

New Mono- and Polynuclear Alkynyl Complexes Containing Phenylacetylide as Terminal or Bridging Ligand. X-ray Structures of the Compounds $\text{NBu}_4[\text{Pt}(\text{CH}_2\text{C}_6\text{H}_4\text{P}(\text{o-tolyl})_2-\kappa\text{C},\text{P})(\text{C}\equiv\text{CPh})_2]$, $[\text{Pt}(\text{CH}_2\text{C}_6\text{H}_4\text{P}(\text{o-tolyl})_2-\kappa\text{C},\text{P})(\text{C}\equiv\text{CPh})(\text{CO})]$, $[\{\text{Pt}(\text{CH}_2\text{C}_6\text{H}_4\text{P}(\text{o-tolyl})_2-\kappa\text{C},\text{P})(\mu\text{-C}\equiv\text{CPh})\}_2]$, and $[\{\text{Pt}(\text{CH}_2\text{C}_6\text{H}_4\text{P}(\text{o-tolyl})_2-\kappa\text{C},\text{P})(\text{C}\equiv\text{CPh})_2\text{Cu}\}_2]$

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This work describes the synthesis of the compounds $\text{Q}[\text{Pt}(\text{C}\wedge\text{P})(\text{C}\equiv\text{CPh})_2]$ ($\text{Q} = \text{Li}^+$ (1), NBu_4^+ (2). $\text{C}\wedge\text{P} = \text{CH}_2\text{C}_6\text{H}_4\text{P}(\text{o-tolyl})_2-\kappa\text{C},\text{P}$) and their use as precursors for the preparation of homo- and heteropolynuclear complexes by reactions with Lewis acid species of transition metals, M ($\text{M} = \text{Cu}(\text{I})$, $\text{Ag}(\text{I})$, $\text{Tl}(\text{I})$, $\text{Pd}(\text{II})$, $\text{Pt}(\text{II})$). These reactions give rise to heteropolynuclear complexes that exhibit different bonding patterns for the bridging alkynyl ligands, depending on M. The reaction of 2 with readily available M^+ ($\text{M} = \text{Cu}$, Ag) species affords the discrete tetranuclear clusters $[\{\text{Pt}(\text{C}\wedge\text{P})(\text{C}\equiv\text{CPh})_2\text{M}\}_2]$ ($\text{M} = \text{Cu}$ (3), Ag (4)). The X-ray structure of 3 shows that in this complex both “ $\text{Pt}(\text{C}\wedge\text{P})(\text{C}\equiv\text{CPh})_2$ ” fragments are connected by two d^{10} metal centers and are stabilized by alkynyl bridging ligands, showing the stronger preference of the M^{I} centers ($\text{M}^{\text{I}} = \text{Cu}$, Ag) for the electron-rich alkynyl units than for the basic $\text{Pt}(\text{II})$ center. However, the reaction of 2 with TlPF_6 rendered the tentatively tetranuclear complex $[\{\text{Pt}(\text{C}\wedge\text{P})(\text{C}\equiv\text{CPh})_2\text{Tl}\}_2]$ (5), containing $\text{Pt}\rightarrow\text{Tl}$ dative bonds, which shows the higher affinity of thallium for the electron density of platinum(II) than for the alkynyl units. Moreover, the reaction of $(\text{NBu}_4)[\text{Pt}(\text{C}\wedge\text{P})(\text{C}\equiv\text{CPh})_2]$ (2) with the neutral complex $[\text{Pd}(\text{C}_6\text{F}_5)_2(\text{THF})_2]$ yields the compound $(\text{NBu}_4)[\text{Pt}(\text{C}\wedge\text{P})(\text{C}\equiv\text{CPh})_2\text{-Pd}(\text{C}_6\text{F}_5)_2]$ (11), in which the two alkynyl ligands are η^2 -bonded to $\text{Pd}(\text{II})$ in such a way that the “ $\text{cis-Pt}(\text{C}\equiv\text{CPh})_2$ ” fragment acts as a chelate ligand toward $\text{Pd}(\text{II})$. Meanwhile the reactions with the cationic and neutral $\text{Pt}(\text{II})$ complexes $[\text{Pt}(\text{C}\wedge\text{P})(\text{THF})_2]^+$ and $[\text{Pt}(\text{C}_6\text{F}_5)_2(\text{THF})_2]$ produce the complexes $[\{\text{Pt}(\text{C}\wedge\text{P})(\mu\text{-C}\equiv\text{CPh})\}_2]$ (6) and $(\text{NBu}_4)[\text{Pt}(\text{C}\wedge\text{P})(\mu\text{-C}\equiv\text{CPh})_2\text{Pt}(\text{C}_6\text{F}_5)_2]$ (12), both containing the double $\mu_2\text{-}\eta^2\text{-(}\sigma,\pi\text{)-alkynyl}$ bridging system “ $\text{Pt}_2(\mu\text{-C}\equiv\text{CPh})_2$ ” as a consequence of an alkynyating process. This bridging system “ $\text{Pt}_2(\mu\text{-C}\equiv\text{CPh})_2$ ” can be broken by neutral ligands, L, to give mono(σ -alkynyl) complexes of $\text{Pt}(\text{II})$. Thus, the complexes $[\text{Pt}(\text{C}\wedge\text{P})(\text{C}\equiv\text{CPh})\text{L}]$ ($\text{L} = \text{CO}$ (7), py (8), tht (9), PPh_3 (10)) have been obtained by reaction of 6 with L in a 1:2 molar ratio. When $\text{L} = \text{PPh}_3$, the substitution reaction takes place with stereoretention, but not when $\text{L} = \text{CO}$, py , tht , as was conclusively established by an X-ray study on the complex $[\text{Pt}(\text{CH}_2\text{C}_6\text{H}_4\text{P}(\text{o-tolyl})_2)(\text{CCPh})(\text{CO})]$ (7). The cis or trans disposition of the two $\sigma\text{-C-donor}$ ligands ($\text{C}(\text{C}\wedge\text{P})$, $\sigma\text{-C}\equiv\text{CPh}$) around the Pt center in complexes 6–10 and 12 seems to depend as much on the transphobia of pairs of trans ligands (T) as on the steric requirements of those in the cis configuration.

Introduction

The chemistry of transition-metal alkynyl complexes and polymers has been intensively studied due to their structural diversity and chemical reactivity.^{1,2} Interest has grown, particularly in recent years, because of their potential application

in supramolecular chemistry and material science.^{3–6} Within this field, square-planar platinum(II) σ -acetylide complexes have attracted much attention in nonlinear optics,⁷ photochemical devices,^{8–13} luminescence,^{14–21} liquid crystals,^{22,23} molecular wires,^{24–26} macrocycles,^{27,28} and dendritic molecules.^{10,29}

Platinum σ -alkynyl complexes with linear $\text{Pt}-\text{C}\equiv\text{CR}$ groups have been used as excellent precursors for the synthesis of

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polynuclear derivatives, since the presence of two orthogonal π C–C bonds allows interaction with transition-metal species (M) to give bridging acetylide compounds. In this field, much attention has been paid to the chemistry of $\text{Pt}^{\text{II}}\text{--M}^{\text{I}}$ ($\text{M}^{\text{I}} = \text{Cu}$, Ag , Tl) heterometallic alkynyl complexes and their spectroscopic behavior, photophysical properties, and structural topology, including metal–metal contacts,^{17,30–63} and also to the chemistry

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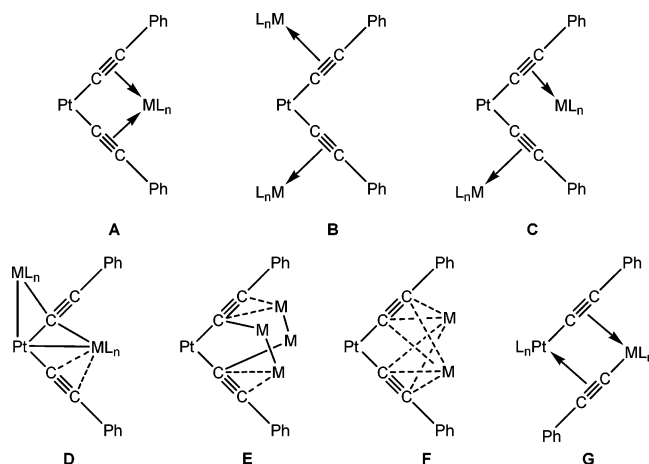
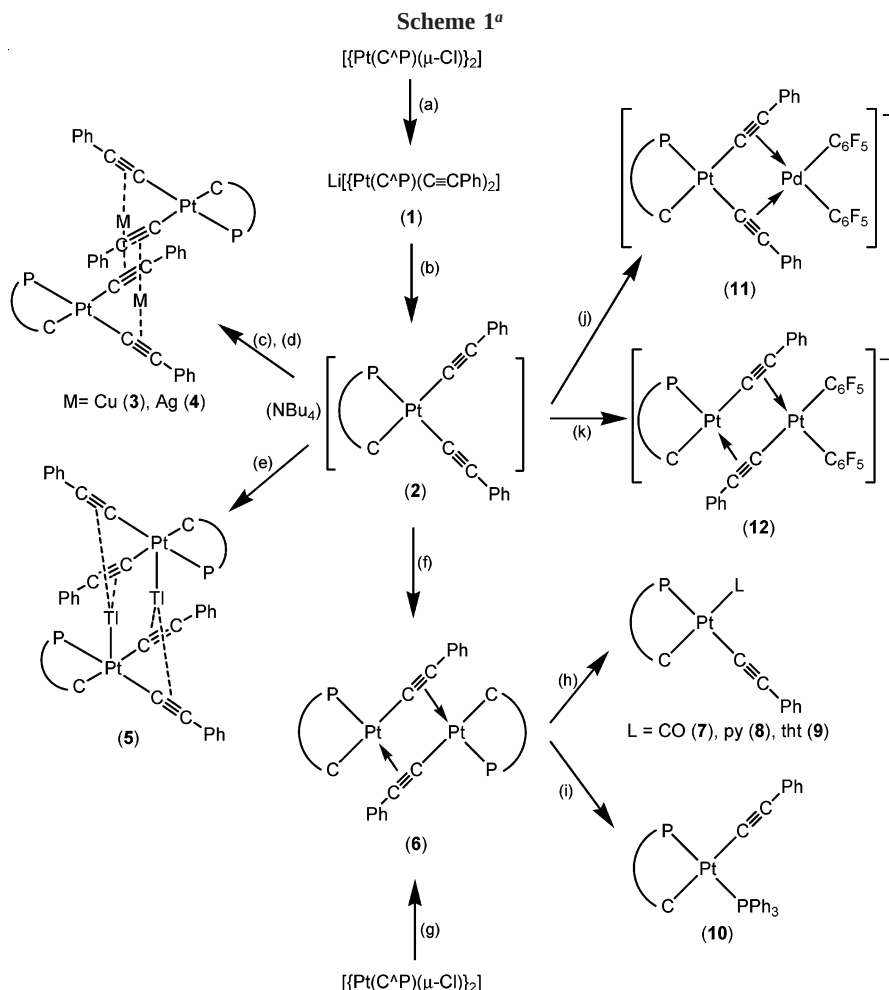


Figure 1.

of polynuclear $\text{Pt}^{\text{II}}\text{--M}^{\text{II}}$ ($\text{M} = \text{Pd}$, Pt) complexes.^{64–70} In particular, when platinum bis(σ -alkynyl) complexes with a cis configuration have been used as starting materials, different bonding situations of the bridging $\text{C}\equiv\text{CR}$ groups (Figure 1) have been found, depending on M and on the platinum ancillary ligands. The reactions of these kinds of complexes with Ag^{I} and Cu^{I} species^{30,34,36,44,46,47,49,52,53,55,57–59,61,63,70} rendered compounds of the types A–E. However, the reactions with Tl^{I} species have given rise to compounds containing donor–acceptor $\text{Pt}\text{--Tl}$ bonds, in which the interaction of Tl^{I} with the acetylenic fragments is very weak.³⁸

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^a Legend: (a) ⁿBuLi (excess); (b) NBu₄Br; (c) [Cu(NCMe)₄]PF₆; (d) AgClO₄; (e) TlPF₆; (f) [Pt(C[∧]P)(THF)₂]ClO₄; (g) ⁿBuLi; (h) L = CO, py, tht; (i) PPh₃; (j) *cis*-[Pd(C₆F₅)₂(THF)₂]; (k) *cis*-[Pt(C₆F₅)₂(THF)₂].

