

mimetics combining the biological activity of β -lactams and the countless bioactive properties of conformationally restricted oligopeptides.

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Double Insertion of Coordinated Phosphanylalkyne Ligands into a Pt–C₆F₅ Bond**

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Carbon–carbon bond forming reactions promoted by transition metals are among the basic goals of organometallic chemistry and play an important role in the design of efficient and selective processes.^[1] The intramolecular coupling of alkyne and related C₂ ligands (alkynyl, vinyl, vinylidene) is particularly interesting because it constitutes an effective method for the synthesis of useful organic products.^[2] The facile migratory insertion of C≡C units into M–H and M–C bonds seems to be decisive not only for these reactions but also for many catalytic processes.^[1, 2] Usually bonds between a metal and a perfluorocarbon atom are quite inert towards insertion reactions, and there is currently little or no knowledge on the insertion of acetylene fragments into the robust M–R_F bonds.^[3]

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Herein we report on the unprecedented double insertion of coordinated (phenylethynyl)phosphane $\text{PPh}_2\text{C}\equiv\text{CPh}$ into a $\text{Pt}-\text{C}_6\text{F}_5$ bond. Phosphanylalkynes $\text{PPh}_2\text{C}\equiv\text{CR}$ are extremely versatile molecules which display a very rich chemistry. They are not only capable of binding in a variety of coordination modes,^[4] but in some cases the ligands undergo cleavage of the $\text{P}-\text{C}$ (alkyne) bond to yield phosphide and alkynyl fragments, which may take part in further coupling reactions in the presence of suitable unsaturated molecules.^[4a,b,5] Insertions into reactive $\text{M}-\text{H}$ or $\text{M}-\text{C}$ bonds are also known,^[6] and several recent papers describe oxidative alkyne coupling processes with these unsaturated phosphorous-substituted alkynes.^[7]

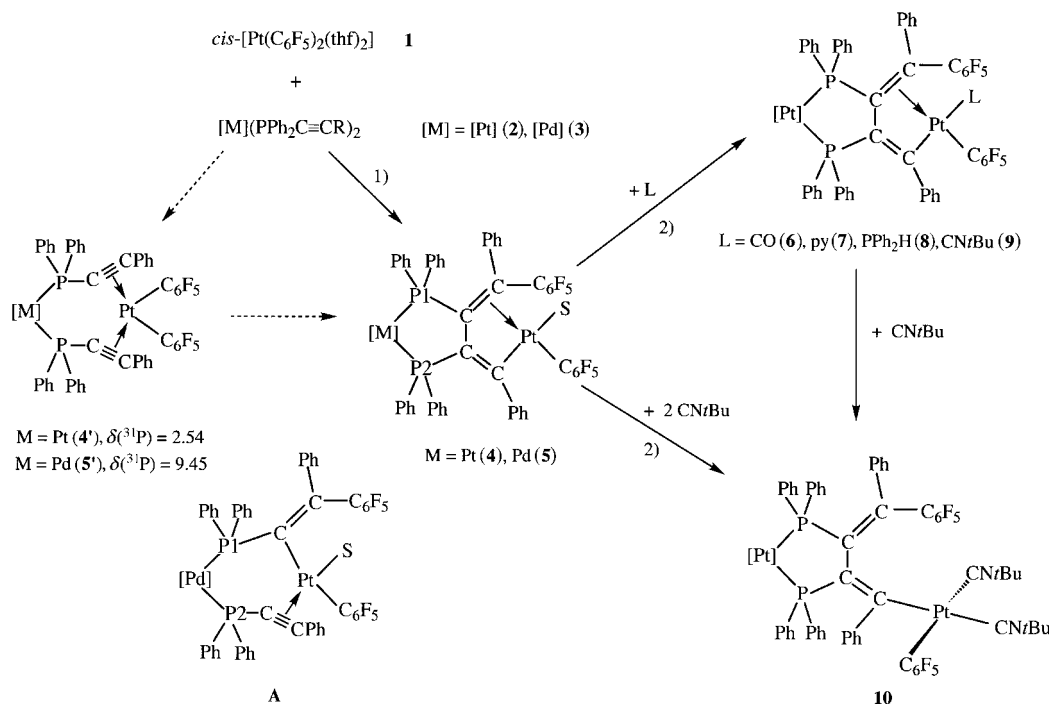
We have recently shown that the tetrahydrofuran molecules of the very reactive compound $\text{cis}[\text{Pt}(\text{C}_6\text{F}_5)_2(\text{thf})_2]$ (**1**) are easily displaced by alkynes^[8a] or alkynylmetal complexes.^[8b-d] However, the reaction of **1** with $\text{cis}[\text{PtX}_2(\text{PPh}_2\text{C}\equiv\text{CR})_2]$ ($\text{X} = \text{Cl}, \text{C}\equiv\text{CR}$; $\text{R}' = \text{Ph}, t\text{Bu}$) yields only homobridged—($\mu\text{-X}$)₂ ($\text{X} = \text{Cl}$,^[8e] $\text{C}\equiv\text{CR}$ ^[8f])—or heterobridged—($\mu\text{-PPh}_2\text{C}\equiv\text{CR}$)($\mu\text{-Cl}$)^[8e]—binuclear complexes. To force the coordination of two $\text{PPh}_2\text{C}\equiv\text{CR}$ molecules as bridging ligands, we have investigated the reaction of **1** with complexes $\text{cis}[\text{M}(\text{C}_6\text{F}_5)_2(\text{PPh}_2\text{C}\equiv\text{CR})_2]$ ($\text{M} = \text{Pt}$ (**2**), Pd (**3**); $\text{R} = \text{Ph}$ (**a**), $t\text{Bu}$ (**b**)), which were prepared by standard methods (see the Supporting Information). To our surprise these reactions did not lead to the expected bis[$\mu\text{-}\kappa\text{P}:(\eta^2)\text{-}(\text{PPh}_2\text{C}\equiv\text{CR})$]-bridged η^2 -alkyne complexes **4'** and **5'** (see Scheme 1), but to unusual coupling products.

