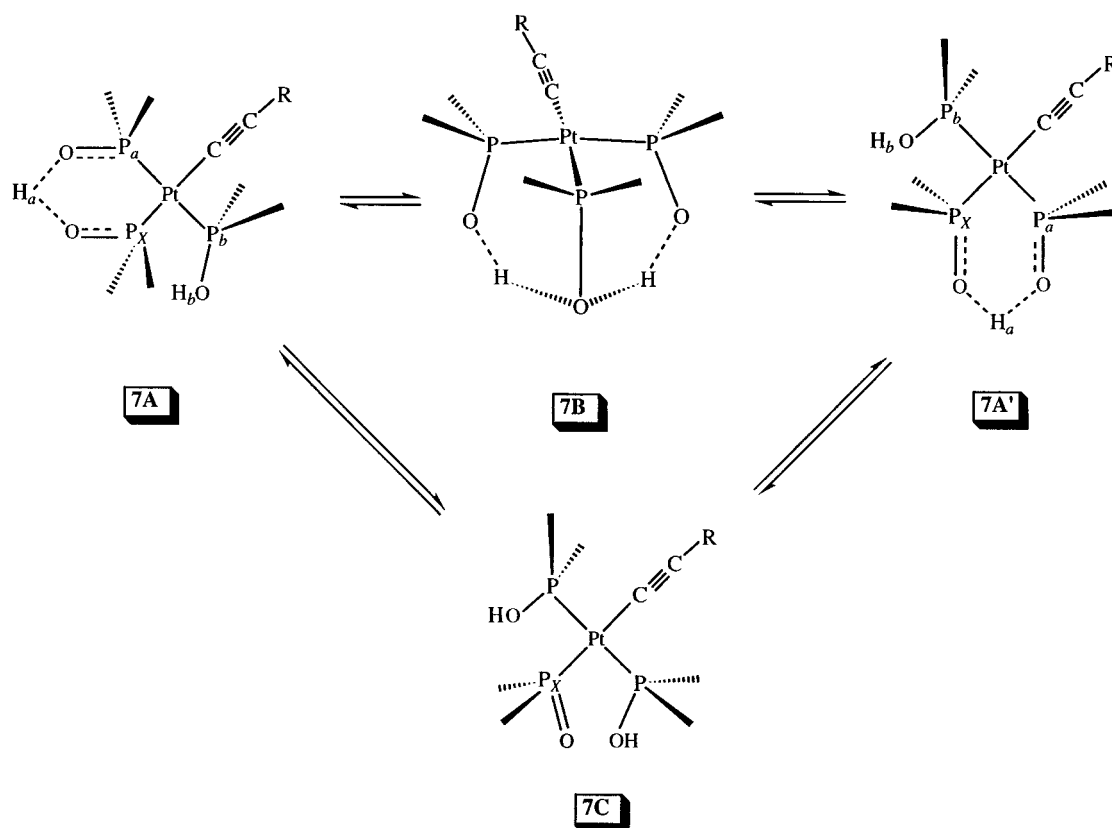


Figure 4. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (CDCl_3) of complex $[\text{Pt}(\text{C}\equiv\text{CtBu})\{(\text{PPh}_2\text{O})_2\text{H}\}(\text{PPh}_2\text{OH})]$ **7a** at different temperatures. At $+50^\circ\text{C}$ the spectrum observed is identical to that at 25°C . ABX system: * X; ∇ 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 $C\equiv CR$ 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 ($\delta = 69.19 - 72.49$ PPh₂O...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 $C\equiv CR$, and the low-frequency signal ($\delta = 60.95 - 66.11$) is then assigned to the phosphorus atom *trans* to $CNtBu$ 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 alkyne ligands is slightly stronger than that of the isoelectronic $CNtBu$ or CN^- groups.

On the other hand, the similarity between these alkyne-phosphinite/bis(hydroxyphosphine) di(acidic) species **7a** and **7b** and the observed deprotonated skeleton in each of the alkyne-tris(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)plati-

nate fragments with the lithium counter ions, yielding the sandwiched Pt_2Li_4 complex **3a** 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 **3a** 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 **3a**. Its 7Li NMR spectrum exhibits a broad signal at room temperature ($\delta = -0.89$, $w_{1/2} = 86$ Hz) which splits at $0^\circ C$ into two signals ($\delta = -0.1, -1.8$; coalescence ca. 3–4 $^\circ C$), 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 $Li_2[Pt(C\equiv CR)_4]$ ($R = tBu, Ph$) 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 alkyne

platinum compounds, which may be inaccessible by other synthetic routes: i) the mononuclear bis(alkynyl) complexes stabilized by PPh₂H ligands [Pt(C≡CR)₂(PPh₂H)₂] (*trans*-**1** or *cis*-**2**); ii) the unexpected mononuclear diphosphine derivative [Pt(C≡CR)₂(PPh₂CHPhCH₂PPh₂)] (**4b**); iii) the phosphido-bridged diplatinum complexes [[Pt(C≡CR)(μ-PPh₂)(PPh₂H)]₂] (**6**), also containing alkynyl and PPh₂H as coligands; iv) the novel mononuclear alkynyl derivatives [Pt(C≡CR){(PPh₂O)₂H}(PPh₂OH)] (**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≡CR)₂(PPh₂O)₂Li₂(μ-H₂O)(Me₂CO)₂]₂] (**2**) and [[Pt(C≡CR)(PPh₂O)₃Li₂(thf)(H₂O)]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 PPh₂H. However, we have also observed that the treatment of complexes **5** with one equivalent of PPh₂H 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 PPh₂⁻ 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(μ-PPh₂)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 (μ-PR₂)(μ-C≡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≡CR){(PPh₂O)₂H}(PPh₂OH)] (**7**), which formally contains two PPh₂(O)H ligands, with Lewis bases such as PET₃,

PPh₂H, 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 (PPh₂H **1**, **5**, **6**, **9** or PPh₂OH **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 (μ-C₂R)/(μ-PPh₂) or (μ-C₂R)/μ-PPh₂O⁻ 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 ARX 300 spectrometer, and chemical shifts are reported relative to external standards (SiMe₄, CFCl₃, 85% H₃PO₄, and LiCl in H₂O). 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 [PtCl₂(tht)₂]^[40] and *cis*-[Pt(C≡CR)₂COD] (R = Ph,^[24] *t*Bu^[10a]) were prepared by published methods. PPh₂H and PPh₂(O)H were purchased from commercial suppliers.

