

Article

A Hydrido η^1 -Alkynyl Diplatinum Complex Obtained from a Phosphinito Phosphanido Complex and Trimethylsilylacetylene

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External Editor: Axel Klein

Received: 11 September 2014; in revised form: 13 October 2014 / Accepted: 14 October 2014 /

Published: 31 October 2014

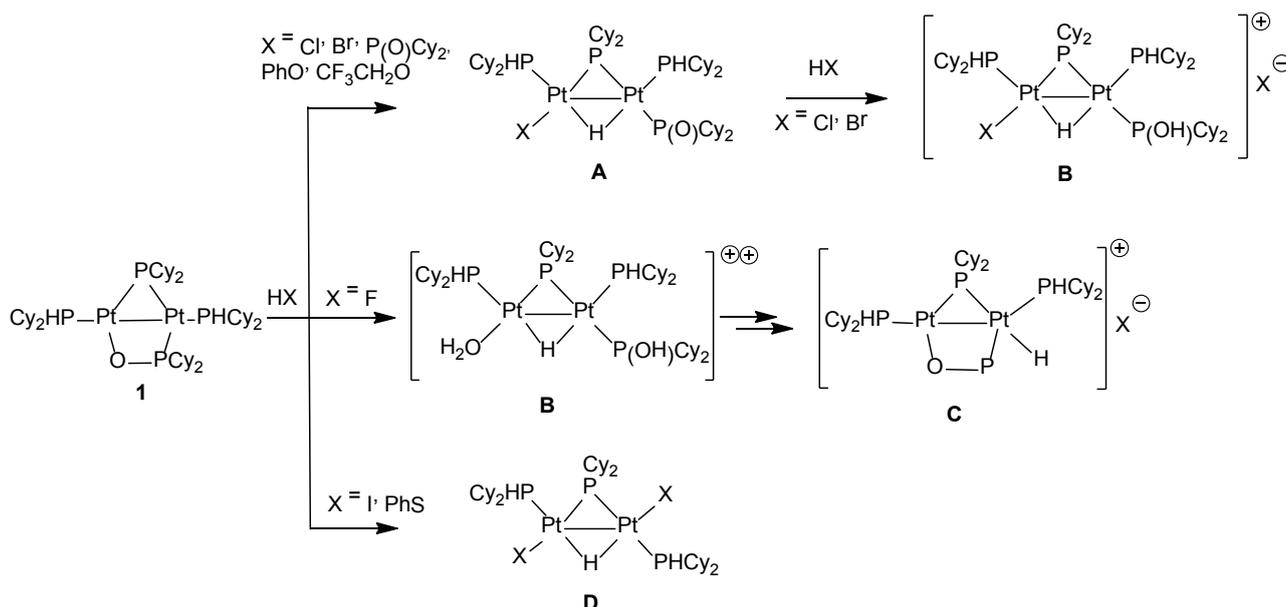
Abstract: The reaction of (trimethylsilyl)acetylene with the phosphinito phosphanido Pt(I) complex $[(\text{PHCy}_2)\text{Pt}(\mu\text{-PCy}_2)\{\kappa^2\text{P},\text{O}-\mu\text{-P}(\text{O})\text{Cy}_2\}\text{Pt}(\text{PHCy}_2)](\text{Pt-Pt})$ (**1**) results in the protonation of the Pt-Pt bond with the formation of the bridging hydride complex $[(\text{PHCy}_2)(\text{Me}_3\text{SiC}\equiv\text{C})\text{Pt}(\mu\text{-PCy}_2)(\mu\text{-H})\text{Pt}(\text{PHCy}_2)\{\kappa\text{P-P}(\text{O})\text{Cy}_2\}](\text{Pt-Pt})$ (**2**), which was characterized by spectroscopic, spectrometric and XRD analyses. Complex **2** exhibits in the solid state at 77 K a long-lived, weak, orange emission assigned as metal-metal to ligand charge transfer (MMLCT) (L = alkynyl) due to the presence of a very short Pt...Pt distance [2.8209(2) Å]. Reaction of **2** with etherate HBF_4 results in the selective protonation of the phosphinito ligand to afford the species $[(\text{PHCy}_2)(\text{Me}_3\text{SiC}\equiv\text{C})\text{Pt}(\mu\text{-PCy}_2)(\mu\text{-H})\text{Pt}(\text{PHCy}_2)\{\kappa\text{P-P}(\text{OH})\text{Cy}_2\}](\text{Pt-Pt})[\text{BF}_4]$ (**3**) $[\text{BF}_4]$.

Keywords: acetylide complexes; phosphinito complexes; bridging hydrides; C-H activation

1. Introduction

It is now well established that the mixed bridge phosphinito-phosphanido Pt(I) complex $[(\text{PHCy}_2)\text{Pt}^1(\mu\text{-PCy}_2)\{\kappa P, O\text{-}\mu\text{-P(O)Cy}_2\}\text{Pt}^2(\text{PHCy}_2)](\text{Pt-Pt})$ (**1**) [1] exhibits an amphiphilic behavior, in that it reacts with both nucleophiles (with initial attack at the Pt^1 center) [2] and electrophiles (with initial attack at the O atom) [3,4]. In particular, reaction of **1** with HX Brønsted acids affords, with the exception of HF, [4] dinuclear compounds endowed with a bridging hydride, a bridging dicyclohexylphosphanide and a covalent bond between Pt^1 and the X residue (Scheme 1).

Scheme 1. Reactivity of Complex **1** with Brønsted acids.



In the framework of platinum chemistry, the interaction of terminal alkynes with mono- or binuclear complexes has been an intense area of research in connection with their involvement in many insertion, coupling and polymerizations reactions [5–10]. On the other hand, platinum alkynyl complexes have been attracting widespread interest for several years, mainly due to their structural variety, remarkable reactivity and photophysical properties [11–18].

Therefore, we decided to explore the reactivity of the Pt(I) Complex **1** with substituted acetylenes possessing the $\text{C}\equiv\text{C-H}$ moiety able to protonate the diplatinum complex and to form new Pt-C bonds. In this paper, we describe for the first time the reaction between a platinum(I) complex and alkynes, which led to the synthesis of the acetylide complex $[(\text{PHCy}_2)(\text{Me}_3\text{Si-C}\equiv\text{C})\text{Pt}(\mu\text{-PCy}_2)\{\kappa P\text{-P(O)Cy}_2\}]\text{Pt}(\text{PHCy}_2)](\text{Pt-Pt})$ (**2**).

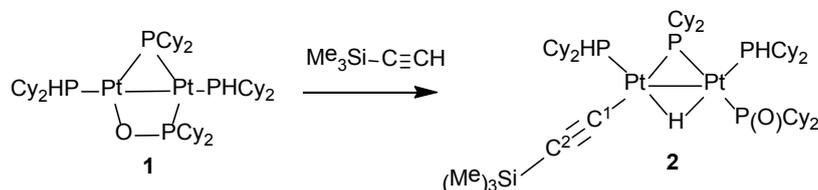
2. Results and Discussion

2.1. Synthesis and Spectroscopic Features of the Hydride/Acetylide Complex **2**

The Pt(I) Complex **1** transformed quantitatively into the bridging hydride complex $[(\text{PHCy}_2)(\eta^1\text{-Me}_3\text{SiC}\equiv\text{C})\text{Pt}(\mu\text{-PCy}_2)(\mu\text{-H})\text{Pt}(\text{PHCy}_2)\{\kappa P\text{-P(O)Cy}_2\}]\text{Pt}(\text{PHCy}_2)](\text{Pt-Pt})$ (**2**) by reaction in *n*-hexane with an equimolar quantity of (trimethylsilyl)acetylene (Scheme 2). This reactivity is similar to that observed