The reactions of the neutral complexes *cis*-[PtL₂(C≡CR)₂] with [M(C₆F₅)₂(THF)₂] (M = Pd, Pt), which contain two weak donor ligands (THF) in *cis* positions easily replaceable by other ones, render dinuclear derivatives of types **A**^{65,66} and **F**⁶⁶ meanwhile the anionic complexes Q₂[*cis*-Pt(C₆F₅)₂(C≡CR)₂] (R = Ph, Q = PMePh₃; R = ^tBu, Q = NBu₄)⁶⁵ give compounds of type **G**, as a consequence of an alkylating process of the “M(C₆F₅)₂” fragment. However, both the neutral complexes *cis*-[PtL₂(C≡CR)₂] and the anionic [*cis*-Pt(C₆F₅)₂(C≡CR)₂]²⁻ give compounds of type **A** when they react with the cationic “Pd(η³-C₃H₅)⁺” species.^{67,69}

As part of our current research on polynuclear complexes, we have recently described the synthesis of neutral Pt(II) complexes of the formulas [Pt(C[∧]P)(L[∧]L)] (C[∧]P = CH₂C₆H₄P-(*o*-tolyl)₂-κC,P, L[∧]L = S₂CNMe₂, S₂COEt, acac-O,O'), [Pt-(C[∧]P)(μ-O₂CCX₃)₂] (X = H, F), and [Pt(C[∧]P)(μ-Rpz)]₂ (Rpz = pz, 3,5-dmpz, 4-Mepz) and we demonstrated their ability to form heteronuclear compounds containing Pt→M donor–acceptor bonds when they react with Lewis acids such as Ag(I), Au(I), and Hg(II) species.^{71–76}

With the aim of obtaining new polynuclear complexes, we decided to prepare compounds that simultaneously contain the

“Pt(C[∧]P)” metallacycle and alkynyl ligands. As part of this work, we have prepared the monoanionic bis(*o*-alkynyl)-platinum(II) complex [Pt(C[∧]P)(C≡CPh)₂]⁻, in which the alkynyl ligands and the platinum center are all electron density rich. Its reactions with transition-metal species, M (M = Cu(I), Ag(I), Tl(I), Pd(II), Pt(II)) yielded new polynuclear complexes exhibiting different bonding patterns for the bridging alkynyl groups, depending on M.

Results and Discussion

Synthesis and Spectroscopic Characterization of the Compounds Q[Pt(C[∧]P)(C≡CPh)₂] (Q = Li⁺ (1), NBu₄⁺ (2)). The compound Li[Pt(C[∧]P)(C≡CPh)₂] (1) was prepared by treating a suspension of the dinuclear chloro-bridged complex [{Pt(C[∧]P)(μ-Cl)}₂] with LiC≡CPh in THF at low temperature (Scheme 1a, see the Experimental Section for details).

If NBu₄Br is added to a freshly prepared solution of 1 in ⁱPrOH (see the Experimental Section), the compound (NBu₄)-[Pt(C[∧]P)(C≡CPh)₂] (2) precipitates “in situ” (Scheme 1b). Compounds 1 and 2 were obtained as air-stable solids and fully characterized by the usual analytical and spectroscopic means

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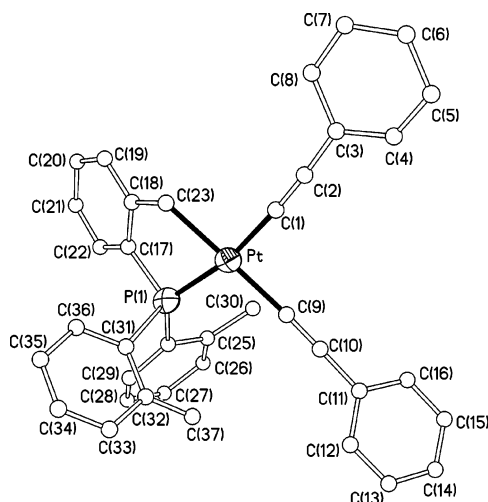
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Table 1. IR and $^{31}\text{P}\{^1\text{H}\}$ NMR Data for Compounds 1–13

complex	$\delta(\text{P})$ (ppm)	$^1J_{\text{Pt-P}}$ (Hz)	Δ_{P} (ppm) ^e	$\Delta J_{\text{Pt-P}}$ (Hz) ^f	$\nu_{\text{C}\equiv\text{C}}$ (cm ⁻¹)
$\text{Li}[\text{Pt}(\text{C}\wedge\text{P})(\text{C}\equiv\text{CPh})_2]$ (1) ^a	32.0 (s)	2746	0.2	143	2078
$\text{NBu}_4[\text{Pt}(\text{C}\wedge\text{P})(\text{C}\equiv\text{CPh})_2]$ (2) ^a	31.8 (s)	2603			2098, 2081
$[\{\text{Pt}(\text{C}\wedge\text{P})(\text{C}\equiv\text{CPh})_2\text{Cu}\}_2]$ (3) ^a	30.2 (s)	3056	-1.6	453	2007, 1971
$[\{\text{Pt}(\text{C}\wedge\text{P})(\text{C}\equiv\text{CPh})_2\text{Ag}\}_2]$ (4) ^b	29.2 (s)	3015	-2.6	412	2019
$[\{\text{Pt}(\text{C}\wedge\text{P})(\text{C}\equiv\text{CPh})_2\text{Ti}\}_2]$ (5) ^a	29.3 (s)	2681	-2.5	78	2088, 2059
$[\{\text{Pt}(\text{C}\wedge\text{P})(\text{C}\equiv\text{CPh})_2\}_2]$ (6) ^c	25.1 (s)	4190	-6.7	1587	1962
$[\text{Pt}(\text{C}\wedge\text{P})(\text{C}\equiv\text{CPh})(\text{CO})]$ (7) ^a	33.6 (s)	2448	+1.8	-155	2127
$[\text{Pt}(\text{C}\wedge\text{P})(\text{C}\equiv\text{CPh})(\text{py})]$ (8) ^a	35.4 (s)	2742	+3.6	139	2102
$[\text{Pt}(\text{C}\wedge\text{P})(\text{C}\equiv\text{CPh})(\text{tht})]$ (9) ^d	31.9 (s)	2696	+0.1	93	2103
$[\text{Pt}(\text{C}\wedge\text{P})(\text{C}\equiv\text{CPh})(\text{PPh}_3)]$ (10) ^b	32.6 (ν_{A}) 25.6 (ν_{B})	2913	+0.8	310	2094
$J_{\text{A-B}} = 433$ Hz					
$(\text{NBu}_4)[\text{Pt}(\text{C}\wedge\text{P})(\text{C}\equiv\text{CPh})_2\text{Pd}(\text{C}_6\text{F}_5)_2]$ (11) ^a	33.3 (s)	3013	+1.5	410	2033
$(\text{NBu}_4)[\text{Pt}(\text{C}\wedge\text{P})(\text{C}\equiv\text{CPh})_2\text{Pt}(\text{C}_6\text{F}_5)_2]$ (12) ^a	27.9 (s)	4223	-3.9	1620	1957
$(\text{NBu}_4)[\text{Pt}(\text{C}_6\text{F}_5)_2(\text{C}\equiv\text{CPh})(\text{PPh}_3)]$ (13) ^b	16.5 (s)	2543			2104

^a Conditions: 300 MHz, CD_2Cl_2 , 293 K. ^b Conditions: 400 MHz, CD_2Cl_2 , 293 K. ^c Conditions: 300 MHz, CDCl_3 , 328 K. ^d Conditions: 300 MHz, CDCl_3 , 293 K. ^e Δ_{P} (ppm) = $\delta(\text{P}) - \delta(\text{P}(2))$. ^f $\Delta J_{\text{Pt-P}}$ (Hz) = $J_{\text{Pt-P}} - J_{\text{Pt-P}}(2)$.

**Figure 2.** Molecular structure of the anion of compound 2.**Table 2.** Selected Bond Distances (Å) and Angles (deg) for $\text{NBu}_4[\text{Pt}(\text{C}\wedge\text{P})(\text{C}\equiv\text{CPh})_2]$ (**2**)

Pt–C1	1.973(5)	Pt–C9	1.998(5)
Pt–C23	2.097(4)	Pt–P(1)	2.2501(13)
C(1)–C(2)	1.198(6)	C(9)–C(10)	1.213(5)
C(1)–Pt–C(9)	91.66(18)	C(1)–Pt–C(23)	88.20(17)
C(9)–Pt–P(1)	99.37(13)	C(23)–Pt–P(1)	80.82(12)
Pt–C(1)–C(2)	174.7(4)	C(1)–C(2)–C(3)	175.8(12)
Pt–C(9)–C(10)	177.5(4)	C(9)–C(10)–C(11)	178.9(6)

(see the Experimental Section). Both complexes give the expected negative ion $[\text{M} - \text{Q}]^-$ (~100%) in their FAB mass spectra, and conductivity measurements in acetone confirm their behavior as 1:1 electrolytes.⁷⁷ The observation of two $\nu_{\text{C}\equiv\text{C}}$ absorptions (Table 1) in the IR spectrum of compound 2 is consistent with a cis arrangement of the σ -alkynyl ligands around the Pt(II) center,^{14,16} which was later confirmed by X-ray crystallography. In the ^{13}C NMR spectrum of 2 the expected signals for two alkynyl ligands are present. The signals due to the C_α and C_β atoms corresponding to the alkynyl group located trans to the P atom are found at higher field. These signals appear as doublets because of the P–C coupling and show larger values for $^1J_{\text{Pt-C}}$ and $^2J_{\text{Pt-C}}$ as a result of the smaller trans influence of P with respect to the cyclometalated C atom.¹⁴

The X-ray structure of 2 (Figure 2, Table 2) shows that in the anionic complex $[\text{Pt}(\text{C}\wedge\text{P})(\text{C}\equiv\text{CPh})_2]^-$ the platinum(II)

center is bonded to two alkynyl carbon atoms and to the phosphorus and carbon donor atoms of the C,P-cyclometalated phosphine ligand, showing a distorted-square-planar geometry. Structural parameters concerning the five-membered metallacycle are similar to those observed in other complexes containing it.^{71–76,78} The Pt–C_{alkynyl} bond lengths observed are identical within experimental error, in spite of the different trans donor atoms (C or P). These distances are similar to those observed in $(\text{NBu}_4)[\text{Pt}(\text{bzq})(\text{C}\equiv\text{CC}_5\text{H}_4\text{N-2})_2]$ ¹⁴ and slightly longer than those reported for some neutral bis(acetylide) complexes.^{15,79–81} The alkynyl groups lie in the platinum coordination plane⁸² and show the expected linear arrangement.

Heteropolynuclear complexes containing alkynyl bridging ligands connecting metals and lithium centers have been previously reported.^{38,83–86} In compound 1, the singlet observed in its ^7Li NMR spectrum proves the presence of the alkali metal. For this compound a structure of the anion similar to that described for 2 can be proposed on the basis of the analytical and spectroscopic data. The observed small shift of the $\nu_{\text{C}\equiv\text{C}}$ absorption to a lower wavenumber, the small enlargement of the Pt–P coupling constant with respect to compound 2 (Table 1), and the absence of Pt–Li coupling in the ^7Li NMR spectrum of 1, even at 193 K in CD_2Cl_2 ,^{38,83} denote that a very weak interaction, if any, occurs between the Li^+ and the alkynyl fragments or platinum. In spite of the structural similarities of these two compounds, 2 is stable in dichloromethane solution at room temperature for a long time, while under the same conditions, 1 decomposes in 1 h to give $[\{\text{Pt}(\text{C}\wedge\text{P})(\mu\text{-C}\equiv\text{CPh})_2\}]$ (**6**), which will be described in full below.

The anionic complex $[\text{Pt}(\text{C}\wedge\text{P})(\text{C}\equiv\text{CPh})_2]^-$ contains two alkynyl groups and a basic metal center, all electron density rich. Thus, it is capable of coordinating to acidic species through

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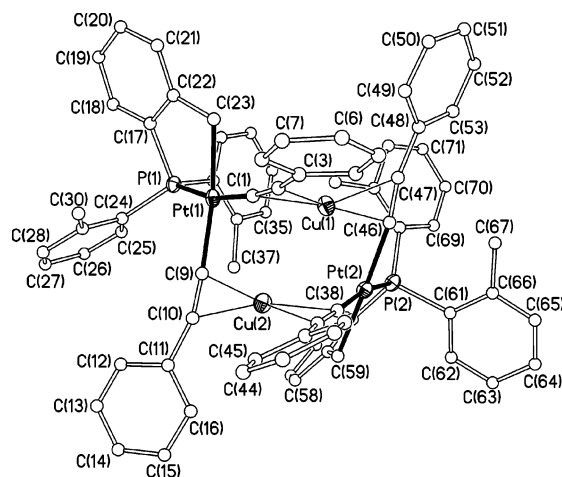


Figure 3. Molecular structure of compound **3**.

different donor atoms. Since compound **2** is more stable and is obtained with a better yield than **1**, it has been used as the starting material in the reactions of the complex anion $[\text{Pt}(\text{C}\equiv\text{P})(\text{C}\equiv\text{CPh})_2]^-$ with Lewis acid species containing transition metals.

Reactivity of $(\text{NBu}_4)[\text{Pt}(\text{C}\equiv\text{P})(\text{C}\equiv\text{CPh})_2]$ (2**) toward Lewis Acid Species of $\text{M}(\text{I})$ ($\text{M} = \text{Cu}, \text{Ag}, \text{Au}, \text{Tl}$).** The reactions of **2** with monovalent metal species such as $[\text{Cu}(\text{NCMe})_4]\text{PF}_6$, AgClO_4 , and TlPF_6 in a 1:1 molar ratio (Scheme 1c–e) allowed the compounds $[\{\text{Pt}(\text{C}\equiv\text{P})(\text{C}\equiv\text{CPh})_2\text{M}\}_2]$ ($\text{M} = \text{Cu}$ (**3**), Ag (**4**), Tl (**5**)) to be obtained in moderate yields (55–69%) as air- and temperature-stable solids. However, the reactions of **2** with $[\text{Au}(\text{tht})_2]\text{ClO}_4$ at different temperatures (–30, 0, 20 °C) render, in all cases, mixtures of species from which we have not been able to isolate and characterize any mixed-metal platinum–gold alkynyl complex.