Reaction of Li₂[Pt(C≡C*t*Bu)₂] with PPh₂H. Preparation of *trans*-[Pt(C≡C*t*Bu)₂(PPh₂H)₂] (1a**), [[Pt(C≡C*t*Bu)₂(PPh₂O)₂Li₂(μ-H₂O)(Me₂CO)₂]₂] (**2a**) and [[Pt(C≡C*t*Bu)(PPh₂O)₃Li₂(thf)(H₂O)]₂] (**3a**):** [PtCl₂(tht)₂] (0.400 g, 0.904 mmol) was added to a fresh solution of LiC≡C*t*Bu (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 Li₂Pt(C≡C*t*Bu)₄ was treated with 25 mL of an acetone/EtOH mixture (1:4; not deoxygenated). The resulting colourless solution was treated with PPh₂H (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≡C*t*Bu)₂(PPh₂H)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≡C*t*Bu)₂(PPh₂O)₂Li₂(H₂O)_n] (n = 3). C₃₆H₄₄Li₂O₅P₂Pt (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≡C*t*Bu)₂(PPh₂O)₂Li₂(μ-H₂O)(Me₂CO)₂]₂] (**2a**) as a microcrystalline solid (40% yield). This solid has a tendency to exchange acetone molecules for H₂O. 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 ³¹P) 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≡C*t*Bu)(PPh₂O)₃Li₂(H₂O)_n] (n = 2). C₄₂H₄₃Li₂O₅P₃Pt (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≡C*t*Bu)(PPh₂O)₃Li₂(H₂O)(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: $^1\text{H NMR}$ (CDCl_3): $\delta = 7.96$ (br, 8H), 7.37 (br, 8H; Ph), 6.46 (AA' part of an AA'XX' system (X = P)); $N = ^1J(\text{P,H}) + ^3J(\text{P',H}) = 400$ Hz, $^2J(\text{Pt,H}) = 26.2$ Hz, PH , 1.05 (s, 18H; *t*Bu); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = -1.99$ ($^1J(\text{Pt,P}) = 2616$ Hz); $^{31}\text{P NMR}$ (CDCl_3): $\delta = -1.97$, (XX' part of an AA'XX' system (A = H)); $^1J(\text{P,H}) = 399.9$ Hz, $^2J(\text{P,P'}) = 484$ Hz, $^3J(\text{P,H'}) = 3.6$ Hz, $J(\text{H,H'}) \sim 0$; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 134.2$ (t, $J(\text{C,P}) = 6.2$ Hz, $^3J(\text{Pt,C}) = 24.5$ Hz; *o*-C, PPh_2H), 130.1 (s; *p*-C, PPh_2H), 128.7 (t, $J(\text{C,P}) = 28.3$ Hz; *i*-C, PPh_2H), 128.0 (t, $J(\text{C,P}) = 5.4$ Hz; *m*-C, PPh_2H), 120.6 (t, $^3J(\text{C}_\beta\text{P}) = 2.6$ Hz, $^2J(\text{Pt,C}_\beta) = 249$ Hz; C_β , $-\text{C}_\alpha=\text{C}_\beta-\text{tBu}$), 85.2 (t, $^2J(\text{C}_\alpha\text{P}) = 15.9$ Hz, $^1J(\text{Pt,C}_\alpha) = 913$ Hz; C_α , $\text{C}_\alpha=\text{C}_\beta-\text{tBu}$), 32.0 (s; C(CH₃)₃), 29.0 (s, $^3J(\text{Pt,C}) = 17.9$ Hz; $-\text{CMe}_3$); IR: $\tilde{\nu} = 2369$ (vs; P-H), 2106 cm^{-1} (m; C=C); MS: m/z (%): 1294 (9) [$[\text{Pt}(\text{PPh}_2\text{H})(\text{C}\equiv\text{CtBu})(\mu\text{-PPh}_2\text{H})_2]^+ = [\text{A}]^+$, 1212 (9) [$[\text{A}-\text{C}\equiv\text{CtBu}-\text{H}]^+$, 1027 (6) [$[\text{A}-\text{C}\equiv\text{CtBu}-\text{PPh}_2\text{H}]^+$, 729 (31) [$[\text{M}^+]$, 647 (33) [$[\text{M}-\text{C}\equiv\text{CtBu}-\text{H}]^+$, 565 (68) [$[\text{Pt}(\text{PPh}_2)_2]^+$, 379 (70) [$[\text{PtPPh}_2-\text{H}]^+$; $\text{C}_{40}\text{H}_{40}\text{P}_2\text{Pt}$ (729.7); calcd C 59.25, H 5.52; found: C 59.12, H 5.54.

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

Data for 3a: $^1\text{H NMR}$ (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; H₂O), 0.49 (s; *t*Bu); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 73.14$ (d, $^1J(\text{Pt,P}_A) = 2723$ Hz, 2P), 58.70 (t, $^1J(\text{Pt,P}_X) = 2673$ Hz, 1P), $^2J(\text{P}_A\text{P}_X) = 29.3$ Hz; $^7\text{Li}\{^1\text{H}\}$ NMR (CDCl_3): at 20 °C, $\delta = -1.03$ (brs); 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) [$[\text{Pt}_2(\text{C}\equiv\text{CtBu})(\text{PPh}_2\text{O})_6\text{Li}]^+$, 882 (100) [$[\text{Pt}(\text{C}\equiv\text{CtBu})(\text{PPh}_2\text{O})_3+3\text{H}]^+$, 806 (27) [$[\text{Pt}(\text{PPh}_2\text{O})_3\text{Li}]^+$, 604 (80) [$[\text{Pt}(\text{PPh}_2\text{O})_2\text{Li}]^+$, 396 (54) [$[\text{Pt}(\text{PPh}_2\text{O})]^+$.

Reaction of $\text{Li}_2[\text{Pt}(\text{C}\equiv\text{CtBu})_4]$ with $\text{PPh}_2(\text{O})\text{H}$: A fresh solution of $\text{Li}_2\text{Pt}(\text{C}\equiv\text{CtBu})_4$ (0.452 mmol) in an acetone/EtOH mixture (25 mL) prepared as described above was treated with $\text{PPh}_2(\text{O})\text{H}$ (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 $[\text{PtCl}_2(\text{tht})_2]$). Removal of the solvent from the filtrate and addition of diethyl ether (5 mL) gave **3'a** (0.168 g, 37% yield).

Reaction of $[\text{Pt}(\text{C}\equiv\text{CtBu})_2(\text{PPh}_2\text{O})_2\text{Li}(\mu\text{-H}_2\text{O})(\text{Me}_2\text{CO})_2]_2$ (2a**) with $\text{PPh}_2(\text{O})\text{H}$:** A white suspension of **2a** (0.050 g, 0.027 mmol) in CHCl_3 (30 mL), was treated with $\text{PPh}_2(\text{O})\text{H}$ (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 ($^{31}\text{P}\{^1\text{H}\}$ 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 $\text{PPh}_2(\text{O})\text{H}$. When the reaction was monitored by $^{31}\text{P}\{^1\text{H}\}$ 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 $\text{trans}[\text{Pt}(\text{C}\equiv\text{CtBu})_2(\text{PPh}_2\text{H})_2]$ (1a**) with LiOH and H₂O₂:** H₂O₂ (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 $^{31}\text{P}\{^1\text{H}\}$ NMR of this solution shows only the presence of starting material. When an excess of LiOH and H₂O₂ (4:4:1 molar ratio) and longer periods of stirring (6 d) are employed, a complex mixture of unidentified platinum complexes is observed by $^{31}\text{P}\{^1\text{H}\}$ NMR.

Preparation of $\text{trans}[\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{PPh}_2\text{H})_2]$ (1b**), $[\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{PPh}_2\text{O})_2\text{Li}_2(\mu\text{-H}_2\text{O})\text{S}_2]_2$ (**2'b**), $[\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{PPh}_2\text{CHPhCH}_2\text{PPh}_2)]$ (**4b**), and $[\text{Pt}(\text{C}\equiv\text{CPh})(\mu\text{-PPh}_2)(\text{PPh}_2\text{H})_2]$ (**6b**)**

a) Reaction of $\text{Li}_2[\text{Pt}(\text{C}\equiv\text{CPh})_4]$ with PPh_2H : A white suspension of $\text{Li}_2[\text{Pt}(\text{C}\equiv\text{CPh})_4]$, prepared from $[\text{PtCl}_2(\text{tht})_2]$ (0.300 g, 0.678 mmol) and $\text{LiC}\equiv\text{CPh}$, (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 $\text{CHCl}_3/\text{hexane}$ 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 ($^{31}\text{P}\{^1\text{H}\}$ NMR) containing mainly **2'b**. However, when a solution of $\text{Li}_2[\text{Pt}(\text{C}\equiv\text{CPh})_4]$ (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 $[\text{PtCl}_2(\text{tht})_2]$ (0.600 g, 1.356 mmol) at low temperature (-20 °C) with a lesser excess of $\text{LiC}\equiv\text{CPh}$ (4.069 mmol, 1:3 molar ratio) slowly (~45 min) yields a suspension [probably mixtures of species of the type $\text{Pt}(\text{C}\equiv\text{CPh})_{4-x}(\text{tht})_{x-2}\text{Li}_{2-x}$, ($x = 0-2$)]. 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 $\text{CHCl}_3/\text{hexane}$, yielding **1b** (0.7 g, 67%) as a yellow microcrystalline solid. The mother liquor ($\text{CH}_2\text{Cl}_2/\text{hexane}$) 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 ($\text{Pt}:\text{PPh}_2\text{H}$), 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 $\text{CHCl}_3/\text{hexane}$ yielding **6b** in very low yield (~15%).