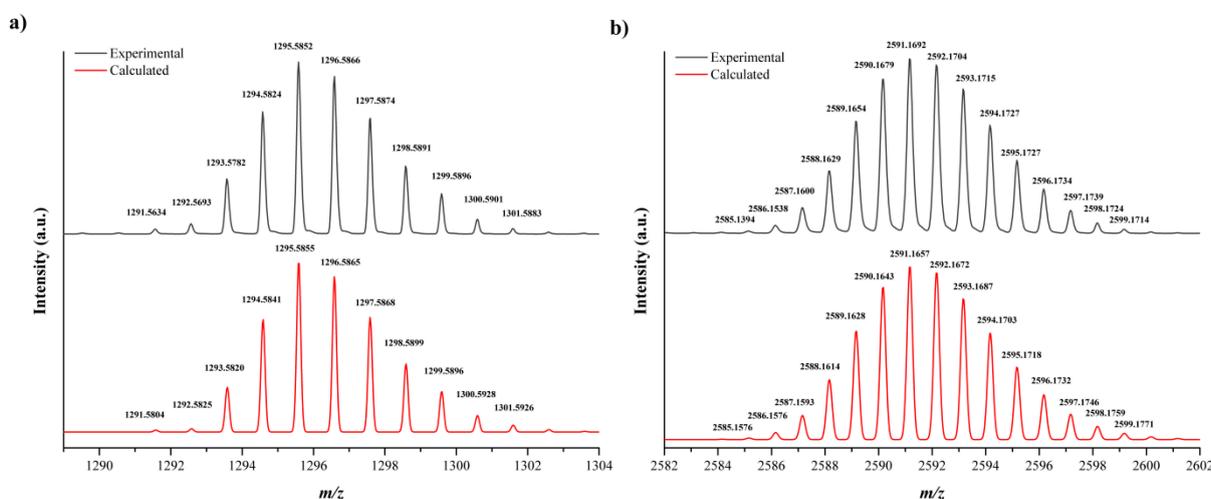
with phenol, trifluoroethanol or dicyclohexylphosphane, [2] and the product is analogous to that obtained in the first stage of reaction of **1** with HCl or HBr (Scheme 1). [3] However, differently from the analogous chlorido or bromido complexes $[(\text{PHCy}_2)(\text{X})\text{Pt}(\mu\text{-PCy}_2)(\mu\text{-H})\text{Pt}(\text{PHCy}_2)\{\kappa\text{P-P}(\text{O})\text{Cy}_2\}](\text{Pt-Pt})$ ($\text{X} = \text{Cl}, \text{Br}$), treatment of **2** with NaOH in dichloromethane did not restore the parent Complex **1**.

Scheme 2. Reactivity of **1** with (trimethylsilyl)acetylene.



Complex **2** is a pale yellow solid soluble in alkanes, aromatic solvents and tetrahydrofuran, which gave, from the HR ESI-MS analysis, an intense peak at m/z 1295.5852 (Figure 1) corresponding to the cation obtained by protonation of **2**, plus a peak at 2591.1691 ascribable to a protonated dimer (exact mass = 2591.1657 Da) [19] formed in the ionization chamber, presumably featuring a hydrogen ion linking two neutral molecules of **2** through the P=O moieties. The MS/MS spectrogram of the peak at m/z 2591.1691 showed only two peaks at 1197.5257 and 1295.5765 ascribable to $[\mathbf{1} + \text{H}]^+$ (exact mass = 1197.5303) and to $[\mathbf{2} + \text{H}]^+$ (exact mass = 1295.5855), respectively. On the other hand, the MS/MS spectrogram of the peak at m/z 1295.5852 showed an intense peak at m/z 1197.5210 due to the loss of (trimethylsilyl)acetylene from **2**, plus a weak peak at 981.3602, due to the contemporary loss of (trimethylsilyl)acetylene and $\text{PH}(\text{O})\text{Cy}_2$ from **2**.

Figure 1. HR ESI-MS spectrograms of **2** showing the peaks due to $[\mathbf{2} + \text{H}]^+$ (A) and $[\mathbf{2} \cdot \mathbf{2} + \text{H}]^+$ (B). The errors between simulated and observed isotopic patterns are 0.7 ppm for $[\mathbf{2} + \text{H}]^+$ and -1.0 ppm for $[\mathbf{2} \cdot \mathbf{2} + \text{H}]^+$.



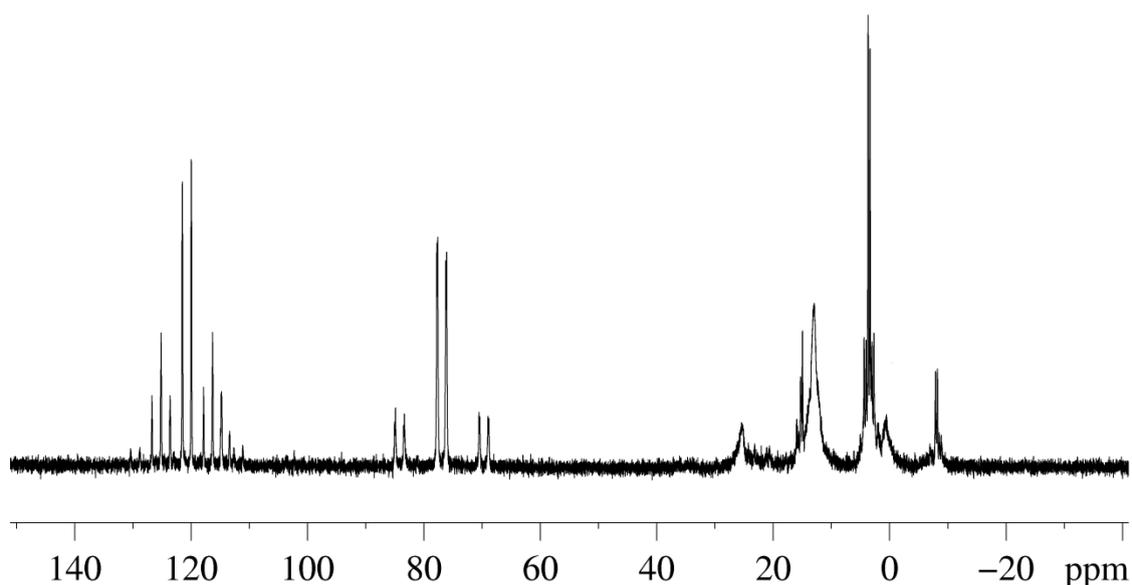
The molecular structure of Complex **2** was deduced from IR, NMR and XRD analyses.

In the IR spectrum (KBr disk), Complex **2** showed, beside the bands of P–H and Pt–H–Pt stretchings at 2329 and 1632 cm^{-1} , respectively, a very strong band at 2042 cm^{-1} attributable to a $\text{C}\equiv\text{C}$ stretching of the (trimethylsilyl)acetylide. This value is in the range commonly observed for platinum

complexes featuring $\eta^1\text{-C}\equiv\text{CSiMe}_3$ (e.g., *trans*-Pt(C \equiv CSiMe₃)₂(PPh₃)₂) 2041 cm⁻¹ [20]; (NBu₄)₂[Pt(C \equiv CSiMe₃)₄] 2015 cm⁻¹) [21]. In fact, the blue-shift of 4 cm⁻¹ observed for the C \equiv C stretching on passing from free Me₃SiC \equiv C-H (ν = 2038 cm⁻¹ in *n*-hexane) to **2** indicates that the C \equiv C bond order in the coordinated acetylide and in the free (trimethylsilyl)acetylene is nearly the same, thus ruling out a possible η^2 -coordination of the C \equiv C triple bond to Pt.