As outlined in Scheme 1 the *tert*-butyl derivatives **2b** and **3b** did not react with **1**, even under reflux conditions (CH_2Cl_2 , 5 h for **2b** or 1 h for **3b**). However, the phenylethynyl complexes **2a** and **3a** react with an equimolar amount of **1** in CH_2Cl_2 to give the yellow binuclear complexes **4** (82%) and **5** (66%), respectively, which contain an unusual 2,3-bis(di-

phenylphosphanyl)-1,3-butadien-1-yl ligand acting as a bis-chelating $\mu\text{-}1(3,4\text{-}\eta,\kappa\text{C}^1):2\kappa^2\text{P,P}'$ bridging ligand. IR and ^{19}F NMR (282.4 MHz) spectroscopy of **4** and **5** clearly established not only the presence of a $\text{C}-\text{C}_6\text{F}_5$ unit, but also the existence of four different types of C_6F_5 moieties, indicating an asymmetrical structure. Similarly two different ^{31}P resonances are seen ($^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, CDCl_3): **4**: $\delta = 24.81$ (d, $^1J_{\text{Pt},\text{P}2} = 2284$, $^3J_{\text{Pt}1,\text{P}2} = 276$ Hz), 36.03 (d, $^1J_{\text{Pt}2,\text{P}1} = 2251$, $J_{\text{P}2,\text{P}1} \approx 7$ Hz); **5**: $\delta = 37.71$ (br, $^3J_{\text{Pt}1,\text{P}2} = 270$ Hz), 42.14 (brs); Pt1 stems from **1**), but X-ray analysis was needed to determine unambiguously the nature of the unsymmetric bridging ligand.

Complex **4** crystallizes easily in different solvent systems, but none of the crystals obtained were suitable for X-ray crystallography. An X-ray crystallographic investigation of **5** was also tried; however, disorder associated with the solvent coordination site at Pt (partial occupancy for thf or H_2O) prevented a satisfactory refinement.^[9] This study notwithstanding indicated that the two acetylenic fragments of the precursor **2** or **3** had condensed with one of the C_6F_5 groups of **1** to form a 2,3-bis(diphenylphosphanyl)butadienyl ligand that bridges the two metal centers (Scheme 1). This is confirmed by X-ray studies on complexes resulting from the substitution of ligand S (see below). A few similar η^3 -butadienyl (3,4- $\eta,\kappa\text{C}^1$) backbones have been previously obtained by insertion of two alkynes into $\text{Ru}-\text{X}$ ($\text{X} = \text{H}, \text{Me}$)^[10a] or $\text{Pd}-\text{X}$ bonds ($\text{X} = \text{Cl}, \text{Ph}$)^[10b,c] or into cyclometalated Pd^{II} or Ni^{II} complexes.^[11] In other systems, the butadienyl unit invariably displays symmetric or asymmetric η^3 -allylic (through $\text{C}2-\text{C}4$) or η^1 (through $\text{C}2$) bonding modes.^[12]

When the reaction of **1** with **2a** or **3a** was monitored at room temperature no intermediates were detected. However, on the basis of preliminary experimental evidence at low