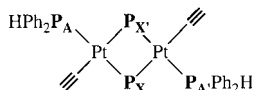
Data for 1b: $^1\text{H NMR}$ (CDCl_3): $\delta = 7.96$, 7.41, 7.11 (m, Ph), ~6.72 (AA' part of an AA'XX' system (X = P), due to overlapping with Ph resonances only $^2J(\text{Pt,H}) = 26.8$ Hz can be calculated; PH); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = -4.26$ ($^1J(\text{Pt,P}) = 2547$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

Data for 2'b: $^1\text{H NMR}$ (CDCl_3): $\delta = 7.78$, 7.14, 6.76, 6.19 (Ph, PPh_2 , $\text{C}\equiv\text{CPh}$), 3.53 (brs, H₂O), signals due to THF are also observed 3.73 (m), 1.84 (m); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 68.07$ (s, $^1J(\text{Pt,P}) = 2395$ Hz); $^7\text{Li}\{^1\text{H}\}$ NMR (CDCl_3): at 20 °C, $\delta = -0.62$ (s), at -20 °C, $\delta = -0.32$ (brs); 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) [$[\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{PPh}_2\text{O})_2+\text{H}]^+$, 498.4 (14) [$[\text{Pt}(\text{C}\equiv\text{CPh})(\text{PPh}_2\text{OH})]^+$; $[\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{PPh}_2\text{O})_2\text{Li}_2(\text{H}_2\text{O})_3]$, $\text{C}_{40}\text{H}_{36}\text{Li}_2\text{O}_3\text{P}_2\text{Pt}$ (867.6); calcd C 55.37, H 4.18; $[\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{PPh}_2\text{O})_2\text{Li}_2(\text{H}_2\text{O})_2(\text{thf})]$, $\text{C}_{44}\text{H}_{42}\text{Li}_2\text{O}_3\text{P}_2\text{Pt}$ (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: $^1\text{H NMR}$ (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; CH₂), 3.19 (dm, $^2J(\text{H,P}) = 47$ Hz, $^3J(\text{Pt,H}) \sim 25$ Hz; CH), 2.53 (m, 1H, CH₂); $^1\text{H}\{^{31}\text{P}\}$ NMR (CDCl_3): Decoupling the $\delta = 21.4$ phosphorus resonance: 8.19 (d, $J(\text{H,H}) = 6.5$ Hz), 7.99 (d, $J(\text{H,H}) = 6.3$ Hz), 7.59–6.90 (m), 6.66 (d, $J(\text{H,H}) = 7.5$ Hz) (Ph), 3.83 (tm, $^2J(\text{H}_a\text{H}_b) \sim ^3J(\text{P,H}_a) = 9.3$ Hz; H_a, CH_aH_b), 3.21 (ddd,

$^2J(\text{P},\text{H}_c) = 47$ Hz, $^3J(\text{H}_c,\text{H}_b) = 14.4$ Hz, $^3J(\text{H}_c,\text{H}_a) = 3.3$ Hz, $^3J(\text{Pt},\text{H}_c) \sim 25$ Hz), 2.53 (td, $^2J(\text{H}_b,\text{H}_c) = 9.3$ Hz, $^3J(\text{H}_b,\text{H}_c) \sim ^3J(\text{H}_b,\text{P}) = 14.4$ Hz; H_b , CH_2H_b). By decoupling the signal at $\delta = 49.24$ under similar conditions the modification of the proton spectrum was negligible. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 49.24$ (d, $^1J(\text{Pt},\text{P}) = 2260$ Hz), 21.53 (d, $^1J(\text{Pt},\text{P}) = 2250$ Hz, $^3J(\text{P},\text{P}) = 13.8$ 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; $\text{C}\equiv\text{C}$); ES-MS(+): m/z (%): 871 (44) $[\text{M}]^+$, 771 (47) $[\text{M} - \text{C}_2\text{Ph} + \text{H}]^+$, 668 (58) $[\text{M} - 2\text{C}_2\text{Ph} - \text{H}]^+$, 565 (100) $[\text{Pt}(\text{PPh}_2)_2]^+$, 487 (90) $[\text{PtPPh}_2\text{PPh} - \text{H}]^+$, 379 (95) $[\text{PtPPh}_2 - \text{H}]^+$; $\text{C}_{48}\text{H}_{38}\text{P}_2\text{Pt}$ (871.9): calcd C 66.12, H 4.39; found C 65.87, H 3.97.

Data for 6b: ^1H NMR (CDCl_3): $\delta = 7.63, 7.28, 7.06, 6.71$ (m, Ph), 5.35 (dm, $J(\text{P},\text{H}) = 372$ Hz, 2H; PH); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): AA'XX' + AA'XX'M ($\text{M} = \text{Pt}$) spin systems $\delta\text{P}_{\text{AA}'} = 1.58$ (PPh₂H), $\delta\text{P}_{\text{XX}'} = -138.7$ ($\mu\text{-PPh}_2$), $[\text{N} = ^2J(\text{P}_A,\text{P}_X) + ^2J(\text{P}_A,\text{P}_X) = 321.4$ Hz, $K = ^4J(\text{P}_A,\text{P}_A) + ^2J(\text{P}_X,\text{P}_X) = 132.6$ Hz, $L = ^2J(\text{P}_A,\text{P}_X) - ^2J(\text{P}_A,\text{P}_X) = 351.9$ Hz, $|^2J(\text{P}_A,\text{P}_X)| = 336.7$ Hz, $|^2J(\text{P}_A,\text{P}_X)| = 15.3$ Hz, $^1J(\text{Pt},\text{P}_X) = 1688$ Hz, $^1J(\text{Pt},\text{P}_A) = 1766$ Hz, $^1J(\text{Pt},\text{P}_A) = 2051$ Hz]; IR: $\tilde{\nu} = 2357$ (w; P–H), 2104 cm^{-1} (s; $\text{C}\equiv\text{C}$); ES-MS (apci +): m/z (%): 666.5 (98) $[\text{Pt}(\text{C}\equiv\text{CPh})(\text{PPh}_2)_2]^+$, 667.5 (100) $[\text{Pt}(\text{C}\equiv\text{CPh})(\text{PPh}_2)(\text{PPh}_2\text{H})]^+$, 566 (15) $[\text{Pt}(\text{PPh}_2)(\text{PPh}_2\text{H})]^+$; $\text{C}_{64}\text{H}_{52}\text{P}_4\text{Pt}_2$ (1335.2): calcd C 57.57, H 3.92; found C 57.73, H 4.42.



Preparation of cis-[Pt(C≡CtBu)₂(PPh₂H)₂] (5a) and [Pt(C≡CtBu)(μ-PPh₂)(PPh₂H)]₂ (6a): A solution of *cis*-[Pt(C≡CtBu)₂(COD)] (1.114 g, 2.393 mmol) in CH_2Cl_2 (10 mL) was treated at -30°C with PPh_2H (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≡CtBu)₂(PPh₂H)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_2Cl_2 /hexane and identified as **6a** 0.031 g, 2% yield). The complex **6a** is also obtained by treatment of **5a** with CH_3COOH : **5a** (0.100 g, 0.1379 mmol) in CH_2Cl_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 ($\sim 25\%$).

Data for 5a: ^1H NMR (CDCl_3): $\delta = 7.65$ (m, 8H), 7.33 (m, 12H) (Ph), 5.88 (dm, $N = ^1J(\text{P},\text{H}) + ^3J(\text{P},\text{H}) = 378$ Hz, 2H; PH), 1.02 (s, 18H, *t*Bu); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = -5.49$ (s, $^1J(\text{Pt},\text{P}) = 2156$ Hz); ^{31}P NMR (CDCl_3): $\delta = -5.49$ (d, $J(\text{P},\text{H}) = 377$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): at 20°C , $\delta = 134.0$ (t, $J(\text{C},\text{P}) = 5.3$ Hz, $J(\text{Pt},\text{C}) = 20.2$ Hz; *o*-C, PPh₂H), 130.3 (s, *p*-C, PPh₂H), 128.1 (t, $J(\text{C},\text{P}) = 5.4$ Hz; *m*-C, PPh₂H), 127.4 (AAXX', $^1J(\text{C},\text{P}) + ^3J(\text{C},\text{P}) = 57.5$ Hz; *i*-C), 118.8 (AAXX', $^3J(\text{C}_\beta,\text{Ptrans}) + ^3J(\text{C}_\beta,\text{Pcis}) \sim 36.3$ Hz, $^2J(\text{Pt},\text{C}_\beta) = 306.4$ Hz; C_β , $-\text{C}_\alpha\equiv\text{C}_\beta\text{tBu}$), 84.3 (dd, $^2J(\text{C}_\alpha,\text{Ptrans}) = 153.0$ Hz, $^2J(\text{C}_\alpha,\text{Pcis}) = 21.2$ Hz, $^1J(\text{Pt},\text{C}_\alpha) = 1122.4$ Hz; C_α , $-\text{C}_\alpha\equiv\text{C}_\beta\text{tBu}$) 31.6 (s, $^4J(\text{Pt},\text{C}) = 8.0$ Hz; $\text{C}(\text{CH}_3)_3$), 28.7 (s, $^3J(\text{Pt},\text{C}) = 20.9$ Hz; $-\text{CMe}_3$); IR: $\tilde{\nu} = 2354$ (m; P–H), 2118 cm^{-1} (w; $\text{C}\equiv\text{C}$); MS: m/z (%): 1214 (8) $[\text{Pt}_2(\text{C}\equiv\text{CtBu})(\mu\text{-PPh}_2)_2(\text{PPh}_2\text{H})_2]^+$, 730 (76) $[\text{M} + \text{H}]^+$, 647 (33) $[\text{M} - \text{C}\equiv\text{CtBu} - \text{H}]^+$, 566 (100) $[\text{Pt}(\text{PPh}_2\text{H})(\text{PPh}_2)]^+$, 379 (42) $[\text{PtPPh}_2 - \text{H}]^+$; $\text{C}_{36}\text{H}_{40}\text{P}_2\text{Pt}$ (729.8): calcd C 59.25, H 5.52; found C 58.99, H 5.65.