The position and the multiplicity of the ³¹P, ¹H and ¹⁹⁵Pt NMR spectral features are similar to those reported for the analogous compounds having Cl, Br, CF₃CH₂O or PhO in place of SiMe₃-C \equiv C and support the structure in which the (trimethylsilyl)acetylide is η^1 -bonded to Pt¹ and the P(O)Cy₂ ligand is κ -P-bonded to Pt². For Complex **2**, the ³¹P{¹H} NMR spectrum showed four mutually-coupled signals at δ 120.9, δ 77.0, δ 13.7 and δ 2.8 (Figure 2). The signal at δ 120.9 is ascribable to a bridging phosphanide subtending a Pt-Pt bond [22], while the signal at δ 77.0 is diagnostic of a dicyclohexylphosphinite P(O)Cy₂ ligand bonded to Pt through the P atom. In fact, Pt-P(O)Cy₂ ³¹P NMR resonances fall in the range of 75–90 ppm, while their protonated analogues Pt-P(OH)Cy₂ give ³¹P NMR signals in the range of 115–135 ppm [3,4,23]. The remaining signals (δ 13.7 and δ 2.8) are ascribed to terminal PHCy₂ ligands. As a consequence of a higher trans influence of the Me₃SiC \equiv C⁻ ligand compared to halogens or alkoxides [24], the value of the Pt¹- μ P¹ direct coupling constant is significantly lower for **2** (¹J_{Pt,P} = 1,680 Hz) than for analogous complexes having chlorine (¹J_{Pt,P} = 2,484 Hz), bromine (¹J_{Pt,P} = 2,465 Hz) or trifluoroethoxide (¹J_{Pt,P} = 2,520 Hz)³ in place of trimethylsilylacetylide.

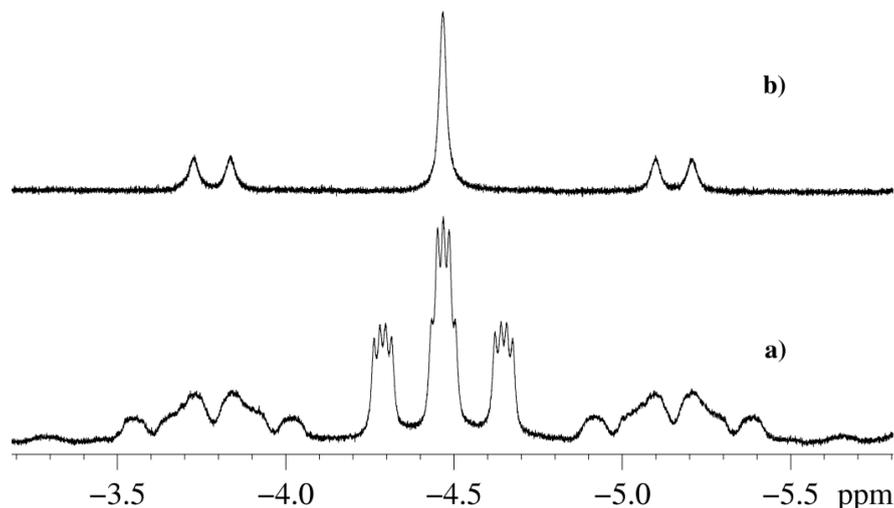
Figure 2. ³¹P{¹H} NMR spectrum of **2** (C₆D₆, 298 K).



In the ¹H NMR spectrum of **2**, the presence of a bridging hydride is attested by a multiplet centered at δ -4.46 flanked by two sets of ¹⁹⁵Pt satellites (Figure 3a). The multiplicity of the central signal is due only to ¹H-³¹P couplings, as indicated by the ¹H{³¹P} spectrum shown in Figure 3b.

The ¹⁹⁵Pt resonances (δ -5,582 and δ -5,562) were attributed to Pt¹ and Pt², respectively, by combined analysis of the ¹⁹⁵Pt{¹H} NMR, ³¹P{¹H} NMR and ¹H-¹⁹⁵Pt HMQC spectra.

Figure 3. Portion of the ^1H (a) and $^1\text{H}\{^{31}\text{P}\}$ (b) spectra of **2** showing the hydride signal (C_6D_6 , 298 K).



The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum in *n*-hexane showed, beside the cyclohexyl signals, a sharp singlet at δ 1.5 attributable to SiMe_3 and two low-field signals flanked by ^{195}Pt satellites at δ 129.9 (doublet of doublets) and at δ 116.6 (doublet) attributable to the quaternary carbons C^1 and C^2 (Scheme 2). The chemical shift and the multiplicity of these signals confirm the σ -coordination of the (trimethylsilyl)acetylide to Pt. In fact, C^1 showed coupling constants $J_{\text{C,P}}$ of 82 Hz (coupling with the bridging phosphanide) and 19 Hz (coupling with one of the PHCy_2), while C^2 showed only a coupling constant $J_{\text{C,P}}$ of 16 Hz, due to the coupling with the bridging phosphanide. Accordingly, the ^{13}C - ^{195}Pt coupling constants are $J_{\text{C,Pt}} = 1011$ Hz for C^1 and $J_{\text{C,Pt}} = 253$ Hz for C^2 , which are comparable to those obtained for platinum complexes featuring terminal bonded alkynyl ligands (e.g., data for $(\text{NBu}_4)_2[\text{PtC}\equiv\text{CSiMe}_3]_4$ δC_α 140.4, $^1J_{\text{Pt-C}\alpha} = 924$ Hz; δC_β 104.4, $^2J_{\text{Pt-C}\beta} = 250.4$ Hz [25]).