The new compounds $[\{\text{Pt}(\text{C}\equiv\text{P})(\text{C}\equiv\text{CPh})_2\text{M}\}_2]$ ($\text{M} = \text{Cu}$ (**3**), Ag (**4**), Tl (**5**)) were characterized by the usual analytical and spectroscopic means (see the Experimental Section).

The spectroscopic data for **3** and **4** are quite similar, indicating that they display the same structure, represented in Scheme 1. The IR spectra of **3** and **4** show $\nu_{\text{C}\equiv\text{C}}$ absorptions shifted to lower wavenumbers with respect to those of the starting material, **2**; additionally, the ^{31}P NMR spectra of **3** and **4** show a Pt–P coupling constant that is more than 400 Hz greater than for **2** (Table 1). According to the literature, these variations in the IR^{48,56,65} and NMR⁶⁵ data with respect to the starting material, **2**, suggest the interaction of the $\text{M}(\text{I})$ atoms with the π electron density of the alkynyl ligands.

The structure of **3** has been established by an X-ray diffraction study (Figure 3, Table 3). It is a tetranuclear complex formed by two square-planar “ $\text{Pt}(\text{C}\equiv\text{P})(\text{C}\equiv\text{CPh})_2$ ” fragments held together by two copper atoms, each one π bonded to two phenylethynyl groups, one from each fragment, in such a way that the dihedral angle between the platinum coordination planes is 56.3(1)°.

The Cu atoms are bonded to the π electron density of the $\text{C}\equiv\text{C}$ triple bond of two alkynyl ligands in a η^2 coordination mode. The Cu atoms can be considered to have a linear coordination environment, since the $\text{C}_0\text{--Cu--C}_{0'}$ (C_0 and $\text{C}_{0'}$ are the midpoints of the $\text{C}\equiv\text{C}$ vectors bonded to each Cu) angles are 160.7(1)° (Cu(1)) and 172.7(1)° (Cu(2)), respectively. The η^2 linkages are somewhat asymmetric, as the Cu– C_α lengths are shorter than the Cu– C_β ones, but all (ca. 2.0 Å) are in the range of distances observed in other compounds containing

Table 3. Selected Bond Distances (Å) and Angles (deg) for $[\{\text{Pt}(\text{C}\equiv\text{P})(\text{C}\equiv\text{CPh})_2\text{Cu}\}_2]$ (**3**)

Pt(1)–C(1)	2.004(4)	Pt(1)–C(9)	2.023(4)
Pt(1)–C(23)	2.090(4)	Pt(1)–P(1)	2.2574(11)
Pt(2)–C(38)	2.007(4)	Pt(2)–C(46)	2.018(5)
Pt(2)–C(60)	2.105(4)	Pt(2)–P(2)	2.2654(11)
Cu(1)–C(1)	2.007(4)	Cu(1)–C(2)	2.106(4)
Cu(1)–C(46)	1.996(4)	Cu(1)–C(47)	2.132(4)
Cu(2)–C(9)	1.970(4)	Cu(2)–C(10)	2.098(4)
Cu(2)–C(38)	2.005(4)	Cu(2)–C(39)	2.128(4)
C(1)–C(2)	1.235(6)	C(9)–C(10)	1.214(6)
C(38)–C(39)	1.222(6)	C(46)–C(47)	1.245(6)
Pt(1)–Cu(1)	3.1793(5)	Pt(1)–Cu(2)	3.1569(5)
Pt(2)–Cu(1)	2.9436(6)	Pt(2)–Cu(2)	3.0413(5)
Cu(1)–Cu(2)	3.0358(7)		
C(1)–Pt(1)–C(9)	96.25(17)	C(1)–Pt(1)–C(23)	85.76(17)
C(9)–Pt(1)–P(1)	95.28(12)	C(23)–Pt(1)–P(1)	82.82(12)
C(38)–Pt(2)–C(46)	92.88(17)	C(38)–Pt(2)–C(60)	89.26(17)
C(46)–Pt(2)–P(2)	96.71(13)	C(60)–Pt(2)–P(2)	81.31(13)
Pt(1)–C(1)–C(2)	172.9(4)	C(1)–C(2)–C(3)	168.1(4)
Pt(1)–C(9)–C(10)	176.1(4)	C(9)–C(10)–C(11)	162.1(5)
Pt(2)–C(38)–C(39)	177.0(4)	C(38)–C(39)–C(40)	165.8(4)
Pt(2)–C(46)–C(47)	170.8(4)	C(46)–C(47)–C(48)	164.6(5)

Cu π bonded to the $\text{C}\equiv\text{C}$ triple bond of two acetylide groups.^{30,40,52,59,87–92}

Each “ $\text{Pt}(\text{C}\equiv\text{P})(\text{C}\equiv\text{CPh})_2$ ” fragment contains a Pt atom in a slightly distorted square planar geometry, with Pt–C,^{71–76,78} Pt–P,^{71–76,78} and Pt–C_{alkynyl}^{14,21,79–81,48,56,93} bond distances similar to those observed in other complexes with the same kinds of ligands. The alkynyl ligands mostly lie in their corresponding platinum coordination planes with angles between the $\text{C}_\alpha\equiv\text{C}_\beta$ vectors and the perpendicular to the platinum coordination planes of 89.56° (C(1)–C(2)), 86.38° (C(9)–C(10)), 89.41° (C(38)–C(39)), and 79.95° (C(46)–C(47)).⁸² The structural details concerning the Pt–alkynyl units $[\text{Pt}–\text{C}_\alpha\equiv\text{C}_\beta–\text{CPh}]$ are typical of $\mu_2\text{--}\eta^2(\sigma,\pi)$ -alkynyl bridging complexes.^{48,60,65,70} In particular, these units deviate from linearity (Table 3), this distortion being more remarkable at the C_β atom, with the $\text{C}_\alpha\equiv\text{C}_\beta$ lengths being longer than those of typical terminal alkynyl complexes and even somewhat longer than those reported for other mixed-metal platinum–copper(I) complexes.²⁰ The $\text{Pt}\cdots\text{Cu}$ (2.944(1)–3.179(1) Å) and $\text{Cu}\cdots\text{Cu}$ (3.036(1) Å) intermetallic distances are long enough to exclude metal–metal bonds.⁹⁴

When we focus on the complex $[\{\text{Pt}(\text{C}\equiv\text{P})(\text{C}\equiv\text{CPh})_2\text{Tl}\}_2]$ (**5**), it can be seen that its IR and NMR spectroscopic data are different from those observed for **3** and **4**, since the $\nu_{\text{C}\equiv\text{C}}$ absorptions and the Pt–P coupling constant scarcely differ from those of the starting material, **2** (Table 1). A structure such as that shown in Scheme 1 is tentatively proposed for **5**, taking into account that $\text{Pt}^{\text{II}}\text{--Tl}^{\text{I}}$ –alkynyl clusters containing donor–acceptor $\text{Pt}^{\text{II}}\text{--Tl}^{\text{I}}$ bonds have been described^{38,39,51} and that the ^{31}P NMR at –80 °C shows one doublet with its corresponding ^{195}Pt satellites as a consequence of a strong coupling of P to a thallium center (400 MHz, CD_2Cl_2 , δ 25.24 ppm, $J_{203,205\text{Tl--P}} = 409.9$ Hz, $J_{195\text{Pt--P}} = 2629.3$ Hz). The proposed structure explains

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the spectroscopic data on the basis of the following considerations: (a) the π coordination of the Pt–alkynyl units of **2** to an acidic metal (Cu(I) and Ag(I)) causes the $\nu_{\text{C}\equiv\text{C}}$ absorption to shift to lower wavenumbers and the $^1J_{\text{Pt-P}}$ value to increase in about 400 Hz and (b) the existence of a Pt→M donor–acceptor bond in complexes containing the metallacycle “Pt(C $\wedge$ P)” causes a decrease in the value of $^1J_{\text{Pt-P}}$ of about 300–700 Hz.^{71,73–75} If in complex **5** the Pt–alkynyl units are π coordinated to an acidic metal atom (Tl) and the Pt center is involved in a Pt→Tl donor–acceptor bond, the effect of both facts would compensate one another, making the $J_{\text{Pt-P}}$ value not much different from that of the starting material, **2**. Also, the existence of Pt→Tl donor–acceptor bonds in complex **5** would cause the weakening of the π Tl–alkynyl interactions, accounting for the small shift of the $\nu_{\text{C}\equiv\text{C}}$ absorptions to lower wavenumbers with respect to **2**.

Reactivity of 2 toward the Lewis Acid Species [Pt(C $\wedge$ P)(THF)₂]⁺. Synthesis and Characterization of [{Pt(C $\wedge$ P)(μ -C $\equiv$ CPh)}₂] (6**).** The bis(σ -alkynyl) complex (NBu₄)[Pt(C $\wedge$ P)(C $\equiv$ CPh)₂] (**2**) reacts with the equimolar amount of the cationic species [Pt(C $\wedge$ P)(THF)₂](ClO₄), which is prepared “in situ” from [{Pt(C $\wedge$ P)(μ -Cl)]₂⁷⁸ and AgClO₄ to give the neutral homodinuclear complex [{Pt(C $\wedge$ P)(μ -C $\equiv$ CPh)}₂] (**6**) (Scheme 1f). Complex **6** results from an alkynylating process of the “Pt(C $\wedge$ P)” fragment and was isolated as an air- and temperature-stable solid in good yield. It can also be prepared straightforwardly by treating the dinuclear chloro-bridged complex [{Pt(C $\wedge$ P)(μ -Cl)]₂ with the stoichiometric amount of LiC $\equiv$ CPh (1:2 molar ratio) in THF at low temperature (Scheme 1g). This one-step synthetic process of **6** is noteworthy, since reactions with organolithium compounds are not usually made in stoichiometric relation to achieve partially alkylated organometallic compounds. In this case the synthesis of **6** could take place through two reaction pathways: (a) monoalkynylation to give the unsaturated fragment “Pt(C $\wedge$ P)(σ -C $\equiv$ CPh)”, which dimerizes to give [{Pt(C $\wedge$ P)(μ -C $\equiv$ CPh)}₂] (**6**) in good yield (61%), or (b) the initial formation of **2** and subsequent reaction with the unreacted [{Pt(C $\wedge$ P)(μ -Cl)]₂. In fact, the reaction of (NBu₄)[Pt(C $\wedge$ P)(C $\equiv$ CPh)₂] (**2**) with [{Pt(C $\wedge$ P)(μ -Cl)]₂ in a 2:1 molar ratio in THF renders [{Pt(C $\wedge$ P)(μ -C $\equiv$ CPh)}₂] (**6**), which was obtained in 78% yield after evaporation to dryness and addition of methanol to the residue.⁹⁵

Compound **6** was fully characterized by the usual analytical and spectroscopic means and also by X-ray crystallography. Its X-ray structure (Figure 4, Table 4) shows that it is a double alkynyl bridged dinuclear complex formed by two identical “Pt(CH₂C₆H₄P(*o*-tolyl)₂)(μ -C $\equiv$ CPh)” fragments held together by the interaction of the Pt atom of one fragment with the π electron density of the alkynyl ligand from the other. Each platinum center shows a distorted-square-planar coordination environment formed by the phosphorus and carbon donor atoms of the C $\wedge$ P ligand, the C of the σ -bonded alkynyl ligand, and C₀ (C₀ being the midpoint of the C $\equiv$ C vector π -bonded), since the angles between cis ligands deviate notably from 90°. The alkynyl ligands adopt the bonding pattern depicted in **G** in Figure 1, each one being trans with respect to the σ -C atom of the C $\wedge$ P. The central C₄Pt₂ core is not planar, and the best least-squares planes defined for Pt, C(1'), C(2'), Pt' and Pt, C(1), C(2), Pt' form a dihedral angle of 131.8(1)°. Similar nonplanar structures have been found previously in [C₆F₅]₂Pt(μ -C $\equiv$ CPh)₂Pt(C₆F₅)₂]²⁻⁶⁵ and [Ir(COD)(C $\equiv$ CPh)]₂.⁹⁶ The Pt–C(1')

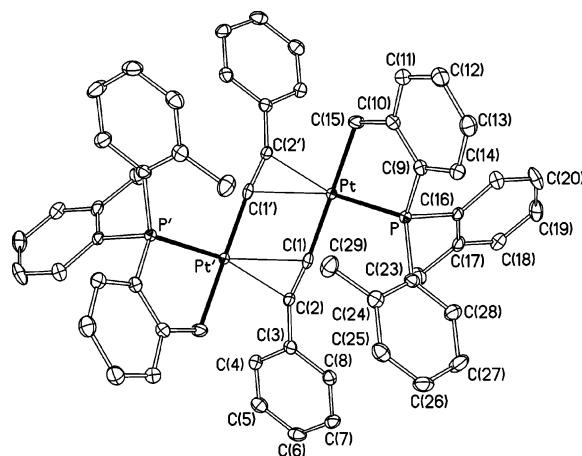


Figure 4. Molecular structure of compound **6** (50% probability ellipsoids).