Data for 6a: ^1H NMR (CDCl_3): $\delta = 7.61$ (m, 16H), 7.27 (m), 7.07 (m) (24H) (Ph), 5.25 (dm, $J = 368$ Hz; 2H; PH), 0.86 (s, 18H, *t*Bu); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): AA'XX' spin system $\delta\text{P}_{\text{AA}'} = 1.36$ (PPh₂H), $\delta\text{P}_{\text{XX}'} = -145.4$ ($\mu\text{-PPh}_2$), $[\text{N} = ^2J(\text{P}_A,\text{P}_X) + ^2J(\text{P}_A,\text{P}_X) = 328.4$ Hz, $K = ^4J(\text{P}_A,\text{P}_A) + ^2J(\text{P}_X,\text{P}_X) = 136.4$ Hz, $L = ^2J(\text{P}_A,\text{P}_X) - ^2J(\text{P}_A,\text{P}_X) = 362$ Hz, $|^2J(\text{P}_A,\text{P}_X)| = 345.2$ Hz, $|^2J(\text{P}_A,\text{P}_X)| = 16.8$ Hz, $^1J(\text{Pt},\text{P}_X) = 1689$ Hz, $^1J(\text{Pt},\text{P}_A) = 1792$ Hz, $^1J(\text{Pt},\text{P}_A) = 2035$ Hz]; IR: $\tilde{\nu} = 2352$ cm^{-1} (s; P–H); MS: m/z (%): 1294 (60) $[\text{A}]^+$, 1213 (100) $[\text{A} - \text{C}\equiv\text{CtBu}]^+$, 1108 (31) $[\text{A} - \text{PPh}_2\text{H} - \text{H}]^+$, 1027 (53) $[\text{A} - \text{C}\equiv\text{CtBu} - \text{PPh}_2\text{H}]^+$; $\text{C}_{60}\text{H}_{60}\text{P}_4\text{Pt}_2$ (1295.2): calcd C 55.64, H 4.67; found C 55.49, H 4.76.

Preparation of cis-[Pt(C≡CPh)₂(PPh₂H)₂] (5b): A yellow solution of *cis*-[Pt(C≡CPh)₂(COD)] (1.004 g, 1.986 mmol) in CH_2Cl_2 (10 mL) was treated at low temperature (-30°C) with PPh_2H (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 diethyl ether and dried under vacuum (1.169 g, 76% yield). ^1H NMR (CDCl_3): $\delta = 7.67$ (m), 7.38 (m), 7.08 (m), (30H; Ph), 6.08 (dm, $N = ^1J(\text{P},\text{H}) + ^3J(\text{P},\text{H}) = 390$ Hz, 2H; PH); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3):

$\delta = -7.07$ (s, $^1J(\text{Pt},\text{P}) = 2169$ Hz); ^{31}P NMR (CDCl_3): $\delta = -7.07$ (d, $J(\text{P},\text{H}) = 383$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): at -50°C , $\delta = 134.2$ (t, $J(\text{C},\text{P}) = 5.2$ Hz; *o*-C, PPh₂H), 131.4 (in this signal, the *o*-C of the $-\text{C}\equiv\text{CPh}$ groups and *p*-C of the ligands PPh₂H probably overlap), 131.1 (s; Ph), 128.6 (t, $J(\text{C},\text{P}) = 5.0$ Hz; *m*-C, PPh₂H), 127.5 (s; *m*-C, Ph, $-\text{C}\equiv\text{CPh}$), 127.3 (s; *i*-C, Ph, $-\text{C}\equiv\text{CPh}$), 126.2 (AAXX', $^1J(\text{C},\text{P}) + ^3J(\text{C},\text{P}) = 59.4$ Hz, *i*-C, PPh₂H), 125.5 (s; *p*-C, Ph, $-\text{C}\equiv\text{CPh}$), 110.6 (AAXX', $^3J(\text{C}_\beta,\text{Ptrans}) + ^3J(\text{C}_\beta,\text{Pcis}) = 36.4$ Hz, $^2J(\text{Pt},\text{C}_\beta) = 308.4$ Hz; C_β , $-\text{C}_\alpha\equiv\text{C}_\beta\text{Ph}$), 99.9 (dd, $^2J(\text{C}_\alpha,\text{Ptrans}) = 148.8$ Hz, $^2J(\text{C}_\alpha,\text{Pcis}) = 21.4$ Hz, $^1J(\text{Pt},\text{C}_\alpha) = 1114.6$ Hz; C_α , $-\text{C}_\alpha\equiv\text{C}_\beta\text{Ph}$); IR: $\tilde{\nu} = 2342$ (m; P–H), 2119 cm^{-1} (m; $\text{C}\equiv\text{C}$); MS: m/z (%): 1334 (10) $[\text{Pt}(\text{C}\equiv\text{CPh})(\mu\text{-PPh}_2)(\text{PPh}_2\text{H})_2]^+ = [\text{B}]^+$, 1233 (14) $[\text{B} - \text{C}\equiv\text{CPh}]^+$, 1133 (11) $[\text{B} - 2\text{C}\equiv\text{CPh} + \text{H}]^+$, 1047 (6) $[\text{B} - \text{C}\equiv\text{CPh} - \text{PPh}_2\text{H}]^+$, 769 (51) $[\text{M}]^+$, 667 (35) $[\text{M} - \text{C}\equiv\text{CPh} - \text{H}]^+$, 566 (100) $[\text{Pt}(\text{PPh}_2\text{H})(\text{PPh}_2)]^+$, 379 (39) $[\text{PtPPh}_2 - \text{H}]^+$; $\text{C}_{40}\text{H}_{32}\text{P}_2\text{Pt}$ (769.7): calcd C 62.42, H 4.19; found C 62.05, H 4.06.

Reactions of cis-[Pt(C≡CR)₂(PPh₂H)₂] with PPh₂H: For $\text{R} = \text{tBu}$; PPh_2H (28.9 μL , 0.167 mmol) was added to a stirred solution of **5a** (0.122 g, 0.167 mmol) in deoxygenated CH_2Cl_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≡CtBu)₂(PPh₂H)₂] **1a** and $[\text{Pt}(\text{C}\equiv\text{CtBu})(\mu\text{-PPh}_2)(\text{PPh}_2\text{H})_2]$ **6a** (3.7:1 ratio). If the initial mixture is stirred for 3 days under aerobic conditions, oxidation of PPh_2H takes place and $\text{PPh}_2(\text{O})\text{H}$ is generated. The ^{31}P NMR spectrum of the final mixture shows the complete transformation of **6a** to $[\text{Pt}(\text{C}\equiv\text{CtBu})(\text{PPh}_2\text{O}_2\text{H})(\text{PPh}_2\text{H})]$ (**9a**). Similar results were obtained starting from **5b** (0.120 g, 0.156 mmol) and 1 equiv of PPh_2H (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(PPh₂H)₂] **1b** with a small amount of $\text{PPh}_2(\text{O})\text{H}$ as impurity.