2.2. X-ray Structure of **2**

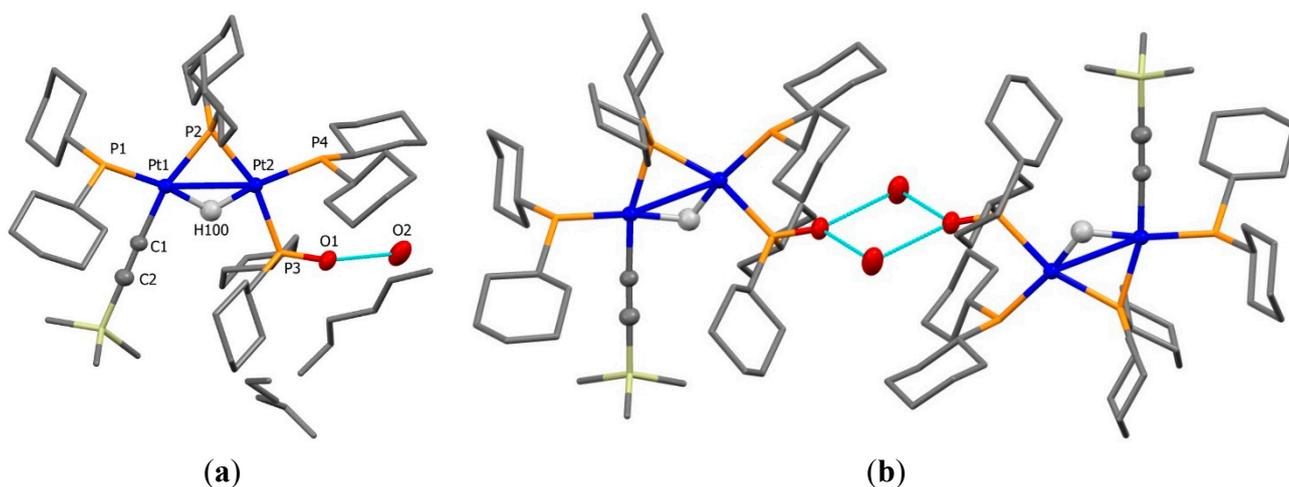
Crystals suitable for XRD analysis were obtained from a saturated solution of **2** in *n*-hexane. Not unexpectedly, due to the presence of phosphinito ligands, Complex **2** incorporates a water molecule and crystallizes as $2 \cdot 2$ *n*-hexane \cdot H_2O . The molecular structure is shown in Figure 4. Selected bond parameters (angles and lengths) and crystallographic data are summarized in Tables 1 and 2. As is shown in Figure 4b, each water molecule is simultaneously hydrogen bonded to two phosphinito ligands of two neighboring diplatinum complexes, giving rise to a dimer generated at equivalent positions ($-x, -y, -z$). A similar feature has been observed in the mononuclear phosphinito complex *trans*- $[\text{Pt}(\text{Cl})(\text{PHCy}_2)_2 \{\kappa\text{P-P}(\text{O})\text{Cy}_2\}]$ [25] and in the dinuclear species $[(\text{PHCy}_2)\{\kappa\text{P-P}(\text{O})\text{Cy}_2\} \text{Pt}(\mu\text{-PCy}_2)(\mu\text{-H})\text{Pt}(\text{PHCy}_2)\{\kappa\text{P-P}(\text{O})\text{Cy}_2\}](\text{Pt-Pt})^2$. The $\text{O1}\cdots\text{O2}$, $\text{O1}\cdots\text{O2}'$ distances of 2.726(5) and 2.775(6) Å found for $2 \cdot 2$ *n*-hexane \cdot H_2O lie in the range of other hydrated systems [26,27]. The central dimetallic core $\text{Pt}(\mu\text{-PCy}_2)(\mu\text{-H})\text{Pt}$ of $2 \cdot 2$ *n*-hexane \cdot H_2O is rather similar to that of $[(\text{PHCy}_2)\{\kappa\text{P-P}(\text{O})\text{Cy}_2\} \text{Pt}(\mu\text{-PCy}_2)(\mu\text{-H})\text{Pt}(\text{PHCy}_2)\{\kappa\text{P-P}(\text{O})\text{Cy}_2\}](\text{Pt-Pt})^2$ with Pt–H distances (Pt(1)–H 1.80(5) Å; Pt(2)–H 1.65(5) Å) essentially identical within experimental error. These values and the Pt \cdots Pt distance (2.8209(2) Å) compare to those found in other $30 e^-$ diplatinum hydride complexes containing mixed $(\mu\text{-X})(\mu\text{-H})$ bridges [22,28–31] for which the existence of a through-ring Pt–Pt bonding interaction has been suggested on the basis of theoretical calculations [32]. The Pt–C(1) (2.036(4) Å)

and Pt-P distances (2.2409(10)–2.3255(10) Å) and structural details of the terminal C≡CSiMe₃ (C≡C 1.192(6) Å; Pt(1)-C(1)-C(2) 177.1(4)°; C(1)-C(2)-Si(1) 177.2(4)°) are unexceptional for these ligands. Although many different types of dimeric hydride bridged platinum complexes have been reported, including systems containing mixed (μ-C≡CR)(μ-H), complexes containing terminal alkynyl as auxiliary ligands are very rare. To the best of our knowledge, only the related complexes [(η¹-C≡CR)(Bu^t₂HP) Pt(μ-PBu^t₂)(μ-H)Pt(CO)(PBu^t₂H)](TfO) (R = Bu^t, Ph) and [Pt₂(C≡Ph)₂(μ-H)(μ-dppm)₂]Cl₂ characterized by spectroscopic means have been reported [33,34].

Table 1. Selected bond lengths and angles for 2·2 *n*-hexane·H₂O. The prime (') character in the atoms labels indicates that these atoms are at equivalent positions (−*x*, −*y*, −*z*).

Distances (Å)			
Pt(1)-C(1)	2.036(4)	Pt(2)-P(3)	2.3255(10)
Pt(1)-P(1)	2.2409(10)	Pt(2)-P(4)	2.2690(10)
Pt(1)-P(2)	2.2864(10)	Pt(2)-P(2)	2.3089(9)
Pt(1)-H(100)	1.80(5)	Pt(2)-H(100)	1.65(5)
Pt(1)-Pt(2)	2.8209(2)	C(1)-C(2)	1.192(6)
O(1)-O(2)	2.726(5)	O(1)-O(2)'	2.775(6)
Angles (°)			
C(1)-Pt(1)-P(1)	90.76(11)	P(3)-Pt(2)-P(4)	93.84(4)
P(1)-Pt(1)-P(2)	104.46(4)	P(4)-Pt(2)-P(2)	102.67(4)
P(2)-Pt(1)-H(100)	84.1(15)	P(2)-Pt(2)-H(100)	86.7(16)
C(1)-Pt(1)-H(100)	80.7(15)	P(3)-Pt(2)-H(100)	77.1(16)
H(100)-Pt(1)-Pt(2)	33.5(15)	H(100)-Pt(2)-Pt(1)	37.0(16)
P(2)-Pt(1)-Pt(2)	52.49(2)	P(2)-Pt(2)-Pt(1)	51.77(2)
Pt(1)-P(2)-Pt(2)	75.74(3)	Pt(1)-H(100)-Pt(2)	109.5(28)
Pt(1)-C(1)-C(2)	177.1(4)	C(1)-C(2)-Si(1)	177.2(4)

Figure 4. View of the molecular structure of 2·2 *n*-hexane·H₂O; (a) the asymmetric unit showing the presence of the oxygen from the H₂O and (b) the dimer generated through four O···H···O bonds and at equivalent positions (−*x*, −*y*, −*z*).

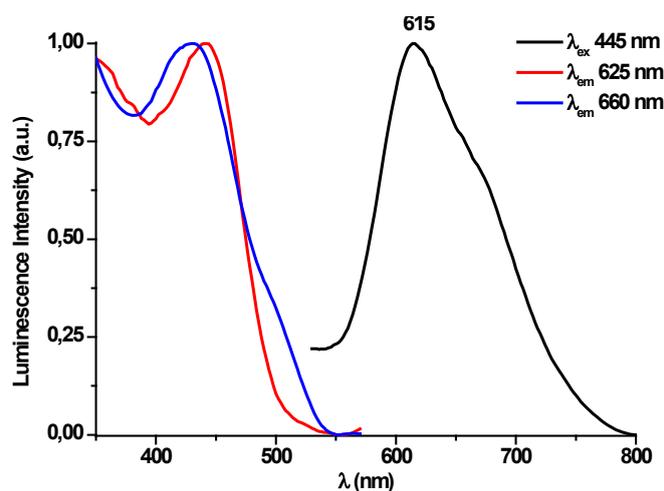


2.3. Photoluminescence of **2**

Due to the presence of the very short Pt··Pt distance, we decided to investigate the photoluminescent properties of Complex **2** in the solid state. The complex is not emissive at room temperature. However, it displays a long-lived, weak emission at 77 K (Figure 5), which fits to a double exponential decay (τ_1 5.6 μ s 55%; τ_2 13.5, μ s 45%). According to previous luminescence studies in alkynyl dinuclear complexes with short Pt··Pt distances [35,36], this emission is tentatively ascribed to an excited state having a metal-metal to alkynyl charge transfer character (3 MMLCT).

The profile of the emission band is asymmetric, and the excitation spectra monitored at two different wavelengths are somewhat different, suggesting the presence of heterogeneity in the bulk solid.

Figure 5. Excitation and emission spectra of **2** in solid state at 77 K. (first line).