Table 4. Selected Bond Distances (Å) and Angles (deg) for [{Pt(C $\wedge$ P)(μ -C $\equiv$ CPh)}₂] (**6**)

Pt–C(1)	2.039(3)	Pt–C(15)	2.150(3)
Pt–C(1')	2.368(3)	Pt–C(2')	2.311(3)
Pt–P	2.2600(7)	C(1)–C(2)	1.255(4)
C(1)–Pt–P	97.05(8)	C(15)–Pt–P	81.88(8)
C ₀ '–Pt–C(1)	83.1(1)	C ₀ '–Pt–C(15)	97.5(1)

and Pt–C(2') lengths are equal within experimental error, indicating the symmetry of the platinum acetylide π -linkages. Symmetrical⁶⁵ and asymmetrical⁷⁰ η^2 -acetylide–platinum linkages have been described previously. The structural details concerning the Pt–alkynyl units [Pt–C α ≡C β –C ϕ] are typical of μ_2 - $\eta^2(\sigma,\pi)$ -alkynyl bridging complexes.^{48,60,65,70} In particular, these units deviate from linearity, this distortion being more pronounced at the C β atom, and the C α ≡C β lengths are slightly elongated with respect to terminal alkynyl complexes.

Structural details concerning the “Pt(C $\wedge$ P)” metallacycle are similar to those observed in other complexes containing it.^{71–76,78} The best plane defined by the metallacycle atoms (Pt, P, C(9), C(10), C(15)) and the platinum coordination plane, defined by Pt, C(1), P, C(15), and C₀ (C₀ being the midpoint of the C $\equiv$ C vector π -bonded), are almost coplanar, the dihedral angle being 19.0(1)°. The intermetallic distance, 3.446(1) Å, is long enough to exclude any Pt–Pt bonding interaction.

The IR spectrum of **6** shows one absorption in the C $\equiv$ C bond region that is perceptibly shifted to lower wavenumbers compared to those observed in complexes with terminal σ -acetylide ligand (complexes **1** and **2**) or even μ_2 - η^2 - σ,π -acetylide ligands (complexes **3** and **4**) attributable to the “Pt(μ -C $\equiv$ C)₂Pt” moiety.^{65,70} The ¹H NMR and ³¹P NMR spectra show the expected signals for a half of the molecule in agreement with its symmetry; however, while the ¹H NMR does not show relevant changes with respect to that of compound **2**, the ³¹P NMR spectrum does, since it strongly depends on the alkynyl bond pattern. Thus, the trans disposition of a π -alkynyl ligand with the P atom causes the ³¹P signal to be shifted to higher field by about 7 ppm with respect to complex **2** and the $J_{\text{Pt-P}}$ value to increase by almost 1600 Hz (Table 1), in agreement with the smaller trans influence of the π -alkynyl with respect to the σ -alkynyl ligand.

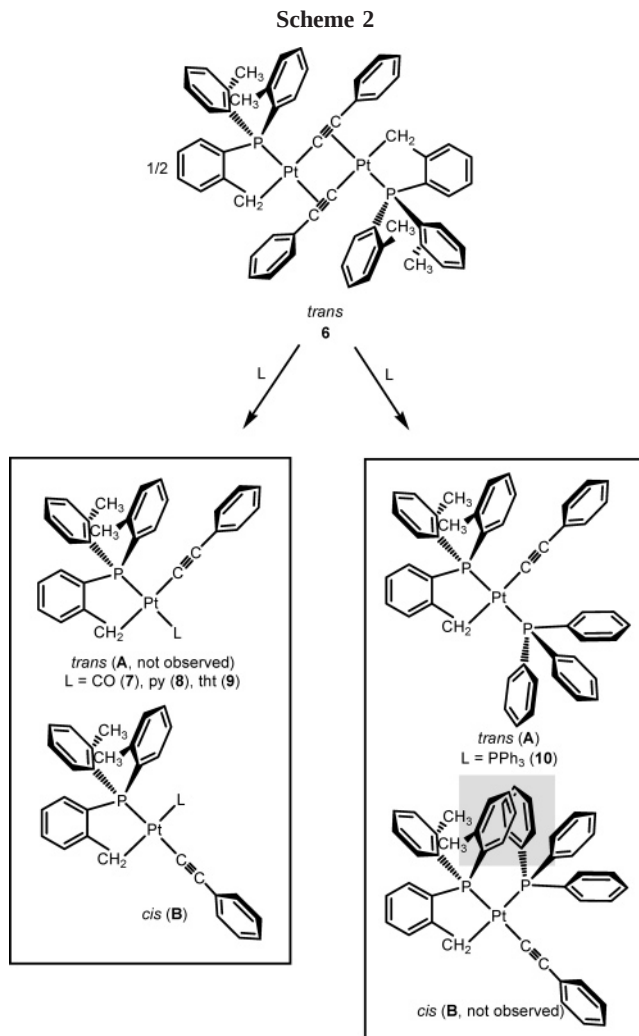
The spectroscopic and X-ray data indicate that the isomer with a trans disposition of the σ -C bonds around the platinum center is the only one obtained by each one of the two synthetic methods described here. The treatment of [{Pt(C $\wedge$ P)(μ -Cl)]₂ with LiC $\equiv$ CPh thus allows not only the monoalkynylation of the platinum fragment “Pt(C $\wedge$ P)” but also the selectivity of it,

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affording the unit *trans*-“Pt(C $\wedge$ P)(σ -C $\equiv$ CPh)”, which dimerizes to $[\{\text{Pt}(\text{C}\wedge\text{P})(\mu\text{-C}\equiv\text{CPh})\}_2]$ (**6**). The high stability of **6** is also evident, considering that it precipitates “in situ” when solutions of **1** are stirred for 1 h or more.

Reactivity of $[\{\text{Pt}(\text{C}\wedge\text{P})(\mu\text{-C}\equiv\text{CPh})\}_2]$ (6**) toward Mono-dentate Ligands.** Complex **6** reacts with several neutral monodentate ligands such as CO, py, tht, and PPh₃ in a 1:2 molar ratio (see the Experimental Section) to give the neutral mononuclear complexes $[\text{Pt}(\text{C}\wedge\text{P})(\text{C}\equiv\text{CPh})\text{L}]$ (L = CO (**7**), py (**8**), tht (**9**), PPh₃ (**10**)) as pure compounds (Scheme 1h,i). Complexes **7–10** were characterized by common analytical and spectroscopic means (see the Experimental Section). All of them are neutral and exhibit one IR absorption of medium intensity close to 2100 cm⁻¹ assignable to the $\nu_{\text{C}\equiv\text{C}}$ absorption of a terminal σ -alkynyl group.^{14,16,21} For complex **7**, the presence of a terminal CO coordinated to platinum is reflected by an absorption at 2079 cm⁻¹ assignable to $\nu(\text{CO})$. Similar values have been reported in carbonyl complexes with the CO trans to a σ -C donor ligand (ν_{CO} : 2086 cm⁻¹, $[\text{Pt}\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-}o,o'\}(\text{CO})]$,⁹⁷ 2079 cm⁻¹, $[\text{Pt}(\text{Et})(\text{CO})(\text{PEt}_3)_2]^+$;⁹⁸ 2078–2092 cm⁻¹, $[(\text{CO})(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-}\eta^2\text{-C}\equiv\text{CR})\text{Pt}(\text{C}\equiv\text{CR})(\text{PR}_3)_2]$ ⁹⁹). The ³¹P NMR spectra of complexes **7–9** show one singlet with the corresponding ¹⁹⁵Pt satellites and the typical signals of an AB system for complex **10**. In agreement with their stoichiometry, the ¹³C NMR spectra show the C $_{\alpha}$ and C $_{\beta}$ resonances of only one alkynyl ligand, in addition to the signals due to the other ligands. For these mononuclear compounds two isomers are possible, depending on the *trans* or *cis* disposition of the two σ -C-donor ligands [C(C $\wedge$ P), σ -C $\equiv$ CPh] around the Pt center, depicted as **A** and **B** in Scheme 2. The *trans* isomer, **A**, results from complex **6** if the substitution of the π -acetylide by the neutral ligand, L, in the coordination sphere of each Pt center proceeds with stereoretention. If not, the *cis* isomer, **B** (Scheme 2), is formed. The ³¹P NMR signals strongly depend on the ligand *trans* to the phosphorus atom. In complex **10**, the magnitude of ²J_{P–P} (433 Hz) is consistent with the *trans* disposition of the two P atoms (**A**).¹⁰⁰ Considering the general observation that a smaller J_{Pt–P} value corresponds to a larger *trans* influence of the ligand *trans* to P, if all the complexes (**7–10**) exhibited the same structure (**A**), the expected values of J_{Pt–P} for complexes **7–9** would be larger than for complex **10**. As complexes **7–9** show smaller Pt–P coupling than **10**, the structure depicted as **B** seems to be more plausible for them. This assumption is supported by several facts. (a) The J_{Pt–P} values in complexes **8** (L = py) and **9** (L = tht) are similar to that observed in complex **2**, in which the P is *trans* to a σ -alkynyl group, and smaller than that expected for the **A** isomer.¹⁰¹ (b) The observed P–C coupling for the C $_{\alpha}$ and C $_{\beta}$ atoms of the alkynyl group (see ¹³C NMR data in the Experimental Section) indicates the *trans* disposition of this ligand with respect to P; this coupling is not observed for complex **10** (L = PPh₃). (c) The values of δ_{CO} and J_{Pt–C} observed in the ¹³C NMR spectrum of **7** indicate the *trans* disposition of CO to an alkyl ligand.¹⁰² The single-crystal X-ray diffraction study carried out on complex



7 (Figure 5, Table 5) confirmed the proposed structure for these complexes (**7–9**).

Assuming the **B** structure for complexes **7–9** (L = CO, py, tht), when the values of J_{Pt–CH₂} in complexes **2** and **7–9** are compared, it can be seen that they decrease in the order L = py (**8**; 637.3 Hz) > tht (**9**; 630.6 Hz) > CO (**7**; 537.4 Hz) > σ -CCPh (**2**; 458.8 Hz). Thus, the *trans* influence should increase as follows: σ -C $\equiv$ CPh > CO > tht > py.

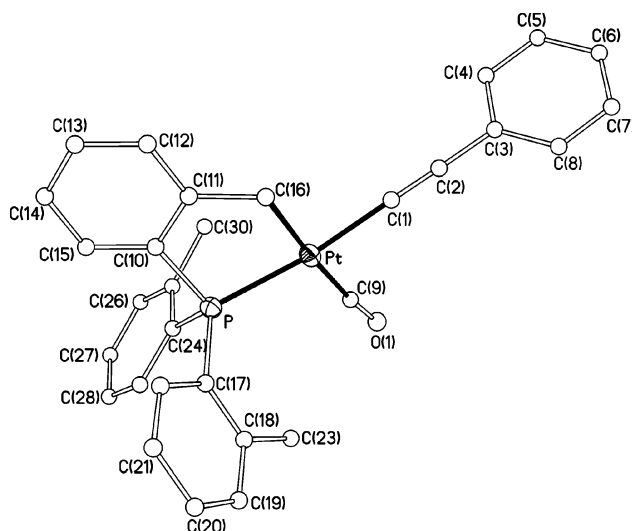


Figure 5. Molecular structure of compound **7**.

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Table 5. Selected Bond Distances (Å) and Angles (deg) for [Pt(C $\wedge$ P)(C $\equiv$ CPh)(CO)] $\cdot$ Me $_2$ CO (7 $\cdot$ Me $_2$ CO)

Pt–C(9)	1.899(5)	Pt–C(1)	2.020(4)
Pt–C(16)	2.096(4)	Pt–P	2.2960(10)
O(1)–C(9)	1.130(6)	C(1)–C(2)	1.192(6)
C(9)–Pt–C(1)	87.39(18)	C(9)–Pt–C(16)	176.37(17)
C(1)–Pt–C(16)	89.10(17)	C(9)–Pt–P	100.97(14)
C(1)–Pt–P	171.53(12)	C(16)–Pt–P	82.51(12)
C(2)–C(1)–Pt	172.0(4)	C(1)–C(2)–C(3)	176.2(4)
O(1)–C(9)–Pt	174.4(4)		

Several spectroscopic facts concerning complex **7** are noteworthy. (a) The low value observed for the ν_{CO} absorption (2079 cm^{-1}) when compared with those of other neutral platinum(II) carbonyl complexes^{103–110} suggests that the metal center in **7** is appreciably electron rich and that there is significant π back-donation to the terminal CO ligand. (b) The high wavenumbers for the $\nu_{\text{C}\equiv\text{C}}$ absorption (2127 cm^{-1}) compared with those in the analogous complexes **8** and **9** and the notable shift of the C_α resonance (101.85 ppm) to a higher field with respect to those in the starting complex, **2** (120.33 ppm, C_α trans to P) indicate the scarce π back-bonding from Pt to the alkynyl ligand (in the remaining mononuclear complexes described in this paper, the C_α resonance appears at a lower field than the C_β resonance, but not in complex **7**), this spectroscopic feature being commonly observed for the compounds *cis*-[Pt(C $_6$ F $_5$) $_2$ -(C $\equiv$ CR) $_2$] $^{2-}$,⁵⁷ [PtCu $_2$ (C $_6$ F $_5$) $_2$ (C $\equiv$ CR) $_2$ (acetone)] $_2$,³⁰ and *cis*-[Pt(C $_6$ F $_5$) $_2$ (μ -C $\equiv$ C'Bu) $_2$]{Cu(bipy)} $_2$.³⁰ (c) The value of $J_{\text{Pt-P(C}\wedge\text{P)}}$ is small in comparison with those in the analogous complexes **8** and **9**. All of these spectroscopic facts can be explained by considering that in complex **7**, the richer π -acceptor character of CO, with respect to σ -alkynyl (**2**), pyridine (**8**), or tht (**9**), is responsible for the scarce π back-bonding to the alkynyl and P $\wedge$ P ligands.