Preparation of [Pt(C≡CR)(PPh₂O₂H)(PPh₂OH)] (R = tBu **7a; R = Ph **7b**):** A suspension of *cis*-[Pt(C≡CtBu)₂(COD)] (0.150 g, 0.322 mmol) in CH_2Cl_2 (20 mL) was treated at -40°C with $\text{PPh}_2(\text{O})\text{H}$ (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 $\text{PPh}_2(\text{O})\text{H}$ (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 (0.215 g, 60%). Similar results were obtained using a $\text{Pt}/\text{PPh}_2(\text{O})\text{H}$ ratio of 1:2 at -20°C (yield: 45% **7a**, 43% **7b**). If *cis*-[Pt(C≡CtBu)₂(COD)] (0.250 g, 0.537 mmol) is treated with two molar equiv of $\text{PPh}_2(\text{O})\text{H}$ (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 $[\text{Pt}(\text{PPh}_2\text{O}_2\text{H})_2]^{[30e]}$ $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 72.33$ ($J(\text{Pt}-\text{P}) = 2454$ Hz).

Data for 7a: ^1H 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 $\text{O}\cdots\text{H}\cdots\text{O}$; $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): at -50°C , ABX pattern $\delta\text{P}_A = 81.75$ (PPh_2O^-), $\delta\text{P}_B = 70.29$ (PPh_2OH), $\delta\text{P}_X = 75.56$ (P *trans* to $\text{C}\equiv\text{CtBu}$), $^2J(\text{P}_A,\text{P}_{\text{trans}}) = 405.4$ Hz, $^2J(\text{P}_A,\text{P}_{\text{cis}}) = 20.4$ Hz, $^2J(\text{P}_B,\text{P}_{\text{cis}}) = 26.3$ Hz, $^1J(\text{Pt},\text{P}_A) = 2223$ Hz, $^1J(\text{Pt},\text{P}_B) = 2537$ Hz, $^1J(\text{Pt},\text{P}_X) = 2713$ Hz; at 25°C , 75.45 (t, $^2J(\text{P}_X,\text{P}_{\text{cis}}) = 23.2$ Hz, $^1J(\text{Pt},\text{P}_X) = 2696$ 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) $[\text{M}]^+$, 800 (16) $[\text{M} - \text{C}\equiv\text{CtBu}]^+$, 598 (50) $[\text{Pt}(\text{PPh}_2\text{O}_2\text{H})_2]^+$, 395 (47) $[\text{PtPPh}_2\text{O} - \text{H}]^+$; $\text{C}_{42}\text{H}_{41}\text{O}_3\text{P}_3\text{Pt}$ (881.8): calcd C 57.21, H 4.69; found C 57.27, H 4.05.

Data for 7b: ^1H NMR (CDCl_3): at -50°C , $\delta = 16.53$ (br; $\text{O}\cdots\text{H}\cdots\text{O}$), 7.76, 7.25, 6.62 (m; Ph); at 25°C , 7.60, 7.32, 7.08, 6.65 (m, Ph); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): at -50°C , ABX pattern, $\delta\text{P}_A = 84.91$ (PPh_2O^-), $\delta\text{P}_B = 70.35$ (PPh_2OH), $\delta\text{P}_X = 75.66$ (P *trans* to $\text{C}\equiv\text{CPh}$), $^2J(\text{P}_A,\text{P}_{\text{trans}}) = 405.3$ Hz, $^1J(\text{Pt},\text{P}_A) = 2246$ Hz, $^1J(\text{Pt},\text{P}_B) = 2512$ Hz, $^1J(\text{Pt},\text{P}_X) = 2670$ Hz); at 25°C , $\delta = 74.81$ (t, $^2J(\text{P}_X,\text{P}_{\text{cis}}) = 23.7$ Hz, $^1J(\text{Pt},\text{P}_X) = 2737$ Hz). A similar pattern was seen at 45°C ; IR: $\tilde{\nu} = 2120$ (w; $\text{C}\equiv\text{C}$), 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) $[\text{M}]^+$, 797 (20) $[\text{Pt}(\text{PPh}_2\text{O}_2\text{H})_2]^+$, 699 (22) $[\text{M} - \text{PPh}_2\text{OH}]^+$, 599 (37) $[\text{Pt}(\text{PPh}_2\text{O}_2\text{H})_2]^+$, 395 (52) $[\text{PtPPh}_2\text{O} - \text{H}]^+$; $\text{C}_{44}\text{H}_{37}\text{O}_3\text{P}_3\text{Pt}$ (901.8): calcd C 58.61, H 4.14; found C 58.31, H 3.86.

Preparation of [Pt(C≡CR)(PPh₂O)₂H]L **8–10:** These complexes were prepared using a common procedure. A typical preparation (R = *t*Bu, L = PEt₃, **8a**) was as follows: A suspension of **7a** (0.15 g, 0.17 mmol) in CH₂Cl₂ (~10 mL) was treated with a stoichiometric amount of PEt₃ (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 appropriate donor ligand. The following amounts were used: For **8b** (R = Ph, PEt₃, **7b** (0.200 g, 0.222 mmol) and PEt₃ (3.01 μL, 0.222 mmol), yield 78%; **10a** (R = *t*Bu, L = CN*t*Bu) **7a** (0.200 g, 0.222 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 = PPh₂H) 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, 0.222 mmol) with PPh₂H (39.5 μL, 0.227 mmol) for complex **9a** (yield 56%) and **7b** (0.128 g, 0.142 mmol) with PPh₂H (24.7 μL, 0.142 mmol) for **9b** (yield 64%), respectively.

Data for 8a: ¹H NMR (CDCl₃): δ = 7.89, 7.68, 7.33 (Ph), 1.55 (m; CH₂, PEt₃), 0.85 (dt, ³J(P,H) = 16 Hz, ²J(H,H) = 7.5 Hz; CH₃, PEt₃), 0.85 (s; *t*Bu, C≡C*t*Bu); ³¹P{¹H} NMR (CDCl₃): AMX spin system, δ = 79.41 (t, ²J(P_X,P_{Mcis}) = 27.4 ~ ²J(P_X,P_{Acis}) = 21.5 Hz, ¹J(Pt,P_X) = 2699 Hz; P_X, P_{trans} to C≡C*t*Bu), 72.49 (dd, ²J(P_A,P_{Mtrans}) = 389.9 Hz, ¹J(Pt,P_M) = 2639.3 Hz; P_M, P_{trans} to PEt₃), 5.14 (dd, ¹J(Pt,P_A) = 1968.2 Hz; P_A, PEt₃); ¹³C{¹H} NMR (CDCl₃): δ = 140.0 (d, ¹J(C,P) = 62.5 Hz, ²J(Pt,C) ~ 47 Hz), 139.99 (dd, ¹J(C,P) = 69.5 Hz, ³J(C,P) = 6.9 Hz, ²J(Pt,C) ~ 31 Hz; *i*-C, PPh₂O⁻), 132.5 (m; *o*-C, PPh₂O⁻), 130.39 (d, ⁴J(C,P) = 1.7 Hz), 129.29 (d, ⁴J(C,P) = 2.3 Hz; *p*-C, PPh₂O⁻), 127.86 (d, ³J(C,P) = 10.5 Hz), 127.12 (d, ³J(C,P) = 11.3 Hz; *m*-C, PPh₂O⁻), 121.04 (dd, ³J(C_β,P_{trans}) = 30.5 Hz, ³J(C_β,P_{cis}) = 1.9 Hz, ²J(Pt,C_β) ~ 235 Hz; C_β, C_α≡C_β*t*Bu), 90.92 (ddd, ²J(C_α,P_{trans}) = 129.1 Hz, ²J(C_α,P_{cis}) = 20.6, 16.8 Hz, ¹J(Pt,C_α) ~ 980 Hz; C_α, C_α≡C_β*t*Bu), 31.01 (s; C(CH₃)₃, *t*Bu), 29.04 (CMe₃, *t*Bu), 15.43 (d, ¹J(C,P) = 31.2 Hz, ²J(Pt,C) = 27 Hz; CH₂, PEt₃), 8.18 (br, ³J(Pt,C) = 19 Hz; CH₃, PEt₃); IR: ν̄ = 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(PPh₂O)₂H]⁺; C₃₆H₄₅O₂P₃Pt (797.8): calcd C 54.20, H 5.68; found C 53.83, H 5.64.