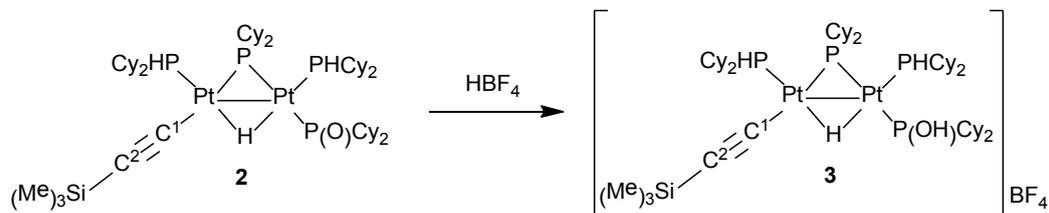
2.4. Reactivity of **2** with HBF_4

Complex **2** possesses several sites susceptible to protonation. In fact, beside the bridging phosphanide, the bridging hydride, the terminal (trimethylsilyl)acetylide (that could give dihydrogen and trimethylsilylacetylene, respectively) and the dicyclohexylphosphinite represent possible protonation sites.

In order to study the site selectivity of the protonation reaction, Complex **2** was treated with $\text{HBF}_4 \cdot \text{Me}_2\text{O}$ in *n*-hexane (Scheme 3). The reaction gave smoothly the corresponding dicyclohexylphosphinic acid complex $[\mathbf{3}]\text{BF}_4$ as the only product, indicating that only the POCy_2 ligand is protonated. The most striking evidence revealing the transformation of the POCy_2 ligand into P(OH)Cy_2 is the presence, in the ^1H NMR spectrum of $[\mathbf{3}]\text{BF}_4$, of a broad peak at δ 6.71 ascribable to the POH proton. Moreover, as reported in related hydrido bridged diplatinum phosphinito species, [3,4] the protonation of the POCy_2 ligand provokes a high field shift of the ^1H NMR hydride resonance (from δ -4.46 (in **2**) to δ -5.83 (in $[\mathbf{3}]\text{BF}_4$)) and a low field shift of the phosphinito ^{31}P NMR resonance (from δ 77.0 (in **2**) to δ 124.3 (in $[\mathbf{3}]\text{BF}_4$)). IR and ^{13}C NMR data confirmed the presence of the η^1 -acetylide bonded to Pt^{I} in $[\mathbf{3}]\text{BF}_4$. In fact, the $\text{C}\equiv\text{C}$ stretching band was found in the IR spectrum at

2045 cm^{-1} , while the $^{13}\text{C}\{^1\text{H}\}$ NMR signals of the coordinated (trimethylsilyl)acetylide were found at δ 126.7 (C^1), δ 118.1 (C^2) and 1.2 (CH_3).

Scheme 3. Protonation of **2** by tetrafluoroboric acid.



3. Experimental Section

Complex **1** was prepared as described [2]. (Trimethylsilyl)acetylene and etherate fluoroboric acid were from commercial suppliers and were used without further purification. All manipulations were carried out under a pure nitrogen atmosphere, using freshly distilled and oxygen-free solvents. C, H elemental analyses were carried out on a Vario Micro-CHNSO elemental analyzer. Infrared spectra were recorded on a Jasco 4200-FTIR spectrometer. NMR spectra were recorded on a Bruker Avance 400 spectrometer; frequencies are referenced to Me_4Si (^1H and ^{13}C), 85% H_3PO_4 (^{31}P) and H_2PtCl_6 (^{195}Pt). The signal attributions (see Schemes 4 and 5 for atom numbering) and coupling constant assessment was made on the basis of a multinuclear NMR analysis, including ^1H - ^{31}P HMQC, ^1H - ^{195}Pt HMQC, COSY and NOESY experiments. The coupling constants not directly extractable from the monodimensional spectra were obtained and attributed by the tilts of the multiplets due to the “passive” nuclei [37] in the aforementioned 2D spectra. High resolution mass spectrometry (HR-MS) analyses were performed using a time-of-flight mass spectrometer equipped with an electrospray ion source (Bruker micrOTOF-Q II). The sample solutions were introduced by continuous infusion with the aid of a syringe pump at a flow-rate of 180 $\mu\text{L}/\text{h}$. The instrument was operated at end plate offset -500 V and capillary -4500 V. Nebulizer pressure was 0.3 bar (N_2) and the drying gas (N_2) flow 4.0 L/min. Capillary exit was 170 V. The drying gas temperature was set at 180 $^\circ\text{C}$. The software used for the simulations is Bruker Daltonics Data Analysis (version 4.0, Bruker Daltonik GmbH, Bremen, Germany). All experimental HRMS signals had an isotope pattern superimposable to that calculated for the relevant formula, on the basis of the natural abundances. Emission and excitation spectra were obtained on a Jobin-Yvon Horiba Fluorog 3-11 Tau-3 spectrofluorometer (Horiba, Kyoto, Japan), with the lifetime measured in the phosphorimeter mode.

3.1. Synthesis of **2**

To a *n*-hexane solution of **1** (164 mg, 0.137 mmol in 4.0 mL), 21 μL of (trimethylsilyl)acetylene (14.8 mg, 0.150 mmol) were added at 298 K and stirred for 12 h. After the reaction, the mixture was taken to dryness under vacuum to eliminate the solvent and the excess (trimethylsilyl)acetylene. The residue was redissolved in 1.0 mL of *n*-hexane, and the procedure was repeated twice. The final pale yellow solid was dried under high vacuum overnight.

Yield: 163 mg (92%).

The complex is air stable in the solid state and is very soluble in halogenated solvents, aromatic solvents, diethyl ether and *n*-hexane.

C₅₃H₁₀₀OP₄Pt₂Si: calcd. C, 49.14; H, 7.78; found C 49.09, H 7.59.

HRMS(+) (*n*-hexane): exact mass calcd. for C₅₃H₁₀₀OP₄Pt₂Si: 1294.5786 da; found: 1295.5852 da [M + H]⁺.

IR (KBr): = 2329 (m, P-H), 2042 (vs, C≡C), 1632 (w, Pt-H-Pt), 1446 (vs), 1342 (m), 1293 (m), 1266 (m), 1241 (s), 1191 (s), 1175 (s), 1117 (s), 1083 (s, P=O), 1044 (m), 1003 (vs, P=O), 916 (s), 888 (s), 858 (vs), 819 (s), 754 (m), 728 (s), 689 (m), 540 (s), 518 (s), 462 (s), 414 (m) cm⁻¹.

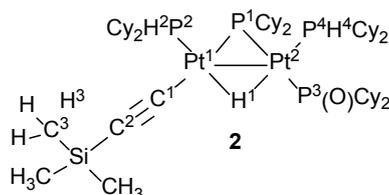
¹H NMR (400 MHz, C₆D₆, 298 K): δ = 5.36 [m, H(4), ¹J_{H(4),P(4)} = 344 Hz, ²J_{H(4),Pt(2)} = 46 Hz], 4.70 [m, H(2), ¹J_{H(2),P(2)} = 376 Hz, ²J_{H(2),Pt(1)} = 83 Hz], 0.44 [s, H(3)], -4.46 [m, H(1), ²J_{H(1),P(4)} = 76 Hz, ²J_{H(1),P(2)} = 68 Hz, ²J_{H(1),Pt(1)} = 13 Hz, ²J_{H(1),Pt(3)} = 7 Hz] ppm.

¹³C{¹H} NMR (100 MHz, *n*-hexane, 298 K, δ): 129.9 (dd, C¹, ²J_{C,P(1)} = 82 Hz, ²J_{C,P} = 19 Hz, ¹J_{C,Pt(1)} = 1011 Hz), 116.6 (d, C², ³J_{C,P(1)} = 16 Hz, ²J_{C,Pt(1)} = 253 Hz), 1.5 (s, C³) ppm.