The X-ray structure of compound **7** (Figure 5) shows that it is a mononuclear complex in which the center of Pt(II) shows a distorted-square-planar environment mainly due to the small bite angle of the C $\wedge$ P ligand (82.5(1) $^\circ$). The trans disposition of the σ -alkynyl and P ligands unambiguously indicates that the substitution of π -alkynyl by CO in complex **6** takes place with isomerization. The Pt–P,^{71–76,78} Pt–C $_{\text{C}\wedge\text{P}}$,^{71–76,78} and Pt–C $_{\text{alkynyl}}$ ^{14,15,79–81} distances are all in the range of those observed in complexes of Pt(II) with the same kinds of ligands. While the Pt–P and Pt–C $_{\text{alkynyl}}$ distances are longer with respect to those in complex **2**, the Pt–C $_{\text{C}\wedge\text{P}}$ distance remains invariable. This fact seems to be logical, taking into account that the neutral nature of complex **7** and the presence of a good π acceptor ligand (CO) will reduce the π back-bonding from Pt(II) to the phosphine and the alkynyl ligand, in agreement with the observed spectroscopic facts for it. The Pt–C $_{\text{CO}}$ and C–O

lengths are in the range of those found in other four-coordinate Pt(II) carbonyl complexes.^{103–110} No lengthening of the CO bond as a consequence of the significant π back-donation to the terminal CO ligand, inferred from the low ν_{CO} value, is observed.

Reactivity of (NBu $_4$)[Pt(C $\wedge$ P)(C $\equiv$ CPh) $_2$] (2**) toward [M(C $_6$ F $_5$) $_2$ (THF) $_2$] (M = Pd, Pt).** The reaction of equimolar amounts of the neutral complexes [M(C $_6$ F $_5$) $_2$ (THF) $_2$] (M = Pd, Pt) and the bis(σ -alkynyl) complex (NBu $_4$)[Pt(C $\wedge$ P)(C $\equiv$ CPh) $_2$] (**2**) at room temperature gave the analytically pure compounds (NBu $_4$)[Pt(C $\wedge$ P)(C $\equiv$ CPh) $_2$ M(C $_6$ F $_5$) $_2$] (M = Pd (**11**), Pt (**12**)) in moderate to good yields as air- and temperature-stable solids (Scheme 1j,k). In a solution of CH $_2$ Cl $_2$, compound **11** decomposes after 1 h, but **12** is stable for a longer time. The two compounds were characterized by elemental analysis, conductivity measurements, and IR and NMR (^1H , ^{19}F , ^{31}P) spectroscopy. Conductivity measurements in acetone are similar to those for compound **2** and confirm their behavior as 1:1 electrolytes.⁷⁷

Significant structural information can be extracted from the IR and ^{31}P NMR spectra of these complexes. Two absorptions assignable to the X-sensitive vibration modes of the C $_6$ F $_5$ groups are observed in the IR spectra, indicating the *cis* arrangement of the "M(C $_6$ F $_5$) $_2$ " moiety¹¹¹ in both **11** and **12**. The IR spectra of compounds **11** and **12** also show $\nu_{\text{C}\equiv\text{C}}$ absorptions, but at quite different wavenumbers. Complex **11** shows one absorption at 2033 cm^{-1} , at wavenumbers similar to those of complexes **3–5**, while compound **12** shows one absorption at 1957 cm^{-1} , comparable with that in complex **6**, which contains a "Pt(μ -C $\equiv$ CPh) $_2$ Pt" moiety. The ^{31}P NMR spectra of **11** and **12** show the expected singlet with the corresponding ^{195}Pt satellites, being $J_{\text{Pt-P}} = 3013$ Hz for complex **11**, similar to the values for complexes **3** and **4**, and 4223 Hz for complex **12**, similar to the value for complex **6** (Table 1). In keeping with the above spectroscopic data, it seems sensible to assign to **11** and **12** the molecular structures depicted in Scheme 1, with the bonding patterns for the acetylide groups being **A** and **G** (Figure 1), respectively.

In agreement with these proposed structures, the ^{19}F NMR spectra of **11** and **12** at room temperature exhibit two sets of signals (2:1:2, typical of a AA'MXX' system in which the two ortho fluorine atoms, as well as the meta atoms, are isochronous or become equivalent) in a 1:1 ratio, indicating the inequivalence of the two C $_6$ F $_5$ groups.

The reaction of complex **11** with PPh $_3$ (Scheme 3) in a 1:2 molar ratio was carried out in CD $_2$ Cl $_2$ and monitored by NMR. The ^{31}P NMR spectra, registered at several interval times, show the presence of [Pd(C $_6$ F $_5$) $_2$ (PPh $_3$) $_2$]¹¹² and (NBu $_4$)[Pt(C $\wedge$ P)(C $\equiv$ CPh) $_2$] (**2**) as the major products and remain invariable even 24 h later. The reaction of compound **12** with PPh $_3$ (Scheme 3) in a 1:2 molar ratio gave [Pt(C $\wedge$ P)(C $\equiv$ CPh)(PPh $_3$)] (**10**) and (NBu $_4$)[Pt(C $_6$ F $_5$) $_2$ (C $\equiv$ CPh)(PPh $_3$)] (**13**). The two compounds could be easily separated, because of their very different solubilities in methanol (see the Experimental Section).

Cis/Trans Disposition of the σ -C Bonds in Complexes **6–10 and **12**.** Two isomers are possible for each one of complexes **6–10** and **12**, depending on the *cis* or *trans* disposition of the two σ -C-donor ligands (C(C $\wedge$ P), σ -C $\equiv$ CPh) around the Pt center (Scheme 2 and Chart 1). Compounds **6** and **12** are each formed by selective transfer of an alkynyl group from complex **2** to the cationic and neutral Pt(II) complexes [Pt(C $\wedge$ P)(THF) $_2$] $^+$ and *cis*-[Pt(C $_6$ F $_5$) $_2$ (THF) $_2$]. Complex **6** is also

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Scheme 3

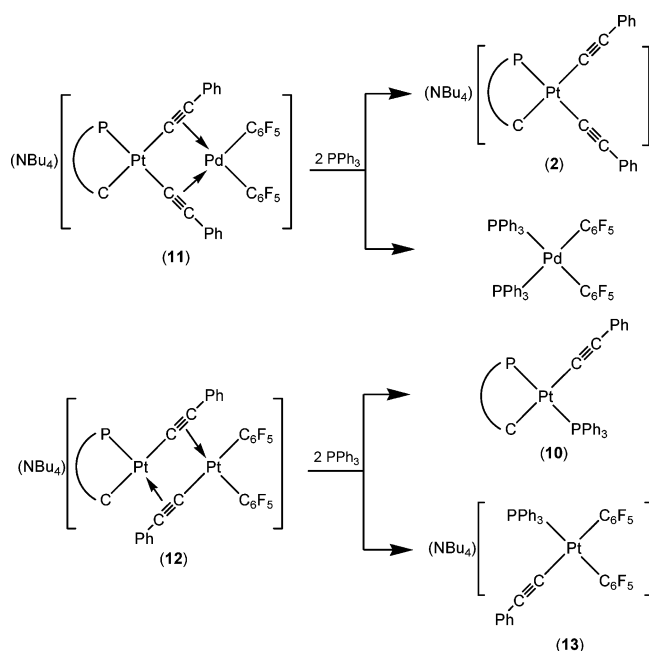
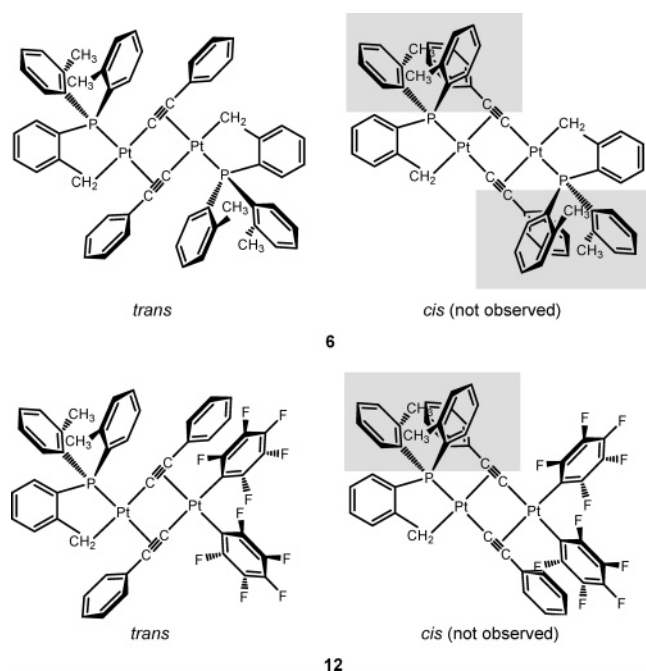


Chart 1



obtained by selective monoalkynylation of a “Pt(C $\wedge$ P)” fragment with LiC $\equiv$ CPh. Complexes 7–10 are obtained by reaction of **6** with 2 equiv of L (L = CO, py, tht, PPh₃) (Scheme 1). In all of these cases, only one of the two possible isomers is formed selectively (Schemes 2 and 3). In an attempt to explain the factors that influence the formation of one isomer instead of the other, we have used the term transphobia (*T*) of pairs of trans ligands, which has been accepted by many authors to explain the geometries of stable square-planar complexes of d⁸ transition metals.^{113–117} The degree of *T* of pairs of trans ligands

has been assumed to be related to the trans influence in such a way that two ligands with large trans influence will suffer a great transphobia. However, the steric requirements of the ligands involved can also play a significant role in determining the geometries of these complexes.^{116,117}

Recent studies on the factors that promote the stability of *cis*- or *trans*-diarylplatinum(II) complexes concluded that “complexes *cis*-[Pt(aryl)₂L₂] are more stable than the *trans* isomers if L ligands are N, O, or S donor ligands because $T[\text{Aryl}/\text{Aryl}] > T[\text{Aryl}/\text{L}(\text{N}, \text{O}, \text{S})]$ unless the aryl or L ligands are highly voluminous. However, because $T[\text{Aryl}/\text{Aryl}]$ is similar to $T[\text{Aryl}/\text{L}(\text{C}, \text{P})]$, the complexes *trans*-[Pt(aryl)₂{L(C,P)}₂] can be more stable than the *cis* isomers if interligand repulsions are important, in such a way that the *cis* isomers can isomerize to their *trans* ones by heating if the temperature required is below their decomposition temperatures and the ligands are sufficiently bulky.”¹¹⁷

Taking into account these assumptions, from the observed $J_{\text{Pt}-\text{P}(\text{C}\wedge\text{P})}$ and $J_{\text{Pt}-\text{C}(\text{alkynyl})}$ values in complexes **2**, **6**, **10**, and **12** the trans influence order must be $\sigma\text{-C}\equiv\text{C} > \text{PPh}_3 > \pi\text{-C}\equiv\text{C}$ and the trans influence of $\sigma\text{-C}(\text{C}\wedge\text{P})$ must be greater than that of P(C $\wedge$ P); then, $T[\text{C}(\sigma\text{-C}\equiv\text{C})/\text{C}(\text{C}\wedge\text{P})]$ is expected to be greater than $T[\text{C}(\sigma\text{-C}\equiv\text{C})/\text{P}(\text{C}\wedge\text{P})]$ and $T[\text{C}(\text{C}\wedge\text{P})/\text{C}(\sigma\text{-C}\equiv\text{C})] > T[\text{C}(\text{C}\wedge\text{P})/\text{L}(\text{PPh}_3)] > T[\text{C}(\text{C}\wedge\text{P})/\text{L}(\pi\text{-C}\equiv\text{C})]$. Thus, the *trans* disposition of the $\sigma\text{-C}$ -donor ligands (C(C $\wedge$ P), $\sigma\text{-C}\equiv\text{C}$) around the Pt center observed in complexes **6** and **12**, despite the expected electronic preferences, can be attributed to the steric hindrance between P(*o*-tolyl)₂ and the Ph group of $\sigma\text{-C}\equiv\text{CPh}$ in the *cis* isomer. The same applies to the other stable *trans* complex [Pt(C $\wedge$ P)(C $\equiv$ CPh)PPh₃] (**10**), which is formed instead of the *cis* isomer, probably because of the crowding associated with the *cis* disposition of P(*o*-tolyl)₂ and PPh₃.