Data for 8b: ¹H NMR (CDCl₃): δ ~ 15.0 (br; H...O...H), 7.92, 7.73, 7.35, 7.10, 6.80 (m; Ph), 1.63 (m; CH₂, PEt₃), 0.91 (dt, ³J(H,P) = 16.6 Hz, ²J(H,H) = 7.2 Hz; CH₃, PEt₃); ³¹P{¹H} NMR (CDCl₃): AMX spin system, δ = 78.36 (t, ²J(P_X,P_{Acis}) = 21.5 ~ ²J(P_X,P_{Mcis}) = 27.1 Hz, ¹J(Pt,P_X) = 2717 Hz; P_X, P_{trans} to C≡CPh), 71.52 (dd, ²J(P_M,P_{Atrans}) = 380.1 Hz, ¹J(Pt,P_M) = 2591 Hz; P_M, P_{trans} to PEt₃), 5.61 (dd, ¹J(Pt,P_A) = 1950 Hz; P_A, PEt₃); ¹³C{¹H} NMR (CDCl₃): δ = 139.78 (dd, ¹J(C,P) = 70.0 Hz, ³J(C,P) = 7.1 Hz, ²J(Pt,C) = 61.6 Hz; *i*-C, PPh₂O⁻ *trans* to C≡C*t*Bu), 139.61 (dd, ¹J(C,P) = 63.2 Hz, ³J(C,P) = 1.3 Hz, ²J(Pt,C) = 48.5 Hz; *i*-C, PPh₂O⁻ *trans* to PEt₃), 132.4 (d, ²J(C,P) = 13 Hz, ³J(Pt,C) = 13.1 Hz), 132.1 (dd, ²J(C,P) = 10.7 Hz, ⁴J(C,P) = 0.6 Hz; *o*-C, PPh₂O⁻), 130.50 (d, ²J(C,P) = 2 Hz), 130.47 (d, ²J(C,P) = 1.2 Hz), 129.47 (d, ²J(C,P) = 2.5 Hz; *p*-C, PPh₂O⁻ and *o*-C, Ph, C≡CPh), 127.96 (d, ³J(C,P) = 10.7 Hz), 127.39 (d, ³J(C,P) = 11.2 Hz; *m*-C, PPh₂O⁻), 127.46 (s; *m*-C, Ph, C≡CPh), 125.66 (s; *p*-C, Ph, C≡CPh), 112.66 (ddd, ³J(C_β,P_{trans}) = 30.8 Hz, ³J(C_β,P_{cis}) = 2.9, 1.1 Hz, ²J(Pt,C_β) = 320.7 Hz; C_β, C_α≡C_βPh), 108.4 (ddd, ²J(C_α,P_{trans}) = 129.7 Hz, ²J(C_α,P_{cis}) = 20.5, 17.0 Hz, ¹J(Pt,C_α) ~ 1010 Hz; C_α, C_α≡C_βPh), 15.57 (dt, ¹J(C,P) = 31.1 Hz, ²J(Pt,C) = 26 Hz; CH₂, PEt₃), 8.2 (t, ²⁺⁴J(C,P) = 3.8 Hz; CH₃, PEt₃); IR: ν̄ = 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(PPh₂O)₂H]⁺; C₃₈H₄₁O₂P₃Pt (817.8): calcd C 55.81, H 5.05; found C 55.88, H 4.84.

Data for 9a: ¹H NMR (CDCl₃): δ = 7.99, 7.52, 7.29, (Ph), 5.38 (ddd, ¹J(H,P) = 364.9 Hz, ³J(H,P_{trans}) = 14.4 Hz, ³J(H,P_{cis}) = 7.3 Hz; PPh₂H), 0.73 (s; *t*Bu); ³¹P{¹H} NMR (CDCl₃): AMX spin system, δ = 76.86 (t, ²J(P_X,P_{Mcis}) ~ 25.5 Hz, ²J(P_X,P_{Acis}) = 21.9 Hz, ¹J(Pt,P_X) = 2521 Hz; P_X, P_{trans} to C≡C*t*Bu), 69.39 (dd, ²J(P_M,P_{Atrans}) = 404.7 Hz, ¹J(Pt,P_M) = 2887 Hz; P_M, P_{trans} to PPh₂H), -3.67 (dd, ¹J(Pt,P_A) = 1982 Hz; P_A, PPh₂H); ¹³C{¹H} NMR (CDCl₃): δ = 138.82 (dd, ¹J(C,P) = 70.5 Hz, ³J(C,P) = 7.4 Hz, ²J(Pt,C) ~ 65 Hz; *i*-C, PPh₂O⁻ *trans* to C≡C*t*Bu), 137.81 (dd, ¹J(C,P) = 66.2 Hz, ³J(C,P) = 1.8 Hz, ²J(Pt,C) = 42 Hz; *i*-C, PPh₂O⁻ *trans* to PPh₂H), 134.00 (d, ²J(C,P) = 9.2 Hz), 132.24 (d, ²J(C,P) = 11.5 Hz), 132.02 (d, ²J(C,P) = 12.5 Hz; *o*-C), 130.62, 130.54, 129.8 (*p*-C), 128.12 (d, ³J(C,P) = 10.6 Hz),

127.31 (d, ³J(C,P) = 11.3 Hz; *m*-C), C_β not observed, 87.27 (ddd, ²J(C_α,P_{trans}) = 124.3 Hz, ²J(C_α,P_{cis}) = 21.16 Hz; C_α, C_α≡C_β*t*Bu), 30.81 (s; C(CH₃)₃), 28.96 (s; CMe₃); IR: ν̄ = 2357 (m; P-H), 1029 (s), 1011(vs), 997 cm⁻¹ (sh; P-O); ES-MS (+): *m/z* (%): 866 (100) [M+H]⁺; C₄₂H₄₁O₂P₃Pt (865.8): calcd C 58.27, H 4.77; found C 58.17, H 4.85.

Data for 9b: ¹H NMR (CDCl₃): δ = 7.96, 7.56, 7.47, 7.28, 7.03, 6.62 (Ph), 5.44 (ddd, ¹J(H,P) = 368.2 Hz, ³J(H,P_{trans}) = 13.8 Hz, ³J(H,P_{cis}) = 6.5 Hz, ²J(Pt,H) ~ 50 Hz; PPh₂H); ³¹P{¹H} NMR (CDCl₃): AMX spin system, δ = 75.68 (t, ²J(P_X,P_{Mcis}) = 24.7 Hz ~ ²J(P_X,P_{Acis}) = 21.9 Hz, ¹J(Pt,P_X) = 2536 Hz; P_X, P_{trans} to C≡CPh), 69.19 (dd, ²J(P_M,P_{Atrans}) = 394.5 Hz, ¹J(Pt,P_M) = 2843 Hz; P_M, P_{trans} to PPh₂H), -2.92 (dd, ¹J(Pt,P_A) = 1960 Hz; P_A, PPh₂H); ¹³C{¹H} NMR (CDCl₃): δ = 138.8 (m; overlapping of *i*-C, PPh₂O⁻, PPh₂H), 134.18 (d, ²J(C,P) = 10.1 Hz), 132.23 (d, ²J(C,P) = 8.2 Hz), 132.07 (d, ²J(C,P) = 8.8 Hz; *o*-C, PPh₂O⁻, PPh₂H), 130.84, 129.94 (*p*-C, PPh₂O⁻), 130.57 (s; *o*-C, Ph, C≡CPh), 128.47 (d, ³J(C,P) = 11.8 Hz), 128.09 (d, ³J(C,P) = 10.8 Hz), 127.59 (d, ³J(C,P) = 11.3 Hz; *m*-C, PPh₂O⁻, PPh₂H), 127.57 (s; *m*-C, Ph, C≡CPh), 126.42 (*i*-C, Ph, C≡CPh), 125.68 (s; Ph, C≡CPh), 117.07 (d, ³J(C_β,P_{trans}) = 32 Hz; C_β, C_α≡C_βPh), ~ 105.4 (poorly resolved signal as dm, ²J(C_α,P_{trans}) ~ 120 Hz; C_α); IR: ν̄ = 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]⁺; C₄₄H₃₇O₂P₃Pt (885.8): calcd C 59.66, H 4.21; found C 59.38, H 4.14.