³¹P{¹H} NMR (161 MHz, C₆D₆, 298 K): δ = 120.8 [d, P(1), ²J_{P(1),P(3)} = 245 Hz, ¹J_{P(1),Pt(1)} = 1680 Hz, ¹J_{P(1),Pt(2)} = 1170 Hz], 77.0 [d, P(3), ²J_{P(3),P(1)} = 245 Hz, ¹J_{P(3),Pt(2)} = 2333 Hz], 13.7 [broad, P(4), ³J_{P(4),P(2)} = 55 Hz, ¹J_{P(4),Pt(2)} = 3946 Hz], 2.8 [d, P(2), ³J_{P(2),P(4)} = 55 Hz, ¹J_{P(2),Pt(1)} = 3726 Hz, ²J_{P(2),Pt(2)} = 209 Hz] ppm.

¹⁹⁵Pt{¹H} NMR (86 MHz, C₆D₆, 298 K): δ = -5582 [ddd, Pt(1), ¹J_{Pt(1),P(1)} = 1680 Hz, ¹J_{Pt(1),P(2)} = 3726 Hz, ²J_{Pt(1),P(4)} = 224 Hz], -5562 [m, Pt(2), ¹J_{Pt(2),P(1)} = 1170 Hz, ²J_{Pt(2),P(2)} = 209 Hz, ¹J_{Pt(2),P(3)} = 2333 Hz, ¹J_{Pt(2),P(4)} = 3946 Hz] ppm.

Scheme 4. Atom numbering for Complex 2.



3.2. Synthesis of [3]BF₄

To an *n*-hexane solution of **2** (104 mg, 0.080 mmol in 2.0 mL), 10 μL of HBF₄·Me₂O (11 mg, 0.080 mmol) were added at 298 K, causing the precipitation of a brownish solid. The solid was filtered off, washed with *n*-hexane (3 × 1 mL) and dried under high vacuum.

Yield: 77 mg (70%).

Complex [3]BF₄ is stable in the solid state, but slowly undergoes a substitution of a chloride for the trimethylsilylacetylide, when it is dissolved in chlorinated solvents. It is soluble in halogenated solvents and insoluble in diethyl ether, in alkanes and in aromatic solvents.

C₅₃H₁₀₁BF₄OP₄Pt₂Si: calcd. C, 46.02; H, 7.36; found C 46.09, H 7.49.

HRMS(+) (*i*-propanol): exact mass calcd. for the cation C₅₃H₁₀₁OP₄Pt₂Si: 1295.5855 da; found: 1295.5808 da [M]⁺.

IR (Nujol mull): = 3358 (broad m, P–O–H), 2662 (w), 2333 (m, P–H), 2045 (vs, C≡C), 1628 (w, Pt–H–Pt), 1452 (vs), 1378 (s), 1295 (m), 1270 (m), 1058 (broad s, BF₄ +PO) 854 (vs), 733 (vs), 518 (s), 467 (s), cm⁻¹.

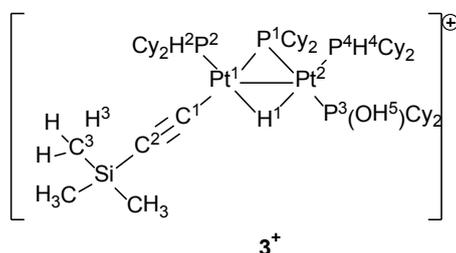
¹H NMR (400 MHz, CD₂Cl₂, 298 K): δ = 6.71 [broad, H(5)], 5.07 [m, H(4), ¹J_{H(4),P(4)} = 372 Hz], 4.93 [m, H(2), ¹J_{H(2),P(2)} = 353 Hz, ²J_{H(2),Pt(1)} = 72 Hz], 0.12 [s, H(3)], -5.83 [m, H(1), ²J_{H(1),P(4)} = 72 Hz, ²J_{H(1),P(2)} = 63 Hz, ²J_{H(1),P(1)} = 18 Hz, ²J_{H(1),P(3)} = 12 Hz] ppm.

¹³C{¹H} NMR (100 MHz, CD₂Cl₂, 298 K, δ): 126.7 (dd, C¹, ²J_{C,P(1)} = 86 Hz, ²J_{C,P} = 15 Hz), 118.1 (d, C², ³J_{C,P(1)} = 20 Hz, ²J_{C,Pt(1)} = 243 Hz), 1.2 (s, C³) ppm.

³¹P{¹H} NMR (161 MHz, CD₂Cl₂, 298 K): δ = 144.4 [d, P(1), ²J_{P(1),P(3)} = 262 Hz, ¹J_{P(1),Pt(1)} = 1742 Hz, ¹J_{P(1),Pt(2)} = 1471 Hz], 124.3 [d, P(3), ²J_{P(3),P(1)} = 262 Hz, ¹J_{P(3),Pt(2)} = 2710 Hz], 2.5 [broad, P(4), ¹J_{P(4),Pt(2)} = 3588 Hz], 0.6 [d, P(2), ³J_{P(2),P(4)} = 49 Hz, ¹J_{P(2),Pt(1)} = 3786 Hz, ²J_{P(2),Pt(2)} = 218 Hz] ppm.

¹⁹⁵Pt{¹H} NMR (86 MHz, CD₂Cl₂, 298 K): δ = -5622 [dd, Pt(1), ¹J_{Pt(1),P(1)} = 1742 Hz, ¹J_{Pt(1),P(2)} = 3786 Hz], -5673 [m, Pt(2), ¹J_{Pt(2),P(1)} = 1471 Hz, ²J_{Pt(2),P(2)} = 262 Hz, ¹J_{Pt(2),P(3)} = 2710 Hz, ¹J_{Pt(2),P(4)} = 3588 Hz] ppm.

Scheme 5. Atom numbering for Complex **3**⁺.



3.3. X-ray Structure Determination

Details of the structural analysis for Complex **2** are summarized in Table 2. Pale yellow crystals were obtained by slow evaporation at 4 °C of a concentrated solution of the complex in *n*-hexane. Two molecules of *n*-hexane and one of water were found in the asymmetric unit. Graphite-monochromatic Mo-K_α radiation was used. X-ray intensity data were collected with a NONIUS-κCCD area-detector diffractometer (CAMCOR, Eugene, OR, USA) and images processed using the DENZO (Academic Press: New York, NY, USA) and SCALEPACK suite of programs [38], carrying out the absorption correction at this point. The structure was solved by direct and Patterson methods using SIR2004 [39] and refined by full-matrix least squares on *F*² with SHELXL-97 [40]. All non-hydrogen atoms were assigned anisotropic displacement parameters. The hydride ligand, H(100), has been located from difference maps and assigned isotropic parameters. The rest of the hydrogen atoms (except the H₂O hydrogens) were constrained to idealized geometries fixing isotropic displacement parameters 1.2-times the *U*_{iso} value of their attached carbon. Several restraints have been used in order to model the *n*-hexane molecules. The hydrogen atoms of the H₂O molecule have been omitted from the density map, but have been included in the empirical formula and in the molecular weight. Finally, the structure showed one residual peaks greater than 1 eÅ⁻³ in the vicinity of the Pt(2) atom, but with no chemical meaning.

4. Conclusions

Reaction of the phosphinito-phosphanido Pt(I) complex [(PHCy₂)Pt(μ-PCy₂){κ²P,O-μ-P(O)Cy₂}Pt(PHCy₂)](*Pt-Pt*) (**1**) with (trimethylsilyl)acetylene results in the C-H bond activation of the alkyne with the formation of the bridging hydride complex [(PHCy₂)(η¹-Me₃SiC≡C)Pt(μ-PCy₂){κP-P(O)Cy₂}Pt(PHCy₂)](*Pt-Pt*) (**2**), which displays a σ-bonded acetylide ligand and a bridging hydride. The reactivity of **1** with (trimethylsilyl)acetylene parallels that already found with PhOH or CF₃CH₂OH, two weak Brønsted acids endowed with a coordinating anion. Complex **2** is stable both in the solid state and in solution, and it is resistant to deprotonation by NaOH. It crystallizes from *n*-hexane as 2·2 *n*-hexane·H₂O. The water molecule is simultaneously hydrogen bonded to two phosphinite ligands of two neighboring diplatinum complexes, giving rise to a dimer. Due to the presence of the short Pt-Pt bond, Complex **2** exhibits a long-lived weak emission at 77 K, which is ascribed to an excited state having a metal-metal to alkynyl charge transfer character (³MMLCT). Despite the number of protonation sites present in Complex **2**, its reaction with HBF₄·Me₂O in toluene gave the phosphinic acid cationic Complex **3**⁺ selectively, still embodying the trimethylsilylacetylide ligand.