However, the substitution reactions at room temperature on complex **6** with the nonbulky ligands CO, py, and tht do not proceed with stereoretention, giving rise to the complexes *cis*-[Pt(C $\wedge$ P)(C $\equiv$ CPh)L] (L = CO (**7**), py (**8**), tht (**9**)), in agreement with $T[\text{C}(\text{C}\wedge\text{P})/\text{C}(\sigma\text{-C}\equiv\text{C})] > T[\text{C}(\text{C}\wedge\text{P})/\text{C}(\text{CO})] > T[\text{C}(\text{C}\wedge\text{P})/\text{L}(\text{py}, \text{tht})]$. This order in the transphobia (*T*) of pairs of *trans* ligands is in agreement with the trans influence order deduced from the $J_{\text{Pt}-\text{C}(\text{C}\wedge\text{P})}$ values in complexes **2** and **7–9**: $\sigma\text{-C}\equiv\text{C} > \text{CO} > \text{py} \approx \text{tht}$.

Summary

This paper describes the synthesis of the monoanionic bis-(σ -alkynyl) complex [Pt(C $\wedge$ P)(C $\equiv$ CPh)₂][−], that has been isolated as its Li⁺ (**1**) and (NBu₄) (**2**) salts, and its reactivity toward Lewis acid species of transition metals, M (M = Cu(I), Ag(I), Au(I), Tl(I), Pd(II), Pt(II)). These reactions give rise, in many cases, to heteropolynuclear complexes and exhibit different bonding patterns for the bridging alkynyl ligands depending on M.

The reactions with [Cu(NCMe)₄]PF₆ and AgClO₄ show the preference of the M^I centers (M = Cu, Ag) for the electron-rich alkynyl units and give tetranuclear compounds (Pt₂M₂, **3** and **4**) of type C (Figure 1). However, the reaction with TlPF₆ rendered a new Pt–Tl complex (**5**) likely to contain Pt→Tl dative bonds, which shows the higher affinity of thallium for the electron density of platinum(II). In agreement with the scarce number of mixed platinum–gold alkynyl compounds, the reactions of compound **2** with Au(I) species proceed with

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alkylation of the gold center, and no mixed platinum–gold alkynyl compounds could be isolated.

In addition, the reactivity of $(\text{NBu}_4)[\text{Pt}(\text{C}\equiv\text{CPh})_2]$ (**2**) toward the neutral $\text{cis-}[\text{Pd}(\text{C}_6\text{F}_5)_2(\text{THF})_2]$ renders the compound $(\text{NBu}_4)[\text{Pt}(\text{C}\equiv\text{CPh})_2\text{Pd}(\text{C}_6\text{F}_5)_2]$ (**11**), with a bonding pattern of type **A** (Figure 1), which has a very limited stability in solution. However, the reactions with the cationic and neutral Pt(II) complexes $[\text{Pt}(\text{C}\equiv\text{CPh})(\text{THF})_2]^+$ and $\text{cis-}[\text{Pt}(\text{C}_6\text{F}_5)_2(\text{THF})_2]$ render compounds **6** and **12** of type **G** (Figure 1) as a consequence of an alkynylating process. These reactions proceed selectively to give only one of the two possible isomers for compounds **6** and **12**. These compounds are highly stable, even in solution. The cleavage of the bridging system “ $\text{Pt}_2(\mu\text{-C}\equiv\text{CPh})_2$ ” can be achieved by some neutral ligands, L. Thus, the reactions of **6** with L at room temperature in a 1:2 molar ratio give the mono(σ -alkynyl) complexes $[\text{Pt}(\text{C}\equiv\text{CPh})\text{L}]$ (L = CO (**7**), py (**8**), tht (**9**), PPh_3 (**10**)). When L = PPh_3 , the substitution reaction takes place with stereoretention, but not when L = CO, py, and tht.

Two isomers are possible for each one of complexes **6–10** and **12**, depending on the cis or trans disposition of the two σ -C-donor ligands (C(C $\equiv$ C), σ -C $\equiv$ CPh) around the Pt center, but only one has been obtained in each case. This seems to depend as much on the transphobia of pairs of trans ligands as on the steric requirements of cis ligands.

Thus, the cis isomer should be observed on the basis of electronic preferences ($T[\text{C}(\sigma\text{-C}\equiv\text{C})/\text{C}(\text{C}\equiv\text{C})] \geq T[\text{C}(\sigma\text{-C}\equiv\text{C})/\text{P}(\text{C}\equiv\text{C})]$; $T[\text{C}(\text{C}\equiv\text{C})/\text{C}(\sigma\text{-C}\equiv\text{C})] > T[\text{C}(\text{C}\equiv\text{C})/\text{L}(\text{PPh}_3)] > T[\text{C}(\text{C}\equiv\text{C})/\text{L}(\pi\text{-C}\equiv\text{C})]$; $T[\text{C}(\text{C}\equiv\text{C})/\text{C}(\sigma\text{-C}\equiv\text{C})] > T[\text{C}(\text{C}\equiv\text{C})/\text{C}(\text{CO})] > T[\text{C}(\text{C}\equiv\text{C})/\text{L}(\text{py}, \text{tht})$). However, the trans disposition of the σ -C-donor ligands (C(C $\equiv$ C), σ -C $\equiv$ C) around the Pt center is observed in complexes **6**, **12**, and **10**, which can be attributed to the steric hindrance between P(o-tolyl)₂ and the Ph group of σ -C $\equiv$ CPh in the cis isomer (complexes **6** and **12**) or P(o-tolyl)₂ and PPh_3 in complex **10**.

When L ligands are the nonbulky CO, py, and tht, the expected more stable cis isomers were obtained.

Experimental Section

General Procedures and Materials. Elemental analyses were carried out in a Perkin-Elmer 240-B microanalyzer. IR spectra were recorded on a Perkin-Elmer 599 spectrophotometer (Nujol mulls between polyethylene plates in the range 350–4000 cm^{-1}). NMR spectra were recorded on Varian Unity-300 and Bruker 400 spectrometers by using the standard references: TMS for ^1H , H_3PO_4 for ^{31}P , and LiCl in H_2O for ^7Li . All of the ^{31}P and ^{13}C NMR experiments were proton-decoupled. Mass spectral analyses were performed with a VG Autospec instrument. THT and phenylacetylene were purchased from Merck, TiPF_6 from Strem Chemicals, and PPh_3 from Fluka. $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$,¹¹⁸ $\text{PPN-}[\text{Au}(\text{acac})_2]$,¹¹⁹ $[\text{Au}(\text{tht})_2]\text{ClO}_4$,¹²⁰ AgClO_4 ,¹²¹ $[\{\text{Pt}(\text{C}\equiv\text{CPh})(\mu\text{-Cl})\}_2]$,⁷⁸ $[\text{cis-Pd}(\text{C}_6\text{F}_5)_2(\text{THF})_2]$,¹²² and $[\text{cis-Pt}(\text{C}_6\text{F}_5)_2(\text{THF})_2]$,¹²² were prepared as described elsewhere.

$[\text{Pt}(\text{C}\equiv\text{CPh})_2]$ (1**).** A solution of $^n\text{BuLi}$ (2.5 mmol) in THF (15 mL) was added to a solution of $\text{HC}\equiv\text{CPh}$ (0.283 mL, 2.50 mmol) in THF at low temperature (ca -20°C) under an argon atmosphere. The mixture was stirred for 15 min, and then

$[\{\text{Pt}(\text{C}\equiv\text{CPh})(\mu\text{-Cl})\}_2]$ (0.667 g, 0.62 mmol) was added and allowed to react at room temperature for 15 h. The resulting mixture was air-evaporated to dryness. CHCl_3 (3×30 mL) was added to the residue at 0°C , the mixture was filtered through Celite, and the resulting solution was evaporated to dryness. The oily residue was treated with $i\text{PrOH}$ (15 mL) and n -hexane (30 mL) and the resulting solution evaporated to dryness. Addition of n -hexane gave **1** as a brown solid. Yield: 0.385 g, 49%. Anal. Calcd for $\text{C}_{37}\text{H}_{30}\text{LiPt}$: C, 62.86; H, 4.24. Found: C, 62.60; H, 4.40. Negative FAB-MS (m/z (%)): 700 (90) $[\text{M} - \text{Li}]^-$. IR (Nujol, cm^{-1}): ν 2078 (m, C $\equiv$ C). ^1H NMR (300 MHz, CD_2Cl_2 , 293 K): δ 6.7–7.7 (m, 22H, Ph groups), 3.1 (s, 2H, CH_2 , $^2J_{\text{Pt-H}} = 63.9$ Hz), 2.64 (s, 6H, Me). ^{31}P NMR (300 MHz, CD_2Cl_2 , 293 K, ppm): δ 32.0 (s, $^1J_{\text{Pt-P}} = 2746$ Hz). ^7Li NMR (400 MHz, CD_2Cl_2 , 293 K, ppm): δ 0.43 (s). $\Lambda_{\text{M}} = 32.31 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ (solution 2.5×10^{-4} M in acetone).

$\text{NBu}_4[\text{Pt}(\text{C}\equiv\text{CPh})_2]$ (2**).** A solution of $^n\text{BuLi}$ (5.0 mmol) in THF (15 mL) was added to a solution of $\text{HC}\equiv\text{CPh}$ (0.566 mL, 5.0 mmol) in THF at low temperature (ca. -20°C) under an argon atmosphere. The mixture was stirred for 15 min, and then $[\{\text{Pt}(\text{C}\equiv\text{CPh})(\mu\text{-Cl})\}_2]$ (1.067 g, 1.00 mmol) was added and allowed to react at room temperature for 15 h. The resulting mixture was air-evaporated to dryness. CHCl_3 (3×30 mL) was added to the residue at 0°C , the mixture was filtered through Celite, and the solution was evaporated to dryness. $i\text{PrOH}$ (50 mL) and NBu_4Br (1.210 g, 3.75 mmol) were added to the residue to give a light brown solid of **2**, which was filtered and washed with n -hexane (10 mL) and Et_2O (10 mL). Yield: 1.49 g, 79%. Anal. Calcd for $\text{C}_{53}\text{H}_{66}\text{NBu}_4\text{Pt}$: C, 67.52; H, 7.06; N, 1.48. Found: C, 67.48; H, 6.94; N, 1.60. Negative FAB-MS (m/z (%)): 700 (100) $[\text{M} - \text{NBu}_4]^+$. IR (Nujol, cm^{-1}): ν 2098 (m, C $\equiv$ C), 2081 (m, C $\equiv$ C). ^1H NMR (300 MHz, CD_2Cl_2 , 293 K, ppm): δ 6.7–7.5 (m, 22 H, Ph groups), 3.09 (m, 8 H, CH_2 , NBu_4^+), 2.96 (s, 2 H, CH_2 , $^2J_{\text{Pt-H}} = 64.8$ Hz), 2.75 (s, 6 H, CH_3), 1.43 (m, 8 H, CH_2 , NBu_4^+), 1.26 (m, 8 H, CH_2 , NBu_4^+), 0.83 (t, $^3J_{\text{H-H}} = 6.9$ Hz, 12 H, CH_3 , NBu_4^+). ^{13}C NMR (400 MHz, CD_2Cl_2 , 293 K, ppm): δ 165–123 (C_{Ph} , $\text{C}_{\alpha}\equiv\text{C}$ trans to C), 120.33 (d, $^2J_{\text{P-C}} = 160.0$ Hz, $J_{\text{Pt-C}} = 1260.0$ Hz, $\text{C}_{\alpha}\equiv\text{C}$ trans to P), 107.86 (s, $^2J_{\text{Pt-C}} = 231.8$ Hz, $\text{C}_{\beta}=\text{C}$ trans to C), 105.69 (d, $^3J_{\text{P-C}} = 39.6$ Hz, $^2J_{\text{Pt-C}} = 354.0$ Hz $\text{C}_{\beta}=\text{C}$ trans to P), 23.40 (s, $J_{\text{Pt-C}} = 458.8$ Hz, CH_2), 23.67 (s, broad, Me). ^{31}P NMR (300 MHz, CD_2Cl_2 , 293 K, ppm): δ 31.8 (s, $^1J_{\text{Pt-P}} = 2603$ Hz). $\Lambda_{\text{M}} = 45.53 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ (solution 5.1×10^{-4} M in acetone).

$[\{\text{Pt}(\text{C}\equiv\text{CPh})_2\text{Cu}\}_2]$ (3**).** **2** (0.208 g, 0.22 mmol) was added to a colorless solution of $[\text{Cu}(\text{NCMe})_4]\text{PF}_6$ (0.082 g, 0.22 mmol) in CH_2Cl_2 (10 mL) under an argon atmosphere in a ice bath, giving rise to a dark orange solution. The mixture was allowed to react for 30 min, and then the solvent was evaporated to dryness. Addition of MeOH (20 mL) to the residue gave **3**, which was filtered, washed with MeOH (10 mL), and air-dried. Yield: 0.117 g, 69%. Anal. Calcd for $\text{C}_{74}\text{H}_{60}\text{Cu}_2\text{P}_2\text{Pt}_2$: C, 58.17; H, 3.92. Found: C, 57.86; H, 3.55. IR (Nujol, cm^{-1}): ν 2007 (w, C $\equiv$ C), 1971 (w, C $\equiv$ C). ^1H NMR (300 MHz, CD_2Cl_2 , 293 K, ppm): δ 6.7–7.6 (m, 44 H, Ph groups), 3.28 (s, 4 H, CH_2 , $^2J_{\text{Pt-H}} = 66.0$ Hz), 2.45 (s, 12 H, Me). ^{31}P NMR (300 MHz, CD_2Cl_2 , 293 K, ppm): δ 30.2 (s, $^1J_{\text{Pt-P}} = 3056$ Hz).