Data for 10a: ¹H NMR (CDCl₃): 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); ³¹P{¹H} NMR (CDCl₃): δ = 70.93 (d, ²J(P_X,P_M) = 25.4 Hz, ¹J(Pt,P) = 2474 Hz; P_{trans} to C≡C*t*Bu), 60.95 (d, ¹J(Pt,P) = 3071 Hz; P_{trans} to CN*t*Bu); ¹³C{¹H} NMR (CDCl₃): signal due to CN⁻ not observed, δ = 140.44 (d, ¹J(C,P) = 66.1 Hz, ²J(Pt,C) = 41.8 Hz; *i*-C, PPh₂O⁻ *trans* to C≡C*t*Bu), 138.5 (d, ¹J(C,P) = 75.2 Hz, ²J(Pt,C) = 64.4 Hz; *i*-C, PPh₂O⁻ *trans* to CN*t*Bu), 132.31 (d, ²J(C,P) = 11.5 Hz), ³J(Pt,C) = 16.4 Hz), 131.64 (d, ²J(C,P) = 12.5 Hz, ³J(Pt,C) = 13.9 Hz (*o*-C, PPh₂O⁻), 130.32 (d, ⁴J(C,P) = 2.04 Hz), 129.00 (d, ⁴J(C,P) = 2.49 Hz; *p*-C, PPh₂O⁻), 127.90 (d, ³J(C,P) = 10.9 Hz), 127.54 (d, ³J(C,P) = 11.6 Hz; *m*-C, PPh₂O⁻), 121.83 (d, ³J(C_β,P_{trans}) = 29.7 Hz; C_β, C_α≡C_β*t*Bu), 55.38 (dd, ²J(C_α,P_{trans}) = 127.9 Hz, ²J(C_α,P_{cis}) = 16.7 Hz; C_α, C_α≡C_β*t*Bu), 88.04 (s; CMe₃, CN*t*Bu), 31.7 (s; C(CH₃)₃, C≡C*t*Bu), 29.29 (s; C(CH₃)₃, CN*t*Bu), 28.99 (s; CMe₃, C≡C*t*Bu); IR: ν̄ = 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]⁺; C₃₅H₃₀NO₂P₂Pt (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: ¹H NMR (CDCl₃): δ = 7.92, 7.66, 7.37, 7.12, 6.98 (m; Ph), 1.23 (s; *t*Bu, CN*t*Bu); ³¹P{¹H} NMR (CDCl₃): δ = 69.85 (d, ²J(P_X,P_{Mcis}) = 24.8 Hz, ¹J(Pt,P) = 2491.5 Hz; P_{trans} to C≡CPh), 61.1 (d, ¹J(Pt,P) = 3045 Hz; P_{trans} to CN*t*Bu); ¹³C{¹H} NMR (CDCl₃): CN⁻ not observed, δ = 139.97 (d, ¹J(C,P) = 67 Hz, ²J(Pt,C) = 42 Hz; *i*-C, PPh₂O⁻ *trans* to C≡CPh), 138.26 (d, ¹J(C,P) = 75.9 Hz, ²J(Pt,C) = 62.6 Hz; *i*-C, PPh₂O⁻ *trans* to CN*t*Bu), 132.19 (d, ²J(C,P) = 11.7 Hz, ³J(Pt,C) = 16.3 Hz), 131.35 (d, ²J(C,P) = 12.5 Hz, ³J(Pt,C) = 13.0 Hz; *o*-C, Ph, PPh₂), 131.07 (s; *o*-C, PPh₂O⁻, C≡CPh), 130.49 (d, ⁴J(C,P) = 1.9 Hz), 130.18 (d, ⁴J(C,P) = 2.26 Hz; *p*-C, Ph, PPh₂O⁻), 128.01 (d, ³J(C,P) = 11 Hz), 127.70 (d, ³J(C,P) = 11.6 Hz; *m*-C, Ph, PPh₂O⁻), 127.67 (s; *m*-C, C≡CPh), 126.72 (d, ⁴J(C,P) ~ 2.34, ³J(Pt,C) ~ 23 Hz; *i*-C, Ph, C≡CPh), 125.97 (s; *p*-C, Ph, C≡CPh), 112.43 (d, ³J(C_β,P_{trans}) = 30.6 Hz, ²J(Pt,C_β) = 260 Hz; C_β, C_α≡C_βPh), 102.6 (dd, ²J(C_α,P_{trans}) = 128.5 Hz, ²J(C_α,P_{cis}) = 16.6 Hz; C_α, C_α≡C_βPh), 58.34 (s; CMe₃, CN*t*Bu), 29.27 (s; C(CH₃)₃, CN*t*Bu); IR: ν̄ = 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(PPh₂O)₂H]⁺, 396 (65) [Pt(PPh₂O)]⁺; C₃₇H₃₅NO₂P₂Pt (782.7): calcd N 1.79, C 56.78, H 4.51; found N 1.82, C 56.18, H 4.54.

Preparation of (NBu₄)[Pt(C≡CR)(CN){(PPh₂O)₂H}] (R = *t*Bu **11a, R = Ph, **11b**):** (NBu₄)CN (0.063 g, 0.227 mmol) was added to a suspension of **7a** (0.200 g, 0.227 mmol) in CH₂Cl₂ (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 (NBu₄)CN (0.078 g, 0.277 mmol), yield 76%.

Data for 11a: ¹H NMR (CDCl₃): δ = 17.2 (br; O...H...O), 7.97, 7.88, 7.26, (m; Ph), 2.92 (m; N-CH₂, NBu₄), 1.26 (m; CH₂, NBu₄), 1.44 (m; CH₂), 0.90 (s; *t*Bu), 0.80 (t; -CH₃, NBu₄); ³¹P{¹H} NMR (CDCl₃): δ = 70.88 (d,