Table 2. Selected crystal data and structure refinement details for 2·2C₆H₁₄·H₂O.

Parameters	2·2C ₆ H ₁₄ ·H ₂ O
empirical formula	C ₆₅ H ₁₃₀ O ₂ P ₄ Pt ₂ Si
<i>F</i> _w	1485.84
<i>T</i> (K)	173(1)
crystal system; space group	triclinic; <i>P</i> -1
<i>a</i> (Å); α (°)	13.1300(3); 67.8780(10)
<i>b</i> (Å); β (°)	16.4810(6); 88.243(2).
<i>c</i> (Å); γ (°)	19.1700(7); 73.174(2).
<i>V</i> (Å ³); <i>Z</i>	3664.0(2); 2
<i>D</i> _{calcd} (Mg/m ³)	1.345
absorption coefficient (mm ⁻¹)	3.954
<i>F</i> (000)	1528
crystal size (mm)	0.6 × 0.2 × 0.05
θ range for data collection (°)	3.19 to 27.48
index ranges	0 ≤ <i>h</i> ≤ 16, -20 ≤ <i>k</i> ≤ 21 -24 ≤ <i>l</i> ≤ 24
No of data/restraints/params	16,496/12/611
goodness of fit on <i>F</i> ² ^a	1.014
final <i>R</i> indexes (<i>I</i> > 2σ(<i>I</i>)) ^a	<i>R</i> ₁ = 0.0329, w <i>R</i> ₂ = 0.0777
<i>R</i> indices (all data) ^a	<i>R</i> ₁ = 0.0441, w <i>R</i> ₂ = 0.082
largest diff. peak and hole (e·Å ⁻³)	1.580 and -1.078

^a *R*₁ = Σ(|*F*_o| - |*F*_c|)/Σ|*F*_o|; w*R*₂ = [Σw(*F*_o² - *F*_c²)²/Σw*F*_o²]^{1/2}; goodness of fit = {Σ[w(*F*_o² - *F*_c²)²]/(N_{obs} - N_{param})^{1/2}; w = [σ²(*F*_o) + (*g*₁*P*)² + *g*₂*P*]⁻¹; *P* = [max(*F*_o²; 0 + 2*F*_c²)/3].

Acknowledgments

We wish to thank Politecnico of Bari for FRA funding and the Spanish MINECO projects (CTQ 2008-06669-C02-02 and CTQ2013-45518-P) for financial support.

Author Contributions

Piero Mastrorilli and Elena Lalinde: Responsibles for research publication. Mario Latronico: Inorganic synthesis. Stefano Todisco: MS and IR analysis. Vito Gallo: NMR. Santiago Ruiz: Crystallographer.

Conflicts of Interest

The authors declare no conflict of interest.

References and Notes

1. Gallo, V.; Latronico, M.; Mastrorilli, P.; Nobile, C.F.; Suranna, G.P.; Ciccarella, G.; Englert, U. Synthesis of phosphido-bridged phosphinito platinum(I) complexes by reaction of *cis*-PtCl₂(PHCy₂)₂ with oxygenated bases—Crystal structure of [(PCy₂OMe)Pt(μ-PCy₂)₂](Pt-Pt). *Eur. J. Inorg. Chem.* **2005**, *22*, 4607–4616.
2. Gallo, V.; Mastrorilli, P.; Polini, F.; Latronico, M.; Re, N.; Englert, U. Reactivity of a phosphinito-bridged Pt^I-Pt^I complex with nucleophiles: Substitution versus addition. *Inorg. Chem.* **2008**, *47*, 4785–4795.
3. Latronico, M.; Polini, F.; Gallo, V.; Mastrorilli, P.; Calmuschi-Cula, B.; Englert, U.; Re, N.; Repo, T.; Raisanen, M. Site selectivity in the protonation of a phosphinito bridged Pt^I-Pt^I complex: A combined NMR and density-functional theory mechanistic study. *Inorg. Chem.* **2008**, *47*, 9779–9796.
4. Latronico, M.; Mastrorilli, P.; Gallo, V.; Dell'Anna, M.M.; Creati, F.; Re, N.; Englert, U. Hydrido phosphanido bridged polynuclear complexes obtained by protonation of a phosphinito bridged Pt(I) complex with HBF₄ and HF. *Inorg. Chem.* **2011**, *50*, 3539–3858.
5. Forniés, J.; Lalinde, E. Platinum–Carbon π-Bonded Complexes. In *Comprehensive Organometallic Chemistry III*; Carbtree, R.H., Mingos, D.M.P., Eds.; Elsevier: Oxford, UK, 2007; pp. 611–673.
6. Belluco, U.; Bertani, R.; Michelin, R.A.; Mozzon, M. Platinum-alkynyl and -alkyne complexes: Old systems with new chemical and physical perspectives. *J. Organomet. Chem.* **2000**, *600*, 37–55.
7. Hahn, C.; Miranda, M.; Chittineni, N.P.B.; Pinion, T.A.; Perez, R. Mechanistic Studies on Platinum(II) Catalyzed Hydroarylation of Alkynes. *Organometallics* **2014**, *33*, 3040–3050.
8. Jourdain, I.; Knorr, M.; Strohmam, C.; Unkelbach, C.; Rojo, S.; Gómez-Iglesias, P.; Villafañe, F. Reactivity of Silyl-Substituted Iron–Platinum Hydride Complexes toward Unsaturated Molecules: 4. Insertion of Fluorinated Aromatic Alkynes into the Platinum-Hydride Bond. Synthesis and Reactivity of Heterobimetallic Dimetallacylopentenone, Dimetallacyclobutene, μ-Vinylidene, and μ²-σ-Alkenyl Complexes. *Organometallics* **2013**, *32*, 5343–5359.