$[\{\text{Pt}(\text{C}\equiv\text{CPh})_2\text{Ag}\}_2]$ (4**).** A solution of **2** (0.2055 g, 0.2179 mmol) in CH_2Cl_2 (15 mL) was added to a colorless solution of AgClO_4 (0.0452 g, 0.2180 mmol) in diethyl ether (8 mL) at room temperature, giving rise to a dark orange solution. The mixture was allowed to react for 2 h in the dark; then the solvent was evaporated to dryness and MeOH (20 mL) was added to the residue. The solid was recrystallized from diethyl ether/methanol to give **4** as an orange solid. Yield: 0.1091 g, 62%. Anal. Calcd for $\text{Ag}_2\text{C}_{74}\text{H}_{60}\text{P}_2\text{Pt}_2$: C, 54.96; H, 3.71. Found: C, 55.08; H, 3.87. IR (Nujol, cm^{-1}): ν 2019 (w, C $\equiv$ C). ^1H NMR (300 MHz, CD_2Cl_2 , 293 K, ppm): δ 6.7–7.6 (m, 44 H, Ph groups), 3.33 (s, 4 H, CH_2 , $^2J_{\text{Pt-H}} = 65.0$ Hz), 2.54 (s, 12 H, Me). ^{31}P NMR (400 MHz, CD_2Cl_2 , 293 K, ppm): δ 29.2 (s, $^1J_{\text{Pt-P}} = 3015$ Hz).

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[Pt(C $\wedge$ P)(C $\equiv$ CPh) $_2$ TI] $_2$ (5). A solution of TlPF $_6$ (0.093 g, 0.266 mmol) in MeOH (10 mL) was added to a solution of **2** (0.250 g, 0.265 mmol) in CH $_2$ Cl $_2$ (20 mL) and the mixture stirred for 1 h in an ice bath. Then, the solvent was evaporated to dryness and acetone (15 mL) was added to the residue. The resulting solution was evaporated to dryness and MeOH (30 mL) added to the residue, to give a solid of **5**, which was washed with Et $_2$ O (30 mL) and MeOH (15 mL). Yield: 0.1310 g, 55%. Anal. Calcd for C $_{74}$ H $_{60}$ P $_2$ Tl $_2$: C, 49.11; H, 3.31. Found: C, 49.02; H, 3.55. IR (Nujol, cm $^{-1}$): ν 2088 (m, C $\equiv$ C), 2059 (m, C $\equiv$ C). 1 H NMR (300 MHz, CD $_2$ Cl $_2$, 293 K, ppm): δ 6.6–7.6 (m, 44 H, Ph groups), 3.21 (s, 4 H, CH $_2$, $^2J_{\text{Pt-H}} = 59.4$ Hz), 2.38 (s, 6 H, Me). ^{31}P NMR (300 MHz, CD $_2$ Cl $_2$, 293 K, ppm): δ 29.3 (s, $^1J_{\text{Pt-P}} = 2681$ Hz).

[Pt(C $\wedge$ P)(μ -C $\equiv$ CPh) $_2$] (6). Method A. A solution of [Pt(C $\wedge$ P)(THF) $_2$]ClO $_4$ (0.513 mmol), prepared “in situ” from [Pt(C $\wedge$ P)(μ -Cl) $_2$] (0.2736 g, 0.256 mmol) and AgClO $_4$ (0.1060 g, 0.5113 mmol) in THF, was evaporated to dryness and the residue treated with CHCl $_3$ (20 mL). Compound **2** (0.4834 g, 0.5126 mmol) was added to the resulting solution. After 2 h of stirring at room temperature, the solvent was evaporated to dryness and MeOH (20 mL) added to the residue to give a solid of **6**, which was filtered and washed with Et $_2$ O (30 mL). Yield: 0.4315 g, 70%. Anal. Calcd for C $_{58}$ H $_{50}$ P $_2$ Tl $_2$: C, 58.12; H, 4.17. Found: C, 58.11; H, 4.53. IR (Nujol, cm $^{-1}$): ν 1962 (m, C $\equiv$ C). 1 H NMR (300 MHz, CDCl $_3$, 328 K, ppm): δ 6.7–7.5 (m, 34 H, Ph groups), 2.93 (s, 4 H, CH $_2$, $^2J_{\text{Pt-H}} = 72.6$ Hz), 2.64 (s, 12 H, Me). ^{31}P NMR (300 MHz, CDCl $_3$, 328 K, ppm): δ 25.1 (s, $^1J_{\text{Pt-P}} = 4190$ Hz).

Method B. A solution of $^n\text{LiBu}$ (1.375 mmol) in THF (15 mL) was added to a solution of HCCPh (0.1555 mL, 1.374 mmol) in THF at low temperature (ca. -20 $^\circ\text{C}$) under an argon atmosphere. After 15 min of stirring, [Pt(C $\wedge$ P)(μ -Cl) $_2$] (0.667 g, 0.625 mmol) was added to it and allowed to react at room temperature for 15 h. The resulting mixture was evaporated to dryness. MeOH (60 mL) was added to the residue to give a solid of **6**, which was filtered and washed with Et $_2$ O (50 mL) and air-dried. Yield: 0.454 g, 61%.

[Pt(C $\wedge$ P)(C $\equiv$ CPh)(CO)] (7). CO(g) was bubbled through a stirred solution of **6** (0.1130 g, 0.1885 mmol) in CHCl $_3$ for 2 h. The resulting solution was evaporated to 3 mL, and CO(g) was additionally bubbled for 30 min. Addition of Et $_2$ O (20 mL) to the resulting solution gives a white solid of **7**. Yield: 0.0795 g; 67%. Anal. Calcd for C $_{30}$ H $_{25}$ OPPt: C, 57.42; H, 3.98. Found: C, 57.26; H, 4.00. IR (Nujol, cm $^{-1}$): ν 2079 (w, C $\equiv$ O), 2127 (w, C $\equiv$ C). 1 H NMR (300 MHz, CD $_2$ Cl $_2$, 293 K, ppm): δ 6.8–7.7 (m, 17 H, Ph groups), 3.64 (s, 2 H, CH $_2$, $^2J_{\text{Pt-H}} = 71.4$ Hz), 2.52 (s, 6 H, Me). ^{13}C NMR (400 MHz, CD $_2$ Cl $_2$, 273 K, ppm): δ 177.72 (d, CO, $^2J_{\text{P-C}} = 5.9$ Hz, $J_{\text{Pt-C}} = 967.0$ Hz), 160–125 (C $_{\text{Ph}}$), 106.82 (d, $^3J_{\text{P-C}} = 29.3$ Hz, C $\equiv$ C β), 101.85 (d, $^2J_{\text{P-C}} = 134.2$ Hz, C $\alpha\equiv$ C), 29.55 (s, $J_{\text{Pt-C}} = 537.4$ Hz, CH $_2$), 23.34 (s, Me), 22.43 (s, Me). ^{31}P NMR (300 MHz, CD $_2$ Cl $_2$, 293 K, ppm): δ 33.6 (s, $^1J_{\text{Pt-P}} = 2448$ Hz).

[Pt(C $\wedge$ P)(C $\equiv$ CPh)(py)] (8). Py (1 mL, 12.41 mmol) was added to a stirred solution of **6** (0.10 g, 0.1668 mmol) in CHCl $_3$. After 1 h of stirring, the solvent was removed and Et $_2$ O (20 mL) was added to the residue to give **8**. Yield: 0.0683 g, 60%; Anal. Calcd for C $_{34}$ H $_{30}$ NPPt: C, 60.20; H, 4.42; N, 2.06. Found: C, 60.10; H, 4.36; N, 2.13. IR (Nujol, cm $^{-1}$): ν 2102 (w, C $\equiv$ C). 1 H NMR (300 MHz, CDCl $_3$, 293 K, ppm): δ 8.73 (d, $^3J_{\text{H}_\text{py}-\text{H}_\text{py}} = 4.8$ Hz, 2 H, H $_o$ (py)), 7.62 (t, $^3J_{\text{H}_\text{py}-\text{H}_\text{py}} = 7.4$ Hz, 1 H, H $_p$ (py)), 6.8–7.7 (m, 19 H, Ph groups, H $_m$ (py)), 3.75 (s, 2 H, CH $_2$, $^2J_{\text{Pt-H}} = 84.0$ Hz), 2.59 (s, 3 H, Me), 1.89 (s, 3 H, Me). ^{13}C NMR (400 MHz, CD $_2$ Cl $_2$, 300 K, ppm): δ 162–123 (C $_{\text{Ph}}$, C $\wedge$ P, py), 121.25 (d, $^2J_{\text{P-C}} = 152.3$ Hz, C $\alpha\equiv$ C), 100.51 (d, $^3J_{\text{P-C}} = 31.7$ Hz, C $\equiv$ C β), 23.14 (s, Me), 21.87 (s, Me), 5.85 (s, $J_{\text{Pt-C}} = 637.3$ Hz, CH $_2$). ^{31}P NMR (300 MHz, CD $_2$ Cl $_2$, 293 K, ppm): δ 35.4 (s, $^1J_{\text{Pt-P}} = 2742$ Hz).

[Pt(C $\wedge$ P)(C $\equiv$ CPh)(tht)] (9). THT (0.3 mL, 3.40 mmol) was added to a stirred solution of **6** (0.1807 g, 0.3015 mmol) in CHCl $_3$ (15 mL) and the mixture allowed to react for 2 h. The resulting solution was evaporated to dryness and MeOH (20 mL) added to

the residue, giving a yellow solid of **9**. Yield: 0.1442 g, 70%. Anal. Calcd for C $_{33}$ H $_{33}$ SPPt: C, 57.66; H, 4.80; S, 4.66. Found: C, 57.44; H, 4.90; S, 4.25. IR (Nujol, cm $^{-1}$): ν 2103 (w, C $\equiv$ C). 1 H NMR (300 MHz, CDCl $_3$, 293 K, ppm): δ 6.8–7.6 (m, 17 H, Ph groups), 3.64 (s, 2 H, CH $_2$, $^2J_{\text{Pt-H}} = 84.0$ Hz), 3.31 (m, 4 H, tht), 2.56 (s, 6 H, Me), 2.07 (m, 4 H, tht). ^{13}C NMR (400 MHz, CD $_2$ Cl $_2$, 293 K, ppm): δ 160–125 (C $_{\text{Ph}}$), 117.16 (d, $^2J_{\text{P-C}} = 179.3$ Hz, C $\alpha\equiv$ C), 103.53 (d, $^3J_{\text{P-C}} = 32.3$ Hz, C $\equiv$ C β), 38.07 (s, tht), 30.44 (s, tht), 22.95 (s, Me), 17.32 (s, $J_{\text{Pt-C}} = 630.6$ Hz, CH $_2$). ^{31}P NMR (300 MHz, CDCl $_3$, 293 K, ppm): δ 31.9 (s, $^1J_{\text{Pt-P}} = 2696$ Hz).

[Pt(C $\wedge$ P)(C $\equiv$ CPh)(PPh $_3$)] (10). PPh $_3$ (0.070 g, 0.267 mmol) was added to a stirred solution of **6** (0.16 g, 0.267 mmol) in CH $_2$ Cl $_2$ (15 mL) and the mixture allowed to react for 1 h. The resulting solution was evaporated to dryness and MeOH (20 mL) added to the residue, giving a white solid of **10**, which was filtered and washed with Et $_2$ O (30 mL). Yield: 0.095 g, 41%. Anal. Calcd for C $_{47}$ H $_{40}$ P $_2$ Pt: C, 65.52; H, 4.64. Found: C, 65.37; H, 4.38. IR (Nujol, cm $^{-1}$): ν 2094 (w, C $\equiv$ C). 1 H NMR (300 MHz, CD $_2$ Cl $_2$, 255 K, ppm): δ 6.3–7.9 (m, 32 H, Ph groups), 2.85 (s, 3 H, Me), 2.69 (s, 2 H, CH $_2$), 2.64 (s, 3 H, Me). ^{13}C NMR (400 MHz, CD $_2$ Cl $_2$, 293 K, ppm): δ 163–124 (C $_{\text{Ph}}$, C $\wedge$ P, PPh $_3$), 116.04 (m, C $\alpha\equiv$ C), 110.32 (s, C $\equiv$ C β), 26.41 (s, $J_{\text{Pt-C}} = 452.6$ Hz, CH $_2$), 23.44 (s, Me). ^{31}P NMR (400 MHz, CD $_2$ Cl $_2$, 293 K, ppm): δ 32.6 (ν_A), 25.6 (ν_B , $^2J_{\text{P}_A-\text{P}_B} = 433$ Hz, $^1J_{\text{Pt-P}} = 2913$ Hz).