$^2J(\text{P},\text{P}_{\text{cis}}) = 24.7$ Hz, $^1J(\text{Pt},\text{P}) = 2506$ Hz; P_{trans} to $\text{C}\equiv\text{CrBu}$, 66.11 (d, $^1J(\text{Pt},\text{P}) = 2844.2$ Hz; P_{trans} to CN); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 141.7$ (d, $^1J(\text{C},\text{P}) = 62.5$ Hz, $^2J(\text{Pt},\text{C}) = 45$ Hz), 140.7 (d, $^1J(\text{C},\text{P}) = 68.2$ Hz, $^2J(\text{Pt},\text{C}) \sim 57$ Hz; *i*-C, PPh_2O^-), 132.36 (d, $^2J(\text{C},\text{P}) = 11.5$ Hz), 131.78 [d, $^2J(\text{C},\text{P}) = 12$ Hz; *o*-C, PPh_2O^-), 128.95 (s; *p*-C, PPh_2O^-), 127.07 (d, $^3J(\text{C},\text{P}) = 10.6$ Hz), 126.76 (d, $^3J(\text{C},\text{P}) = 10.9$ Hz; *m*-C, PPh_2O^-), 118.67 (dd, $^3J(\text{C}_{\beta},\text{P}_{\text{trans}}) = 32.3$ Hz, $^3J(\text{C}_{\beta},\text{P}_{\text{cis}}) = 1.7$ Hz, $^2J(\text{Pt},\text{C}_{\beta}) = 269$ Hz; C_{β} , $\text{C}_{\alpha}\equiv\text{C}_{\beta}\text{tBu}$), 89.5 (dd, $^2J(\text{C}_{\alpha},\text{P}_{\text{trans}}) = 139.6$ Hz, $^2J(\text{C}_{\alpha},\text{P}_{\text{cis}}) = 16.9$ Hz, $^1J(\text{Pt},\text{C}_{\alpha}) \sim 1000$ Hz; C_{α} , $\text{C}_{\alpha}\equiv\text{C}_{\beta}\text{tBu}$), 57.72 (N-CH₂, *n*Bu), 31.6 (C(CH₃)₃, *t*Bu), 23.39 (-CH₂, *n*Bu), 19.15 (CH₂, *n*Bu), 28.6 (m; CMe_3 , *t*Bu), 13.39 (CH₃, *n*Bu); IR (KBr): $\tilde{\nu} = 2127$ (s; $\text{C}\equiv\text{C}$ or $\text{C}\equiv\text{N}$), 1029.5 (s), 993 cm^{-1} (s; $\text{P}-\text{O}$); ES-MS (-): *m/z* (%): 705 (100) $[\text{Pt}(\text{C}\equiv\text{CrBu})(\text{CN})\{\text{PPh}_2\text{O}\}_2\text{H}]^- = [\text{M}]^-$, 623 (13) $[\text{M} - (\text{C}\equiv\text{CrBu})]^-$; $\text{C}_{47}\text{H}_{66}\text{N}_2\text{O}_2\text{P}_2\text{Pt}$ (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: ^1H NMR (CDCl_3): $\delta = 17.28$ (br; $\text{O}\cdots\text{H}\cdots\text{O}$), 7.91, 7.27, 7.06, 6.94 (m; Ph), 2.94 (m; N-CH₂, *n*Bu₄), 1.23 (m; CH₂, *n*Bu₄), 1.12 (m; CH₂), 0.78 (m; -CH₃, *n*Bu₄); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 70.20$ (d, $^2J(\text{P},\text{P}_{\text{cis}}) = 24.43$ Hz, $^1J(\text{Pt},\text{P}) = 2540$ Hz; P_{trans} to $\text{C}\equiv\text{CPh}$), 64.81 (d, $^1J(\text{Pt},\text{P}) = 2816$ Hz; P_{trans} to CN); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 141.36$ (d, $^1J(\text{C},\text{P}) = 64.08$ Hz), 140.86 (d, $^1J(\text{C},\text{P}) = 68.6$ Hz; *i*-C, PPh_2O^-), 132.2 (d, $^2J(\text{C},\text{P}) = 11.5$ Hz), 131.9 (d, $^2J(\text{C},\text{P}) = 12$ Hz; *o*-C, PPh_2O^-), 130.6 (s; *o*-C, Ph, $\text{C}\equiv\text{CPh}$), 129.31 (d), 129.2 (d, $^4J(\text{C},\text{P}) = 1.9$ Hz, *p*-C, PPh_2O^-), 127.5 (d, $^3J(\text{C},\text{P}) = 17$ Hz), 127.15 (d, $^3J(\text{C},\text{P}) = 16.6$ Hz; *m*-C, PPh_2O^-), 127.16 (s; *m*-C, Ph, $\text{C}\equiv\text{CPh}$), 125.08 (s; *p*-C, Ph, $\text{C}\equiv\text{CPh}$), 110.6 (dd, $^3J(\text{C}_{\beta},\text{P}_{\text{trans}}) = 33$ Hz, $^3J(\text{C}_{\beta},\text{P}_{\text{cis}}) = 1.4$ Hz; C_{β} , $\text{C}_{\alpha}\equiv\text{C}_{\beta}\text{Ph}$), 109.28 (dd, $^2J(\text{C}_{\alpha},\text{P}_{\text{trans}}) = 139.6$ Hz, $^2J(\text{C}_{\alpha},\text{P}_{\text{cis}}) = 16.7$ Hz; C_{α} , $\text{C}_{\alpha}\equiv\text{C}_{\beta}\text{Ph}$), 57.9 (N-CH₂, *n*Bu), 23.4 (-CH₂, *n*Bu), 19.3 (CH₂, *n*Bu), 13.50 (CH₃, *n*Bu); IR (KBr): $\tilde{\nu} = 2127$ (m), 2109 (s; $\text{C}\equiv\text{C}$, $\text{C}\equiv\text{N}$), 1028.5 (s), 1006 (vs), 993 cm^{-1} (vs; $\text{P}-\text{O}$); ES-MS (-): *m/z* (%): 725 (100) $[\text{M}]^-$; $\text{C}_{49}\text{H}_{62}\text{N}_2\text{O}_2\text{P}_2\text{Pt}$ (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 $[\text{Pt}(\text{C}\equiv\text{CR})(\text{PPh}_2\text{O})_3\text{Li}_2(\text{thf})(\text{H}_2\text{O})_2]$ (R = *t*Bu 3a; R = Ph 3b): LiOH · H₂O (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).

$[\text{Pt}(\text{C}\equiv\text{CPh})(\text{PPh}_2\text{O})_3\text{Li}_2(\text{thf})(\text{H}_2\text{O})_2]$ (**3b**): ^1H NMR (CDCl_3): $\delta = 7.96$, 7.52, 7.21, 6.88, 6.69, 6.41 (m; Ph); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 73.20$ (d, $^1J(\text{Pt},\text{P}) = 2679$ Hz, 2P), 58.8 (t, $^1J(\text{Pt},\text{P}) = 2704$ Hz, $^2J(\text{P},\text{P}_{\text{cis}}) = 29.02$ Hz, 1P); $^7\text{Li}\{^1\text{H}\}$ NMR (CDCl_3): at 20 °C, $\delta = -0.89$ (s); at 0 °C, $\delta = -0.1$ (brs), -1.8 (brs); at -20 °C, $\delta = -0.23$ (brs), -1.96 (s); IR: $\tilde{\nu} = 3615$ (br), 3362 (br; OH), 2109 (m; $\text{C}\equiv\text{C}$), 1037 (s), 1025 (m), 998 cm^{-1} (w; $\text{P}-\text{O}$); MS: *m/z* (%): 1826 (10) $[\text{Pt}_2(\text{C}\equiv\text{CPh})_2(\text{PPh}_2\text{O})_6\text{Li}_4]^+$, 1726 (5) $[\text{Pt}_2(\text{C}\equiv\text{CPh})(\text{PPh}_2\text{O})_6\text{Li}_4]^+$, 907 (40) $[\text{Pt}(\text{C}\equiv\text{CPh})(\text{PPh}_2\text{O})_3\text{Li}]^+$, 806 (10) $[\text{Pt}(\text{PPh}_2\text{O})_3\text{Li}]^+$, 604 (58) $[\text{Pt}(\text{PPh}_2\text{O})_2\text{Li}]^+$, 401 (35) $[\text{Pt}(\text{PPh}_2\text{O})\text{Li} - 2\text{H}]^+$; $\text{C}_{96}\text{H}_{90}\text{Li}_4\text{O}_{10}\text{P}_6\text{Pt}_2$ (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 Et₂O 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 Et₂O, 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 $[\text{Pt}(\text{C}\equiv\text{CrBu})(\text{PPh}_2\text{O})_3\text{Li}_2(\text{thf})(\text{H}_2\text{O})_2] \cdot 1.75 \text{Et}_2\text{O}$ (**3a** · 1.75 Et₂O), $[\text{Pt}(\text{C}\equiv\text{CPh})_2\{\text{Ph}_2\text{P}(\text{CHPh})(\text{CH}_2)\text{PPh}_2\}]$ (**4b**), and $[\text{Pt}_2(\mu\text{-PPh}_2)_2(\text{C}\equiv\text{CrBu})_2(\text{PPh}_2\text{H}_2)]$ (**6a**).

	3a · 1.75 Et ₂ O	4b	6a
formula	$\text{C}_{92}\text{H}_{98}\text{Li}_4\text{O}_{10}\text{P}_6\text{Pt}_2 \cdot 1.75 \text{Et}_2\text{O}$	$\text{C}_{48}\text{H}_{38}\text{P}_2\text{Pt}$	$\text{C}_{60}\text{H}_{60}\text{P}_4\text{Pt}_2$
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	$P\bar{1}$	$R\bar{3}$	$P\bar{1}$
<i>a</i> [Å]	16.1646(13)	40.727(6)	9.122(2)
<i>b</i> [Å]	17.1032(10)	40.727(6)	12.419(3)
<i>c</i> [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)
<i>V</i> [Å ³]	5076.2(6)	18133(4)	1275.7(5)
<i>Z</i>	2	18	1
M_{R}	2097.17	871.81	1295.14
ρ_{calcd} [g cm ⁻³]	1.372	1.437	1.686
μ (MoK α) [mm ⁻¹]	2.902	3.593	5.641
λ [Å]		MoK α , graphite monochromated, 0.71073	
<i>T</i> [K]	150(1)	293(2)	150(1)
$2\theta_{\text{max}}$ [°]	50	50	50
scan method	ω/θ	ω	ω
<i>hkl</i> 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 [<i>R</i> (int) = 0.0565]	7082 [<i>R</i> (int) = 0.0516]	4484 [<i>R</i> (int) = 0.0225]
observed reflections [<i>I</i> > 2 σ (<i>I</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
<i>R</i> (observed reflections only)	0.0576	0.0608	0.0203
<i>wR</i> 2 (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
($w = [\sigma^2(F_o^2) + (\text{AP})^2 + \text{BP}]^{-1}$)			
A, B	0.0723, 7.43	0.0655, 48.61	0.0317, 0
P		$[\text{max}\{F_o^2, 0\} + 2F_c^2]/3$	

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 appropriate. 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 anisotropic 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 CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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