9. Berenguer, J.R.; Fernández, J.; Giménez, N.; Lalinde, E.; Moreno, M.T.; Sánchez, S. Unexpected Formation of Ferrocenyl(vinyl)benzoquinoline Ligands by Oxidation of an Alkyne Benzoquinolate Platinum(II) Complex. *Organometallics* **2013**, *32*, 3943–3953.
10. West, N.M.; White, P.S.; Templeton, J.L. Alkyne Insertion into the Pt-H Bond of Pt(H)(1-pentene)(β -diimine) Initiates a Reaction Cascade That Results in C-H Activation or C-C Coupling. *Organometallics* **2008**, *27*, 5252–5262.
11. Wang, W.; Yang, H.B. Linear neutral platinum-acetylide moiety: Beyond the links. *Chem. Commun.* **2014**, *50*, 5171–5186.
12. Muro, M.L.; Rachford, A.A.; Wang, X.; Castellano, F.N. Platinum^{II} Acetylide Photophysics. *Top. Organomet. Chem.* **2010**, *29*, 159–191.
13. Berenguer, J.R.; Lalinde, E.; Moreno, M.T. An overview of the chemistry of homo and heteropolynuclear platinum complexes containing bridging acetylide (μ -C \equiv CR) ligands. *Coord. Chem. Rev.* **2010**, *254*, 832–875.
14. Canty, A.J.; Sharma, M. η^1 -Alkynyl Chemistry for the Higher Oxidation State of Palladium and Platinum. *Top. Organomet. Chem.* **2011**, *35*, 111–128.
15. Long, N.J.; Willians, C.K. Metal Alkynyl σ Complexes: Synthesis and Materials. *Angew. Chem. Int. Ed.* **2003**, *42*, 2586–2617.
16. Tao, C.H.; Yam, V.W.W. Branched carbon-rich luminescent multinuclear platinum(II) and palladium(II) alkynyl complexes with phosphine ligands. *J. Photochem. Photobio. C* **2009**, *10*, 130–140.
17. Wong, K.M.; Yam, V.W.W. Self-Assembly of Luminescent Alkynylplatinum(II) Terpyridyl Complexes: Modulation of Photophysical Properties through Aggregation Behavior. *Acc. Chem. Res.* **2011**, *44*, 424–434.
18. Wong, W.Y. Luminescent organometallic poly(aryleneethynylene)s: Functional properties towards implications in molecular optoelectronics. *Dalton Trans.* **2007**, 4495–4510.
19. Throughout the paper, the calculated (exact mass) and the experimental (accurate) m/z values have been compared considering the principal ion (which gives the most intense peak) of the isotope pattern.
20. Berenguer, J.R.; Forniés, J.; Martínez, F.; Cubero, J.C.; Lalinde, E.; Moreno, M.T.; Welch, A.J. Synthesis and reactivity of bimetallic acetylide-bridged Pt-Pt complexes. Crystal and molecular structure of [(PPh₃)(C₆F₅)Pt(μ -C \equiv CPh)₂Pt(C₆F₅)(PPh₃)]. *Polyhedron* **1993**, *12*, 1797–1804.
21. Benito, J.; Berenguer, J.R.; Forniés, J.; Gil, B.; Gómez, J.; Lalinde, E. Synthesis, characterization and luminescence properties of homoleptic platinum(II) acetylide complexes. *Dalton Trans.* **2003**, doi:10.1039/B308291A.
22. Mastrorilli, P. Bridging and Terminal (Phosphanido)platinum Complexes. *Eur. J. Inorg. Chem.* **2008**, *31*, 4835–4850.
23. Mastrorilli, P.; Latronico, M.; Gallo, V.; Polini, F.; Re, N.; Marrone, A.; Gobetto, R.; Ellena, S. Facile Activation of Dihydrogen by a Phosphinito-Bridged Pt(I)-Pt(I) Complex. *J. Am. Chem. Soc.* **2010**, *132*, 4752–4765.
24. Furlani, A.; Licocchia, S.; Russo, M.V.; Chiesi, V.A.; Guastini, C. New platinum hydrido acetylides. Crystal and molecular structure of [PtH{C \equiv C-C(OH)MeEt}(PPh₃)₂]. *Dalton Trans.* **1982**, doi:10.1039/DT9820002449.

25. Mastrorilli, P.; Nobile, C.F.; Latronico, M.; Gallo, V.; Englert, U.; Fanizzi, F.P.; Sciacovelli, O.; Multinuclear and dynamic NMR study of *trans*-[Pt(Cl)(PHCy₂)₂(PCy₂)], [Pt(Cl)(PHCy₂)₃][BF₄], [Pt(Cl)(PHCy₂)₃][Cl], *trans*-[Pt(Cl)(PHCy₂)₂{P(S)Cy₂}], and *trans*-[Pt(Cl)(PHCy₂)₂{P(O)Cy₂}]. *Inorg. Chem.* **2005**, *44*, 9097–9104.
26. Desiraju, G.R.; Steiner, T. *The Weak Hydrogen Bond in Structural Chemistry and Biology*; Oxford University Press: Oxford, UK, 1999.
27. Nishio, M. *Weak Hydrogen Bonds in Encyclopedia of Supramolecular Chemistry*; Atwood, J.L., Steed, J.L., Eds.; Marcel Dekker Inc.: New York, NY, USA, 2004.
28. Ara, I.; Falvello, L.R.; Fornies, J.; Lalinde, E.; Martínez, F.; Moreno, M.T. Synthesis and Structure of New Neutral Bimetallic Platinum Hydride Complexes. *Organometallics* **1997**, *16*, 5392–5405.
29. Berenguer, J.R.; Bernechea, M.; Lalinde, E. Rearrangement or C-H Activation Processes Promoted by Reaction with the Solvate [*cis*-Pt(C₆F₅)₂(thf)₂]. *Organometallics* **2007**, *26*, 1161–1172.
30. Leoni, P.; Manetti, S.; Pasquali, M. Synthesis of New Neutral and Cationic Phosphido-Bridged Dinuclear Platinum(II) Hydride. *Inorg. Chem.* **1995**, *34*, 749–752.
31. Berenguer, J.R.; Bernechea, M.; Lalinde, E. C-H and P-C(Ph) activation competitive processes caused by interaction with the solvate [*cis*-Pt(C₆F₅)₂(thf)₂]. *Dalton Trans.* **2007**, 2384–2393.
32. Aullón, G.; Alemany, P.; Alvarez, S. Through-ring bonding in edge-sharing dimers of square planar complexes. *J. Organomet. Chem.* **1994**, *478*, 75–83.
33. Crementieri, S.; Leoni, P.; Marchetti, F.; Marchetti, L.; Pasquali, M. Stable η^1 -Alkynyl- μ, η^1 : η^2 -Alkenyl Complexes from the Reaction of Terminal Alkynes with Encumbered Dinuclear Platinum Compounds and Their Formyl, Methoxycarbonyl, and Hydride Derivatives. *Organometallics* **2002**, *21*, 2575–2577.
34. Langrick, C.R.; Pringle, P.G.; Shaw, B.L. Bimetallic systems. Part 10. Synthesis of complexes of type [(RC≡C)Pt(μ -dppm)₂Pt(C≡CR)] (dppm = Ph₂PCH₂PPh₂, R = Ph or p-tolyl) and their corresponding “A frames” [(RC≡C)Pt(μ -dppm)₂(μ -H)Pt(C≡CR)]Cl or [(RC≡C)Pt(μ -dppm)₂(μ -X)Pt(C≡CR)] with X = CS₂ or MeOOC≡CCOOMe. *Dalton Trans.* **1985**, doi:10.1039/DT9850001015.
35. Lam, W.H.; Yam, V.W.W. Computational Studies on the Photophysical Properties and NMR Fluxionality of Dinuclear Platinum(II) A-Frame Alkynyl Diphosphine Complexes. *Inorg. Chem.* **2010**, *49*, 10930–10939.
36. Wong, K.M.C.; Hui, K.C.; Yu, L.K.; Yam, V.W.W. Luminescence studies of dinuclear platinum(II) alkynyl complexes and their mixed-metal platinum(II) -copper(I) and -silver(I) complexes. *Coord. Chem. Rev.* **2002**, *229*, 123–132.
37. Carlton, L. Relative Sign of *J* Couplings from Two-Dimensional NMR Spectra. *Bruker Rep.* **2000**, *148*, 28–29.
38. Otwinowski, Z.; Minor, W. *Macromolecular Crystallography, Part A*; Carter, C.W., Jr., Sweet, R.M., Eds.; Academic Press: New York, NY, USA, 1997; Volume 276, pp. 307–326.
39. Burla, M.C.; Caliandro, R.; Camalli, M.; Carrozzini, B.; Cascarano, G.L.; De Caro, L.; Giacovazzo, C.; Polidori, G.; Spagna, R. SIR2004: An improved tool for crystal structure determination and refinement. *J. Appl. Crystallogr.* **2005**, *38*, 381–388.

40. Sheldrick, G.M. *SHELXL-97*; University of Göttingen: Göttingen, Germany, 1997.

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