(NBu $_4$)[Pt(C $\wedge$ P)(C $\equiv$ CPh) $_2$ Pd(C $_6$ F $_5$) $_2$] (11). [Pd(C $_6$ F $_5$) $_2$ (THF) $_2$] (0.0815 g, 0.139 mmol) was added to a solution of **2** (0.1314 g, 0.139 mmol) in CH $_2$ Cl $_2$ (20 mL) under an Ar atmosphere. After 25 min of stirring, the solvent was evaporated to dryness and *n*-hexane (15 mL) added to the residue to give **11**. Yield: 0.16 g, 83%. Anal. Calcd for C $_{65}$ F $_{10}$ H $_{66}$ NPPdPt: C, 56.43; H, 4.81; N, 1.01. Found: C, 55.94; H, 4.34; N, 0.92. IR (Nujol, cm $^{-1}$): ν 2033 (m, C $\equiv$ C), 788 (s, C $_6$ F $_5$, X-sensitive), 775 (s, C $_6$ F $_5$, X-sensitive). 1 H NMR (300 MHz, CD $_2$ Cl $_2$, 293 K) δ (ppm): 6.8–7.7 (m, 22 H, Ph groups), 3.34 (s, 2 H, CH $_2$, $^2J_{\text{Pt-H}} = 67.5$ Hz), 2.98 (m, 8 H, CH $_2$, NBu $_4^+$), 2.83 (s, br, 3 H, CH $_3$), 2.60 (s, br, 3 H, CH $_3$), 1.48 (m, 8 H, CH $_2$, NBu $_4^+$), 1.33 (m, 8 H, CH $_2$, NBu $_4^+$), 0.94 (t, $^3J_{\text{H-H}} = 7.2$ Hz, 12 H, CH $_3$, NBu $_4^+$). ^{19}F NMR (300 MHz, CD $_2$ Cl $_2$, 293 K): δ -113.06 (d, 2 F $_o$, $J_{o-m} = 210.05$ Hz), -114.03 (d, 2 F $_o$, $J_{o-m} = 210.05$ Hz), -165.51 (t, 1 F $_p$, $J_{p-m} = 20.08$ Hz), -165.76 (t, 1 F $_p$, $J_{p-m} = 20.08$ Hz), -166.59 (m, 2 F $_m$), -166.97 (m, 2 F $_m$) ppm. ^{31}P NMR (300 MHz, CD $_2$ Cl $_2$, 293 K): δ 33.3 (s, $^1J_{\text{Pt-P}} = 3013$ Hz). $\Lambda_M = 47.92$ Ω^{-1} cm 2 mol $^{-1}$ (solution 5.06×10^{-4} M in acetone).

(NBu $_4$)[Pt(C $\wedge$ P)(C $\equiv$ CPh) $_2$ Pt(C $_6$ F $_5$) $_2$] (12). [Pt(C $_6$ F $_5$) $_2$ (THF) $_2$] (0.0885 g, 0.131 mmol) was added to a solution of **2** (0.1240 g, 0.131 mmol) in CH $_2$ Cl $_2$ (20 mL) under an Ar atmosphere. After 30 min of stirring, the solvent was evaporated to dryness and MeOH (15 mL) added to the residue. The MeOH solution was evaporated to dryness and diethyl ether added to the residue to give **12**. Yield: 0.0635 g, 41%. Anal. Calcd for C $_{65}$ H $_{66}$ F $_{10}$ NPPt $_2$: C, 53.03; H, 4.48; N, 0.95. Found: C, 53.16; H, 4.29; N, 0.90. IR (Nujol, cm $^{-1}$): ν 1957 (m, C $\equiv$ C), 800 (s, C $_6$ F $_5$, X-sensitive), 789 (s, C $_6$ F $_5$, X-sensitive). 1 H NMR (300 MHz, CD $_2$ Cl $_2$, 293 K, ppm): δ 6.5–7.6 (m, 22 H, Ph groups), 3.04 (m, 10 H, CH $_2$, C $\wedge$ P and NBu $_4^+$), 2.75 (s, 6 H, Me, C $\wedge$ P), 1.52 (m, 8 H, CH $_2$, NBu $_4^+$), 1.37 (m, 8 H, CH $_2$, NBu $_4^+$), 0.95 (t, $^3J_{\text{H-H}} = 7.2$ Hz, 12 H, Me, NBu $_4^+$). ^{19}F NMR (300 MHz, CD $_2$ Cl $_2$, 293 K, ppm): δ -116.69 (d, 2 F $_o$, $J_{o-m} = 23.7$ Hz, $J_{\text{Pt-F}} = 492.8$ Hz), -116.98 (d, 2 F $_o$, $J_{o-m} = 23.7$ Hz, $J_{\text{Pt-F}} = 359.6$ Hz), -166.991 (t, 1 F $_p$, $J_{p-m} = 20.08$ Hz), -167.49 (m, 2 F $_m$), -167.72 (t, 1 F $_p$, $J_{p-m} = 20.08$ Hz), -168.29 (m, 2 F $_m$). ^{31}P NMR (300 MHz, CD $_2$ Cl $_2$, 293 K, ppm): δ 27.9 (s, $^1J_{\text{Pt-P}} = 4223$ Hz). $\Lambda_M = 45.11$ Ω^{-1} cm 2 mol $^{-1}$ (solution 5.5×10^{-4} M in acetone).

(NBu $_4$)[Pt(C $_6$ F $_5$) $_2$ (C $\equiv$ CPh)(PPh $_3$)] (13). PPh $_3$ (0.088 g, 0.335 mmol) was added to a stirred solution of (NBu $_4$)[Pt(C $\wedge$ P)(C $\equiv$ CPh) $_2$ -Pt(C $_6$ F $_5$) $_2$] (**12**; 0.16 g, 0.167 mmol) in distilled CH $_2$ Cl $_2$ (15 mL), and the mixture was allowed to react for 1 h. The solvent was

Table 6. Crystal Data and Structure Refinement for [NBu₄][Pt(C $\wedge$ P)(C $\equiv$ CPh)₂] (**2**), [{Pt(C $\wedge$ P)(C $\equiv$ CPh)₂Cu]₂] (**3**), [{Pt(C $\wedge$ P)(μ -C $\equiv$ CPh)₂] (**6**), and [Pt(C $\wedge$ P)(C $\equiv$ CPh)(CO)] $\cdot$ Me₂CO (**7** $\cdot$ Me₂CO)

	2	3	6	7$\cdot$Me₂CO
empirical formula	C ₅₃ H ₆₆ NNPt	C ₇₄ H ₆₀ Cu ₂ P ₂ Pt ₂	C ₅₈ H ₅₀ P ₂ Pt ₂	C ₃₀ H ₂₆ OPPt $\cdot$ Me ₂ CO
unit cell dimens				
<i>a</i> (Å)	13.0788(7)	12.3290(4)	13.7767(4)	23.401(4)
<i>b</i> (Å)	24.1198(12)	12.3290(4)	7.8071(3)	14.738(2)
<i>c</i> (Å)	15.2094(7)	39.6043(17)	22.3544(6)	6.089(2)
β (deg)	108.200(1)	90	99.827(2)	101.186(3)
<i>V</i> (Å ³), <i>Z</i>	6020.0(4), 4	6020.0(4), 4	2369.07(13), 2	5443.4(14), 8
wavelength (Å)			0.710 73	
temp (K)			100(1)	
radiation		graphite monochromated Mo K α		
cryst syst	monoclinic	tetragonal	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 4 ₁	<i>P</i> 2/ <i>n</i>	<i>C</i> 2/ <i>c</i>
cryst dimens (mm)	0.39 $\times$ 0.31 $\times$ 0.21	0.40 $\times$ 0.40 $\times$ 0.28	0.39 $\times$ 0.12 $\times$ 0.02	0.42 $\times$ 0.38 $\times$ 0.12
abs coeff (mm ⁻¹)	3.149	5.426	6.004	5.243
diffractometer	Bruker SMART	Bruker SMART	Oxford Diffraction Xcalibur	Bruker SMART
2 θ range for data collectn (deg)	3.28–50.08	3.30–50.02	3.92–49.34	3.18–50.02
no. of rflns collected	25 060	33 378	14 214	14 621
no. of indep rflns (<i>R</i> (int))	8050 (0.0347)	10 293 (0.0218)	3984 (0.0211)	4788 (0.0190)
refinement method		full-matrix least squares on <i>F</i> ²		
goodness of fit on <i>F</i> ² ^b	1.007	1.023	1.023	1.023
final <i>R</i> indices (<i>I</i> > 2 σ (<i>I</i>)) ^a				
<i>R</i> 1	0.0319	0.0188	0.0180	0.0274
<i>wR</i> 2	0.0487	0.0454	0.0398	0.0726
<i>R</i> indices (all data)				
<i>R</i> 1	0.0467	0.0194	0.0206	0.0305
<i>wR</i> 2	0.0506	0.0455	0.0407	0.0745

^a *R*1 = $\sum(|F_o| - |F_c|)/\sum|F_o|$. *wR*2 = $[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$. ^b Goodness of fit = $[\sum w(F_o^2 - F_c^2)/(n_{\text{observns}} - n_{\text{params}})]^{1/2}$.

evaporated to dryness and MeOH (20 mL) added to the residue, to eliminate the solid (**10**). From the filtered solution, the evaporation of the solvent to dryness and addition of Et₂O (20 mL) rendered a white solid of **13**. Yield: 0.1170 g, 62%. Anal. Calcd for C₅₄H₅₆F₁₀NNPt: C, 57.14; H, 4.97; N, 1.23. Found: C, 56.94; H, 4.40; N, 1.13. IR (Nujol, cm⁻¹): ν 2104 (m, C $\equiv$ C), 800 (s, C₆F₅, X-sensitive), 777 (s, C₆F₅, X-sensitive). ¹H NMR (300 MHz, CD₂Cl₂, 293 K, ppm): δ 7.74 (m, 6 H, PPh₃), 7.32 (m, 9 H, PPh₃), 6.97 (m, 3 H, C $\equiv$ CPh), 6.74 (m, 2 H, C $\equiv$ CPh), 3.0 (m, 8 H, CH₂, NBu₄⁺), 1.51 (m, 8 H, CH₂, NBu₄⁺), 1.37 (m, 8 H, CH₂, NBu₄⁺), 0.99 (t, ³J_{H-H} = 7.2 Hz, 12 H, Me, NBu₄⁺). ¹⁹F NMR (300 MHz, CD₂Cl₂, 293 K): δ -116.49 (m, 2 F_o, *J*_{Pt-F} = 422.4 Hz), -116.82 (d, 2 F_o, *J*_{O-m} = 27.9 Hz, *J*_{Pt-F} = 349.4 Hz), -166.77 (m, 2 F_m), -166.99 (m, 1 F_p), -167.41 (m, 2 F_m), -168.09 (t, 1 F_p, *J*_{p-m} = 19.9 Hz). ³¹P NMR (400 MHz, CD₂Cl₂, 293 K, ppm): δ 16.5 (s, ¹J_{Pt-P} = 2543 Hz).

X-ray Structure Determination. Crystal data and other details of the structure analysis are presented in Table 6. Suitable crystals of **2**, **3**, **6**, and **7** $\cdot$ Me₂CO were obtained by slow diffusion of *n*-hexane into a CH₂Cl₂ solution at 5 °C of complexes **2** and **6**, by slow diffusion of methanol in a CHCl₃ solution of complex **3** (at 5 °C), and by slow diffusion of methanol in an acetone solution of complex **7** (at -30 °C). Crystals were mounted at the end of a glass fiber. For **2**, unit cell dimensions were determined from the positions of 6094 reflections from the main data set. For **3**, unit cell dimensions were determined from the positions of 7887 reflections from the main data set. For **6**, unit cell dimensions were determined from the positions of 17 793 reflections from the main data set. For **7** $\cdot$ Me₂CO, unit cell dimensions were determined from the positions of 914 reflections from the main data set. The diffraction frames were integrated using the SAINT package⁵⁹ for **2**, **3**, and **7** $\cdot$ Me₂CO and the CrysAlis RED package¹²³ for **6** and corrected for absorption with SADABS¹²⁴ in the three cases. Lorentz and polarization corrections were applied for the three structures.

(123) CrysAlis RED, CCD Camera Data Reduction Program; Oxford Diffraction, Oxford, U.K., 2004.

The structures were solved by Patterson and Fourier methods. All refinements were carried out using the program SHELXL-97.¹²⁵ All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints, except as noted below. All hydrogen atoms were constrained to idealized geometries and assigned isotropic displacement parameters 1.2 times the *U*_{iso} value of their attached carbon atoms (1.5 times for methyl hydrogen atoms). For **2**, during the refinement of the structure it was found that one of the acetylide groups and the *o*-tolyl groups of the phosphine ligand are disordered over two positions with 0.5 occupancy. Several models were tested, and finally the one that gave the best results was kept. In this model, the pairs of homologous atoms of the two sets were refined with the same anisotropic displacement parameters. It was also found that a -CH₂CH₃ fragment of the NBu₄⁺ cation was disordered over two positions with partial occupancy 0.7/0.3. The interatomic distances of these disordered fragments were constrained to sensible values. Full-matrix least-squares refinement of these models against *F*² converged to the final residual indices given in Table 6.

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Supporting Information Available: CIF files giving X-ray structural data for **2**, **3**, **6**, and **7** $\cdot$ Me₂CO. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(124) Sheldrick, G. M. SADABS, Empirical Absorption Correction Program; University of Göttingen, Göttingen, Germany, 1996.

(125) Sheldrick, G. M. SHELXL-97, a Program for Crystal Structure Determination; University of Göttingen, Göttingen, Germany, 1997.