Scheme 1. Synthesis of **4**–**10**. 1) CH_2Cl_2 , 0–10 °C, 45 min. 2) CH_2Cl_2 , room temperature, 5–30 min. [$\text{M} = \text{cis-M}(\text{C}_6\text{F}_5)_2$, $\text{M} = \text{Pt}, \text{Pd}$; $\text{R} = \text{Ph}$ (**a**), $t\text{Bu}$ (**b**). py = pyridine, S = $(\text{thf})_x(\text{H}_2\text{O})_{1-x}$. ^{31}P NMR data at –30 °C.

temperature (^{31}P and ^{19}F NMR spectroscopy between -50 and -10°C) we postulate that the formation of **4** and **5** proceeds stepwise. Thus when the reaction between **2a** and **1** was performed at -50°C , the expected η^2 -alkyne adduct **4'** was detected together with the precursors (**2a**:**1**:**4'** \approx 1:1:0.4) and fully characterized ($\delta(^{31}\text{P})=2.15$ ($^1J_{\text{Pt,P}}=2341$ Hz); $\delta(^{19}\text{F})\approx -116.1$ (br), -120.1 (br, *o*-F), -153.98 (t), -160.5 (*p*-F, overlap with the signal for *p*-F of **1**), -163.0 (m, *m*-F)). The presence of complex **4** was detected at -20°C . Its formation, accompanied by the gradual and simultaneous disappearance of **4'** and reactants, is clean at -10°C and complete within about 6 h.

In the **2a/1** system no other intermediate could be observed. However, in the reaction of **3a** with **1**, the ^{31}P and ^{19}F NMR spectra recorded at -50°C reveal that in addition to the precursors and the η^2 -alkyne adduct **5'** ($\delta(\text{P})=9.27$), a new intermediate (**A**, Scheme 1) is also formed (**3a**:**5'**:**A** \approx 0.54:0.29:0.17). This intermediate shows two different ^{31}P resonances ($\delta(\text{P})=11.16$ (br), -3.29 (br)), and particularly the ^{19}F resonances for one C_6F_5 group ($\delta(\text{F})=-127.14$, -129.5 (*o*-F), -151.5 (*p*-F), -156.8 , -158.6 (*m*-F)) are at chemical shifts typical of a $\text{C}-\text{C}_6\text{F}_5$ unit and support a formulation of the monoinserted alkyne/vinyl species **A**. If the reaction temperature is allowed to increase, the formation of **5** can be observed clearly at -10°C . At this temperature the NMR signals of **3a**, **5'**, and **A** gradually disappear (with a nearly constant ratio), and the signals due to **5** grow concomitantly. Again the transformation is very slow, requiring around 12 h to go to completion.

Although we have no experimental evidence of an analogous monoinserted product in the Pt/Pt system and the structural assignment of the intermediate **A** is only tentative, the participation of **A** in the proposed reaction pathway seems reasonable on chemical grounds and is in agreement with previous results on cyclometalated palladium(II) complexes and acetylenes.^[11b] Curiously, in a donor solvent such as acetone there is formation of neither **4/5** nor **4'/5'**, suggesting that the proximity of the acetylene fragments in the initial adduct probably play a major role in the activation process. The formation of asymmetric diphosphanes by activation^[13] or coupling^[7a,c] of two alkynylphosphanes mediated by metal centers has been previously reported, but, as far as we know, the migratory insertion of an acetylenic fragment into a $\text{M}-\text{C}_6\text{F}_5$ bond has no precedent. In this context it is worth noting that a few examples of pentafluorobenzimidoyl derivatives ($\text{C}(\text{C}_6\text{F}_5)=\text{NR}$) of Ti and Pd have been obtained through insertion reactions of isocyanides into $\text{M}-\text{C}_6\text{F}_5$ bonds.^[14] More recently Espinet et al. have shown that the addition of $\text{Pd}-\text{C}_6\text{F}_5$ to coordinated olefins is also a relatively easy process.^[15]

To confirm the structure of the new bridging ligand we have explored the reactivity of the more stable complex **4** towards different neutral ligands. As expected, the diplatinum derivatives **6–9** (Scheme 1) are easily obtained as yellow (**6**, **9**) or orange (**7**, **8**) air-stable microcrystalline solids by treatment of **4** with stoichiometric amounts of the corresponding ligands L (see the Supporting Information for details). The η^2 -olefin interaction seems to be rather strong because only the reaction of **4** with $\text{CN}i\text{Bu}$ (1:2 molar ratio) results in the

opening of the chelating ring to give **10** as a lemon yellow microcrystalline solid (78% yield).

In addition to full spectroscopic and analytical characterization of complexes **6–10**, the solid-state structures of **8** and **10** were determined by single-crystal X-ray diffraction.^[16] The molecular structure of **8** (Figure 1) confirms unequivocally

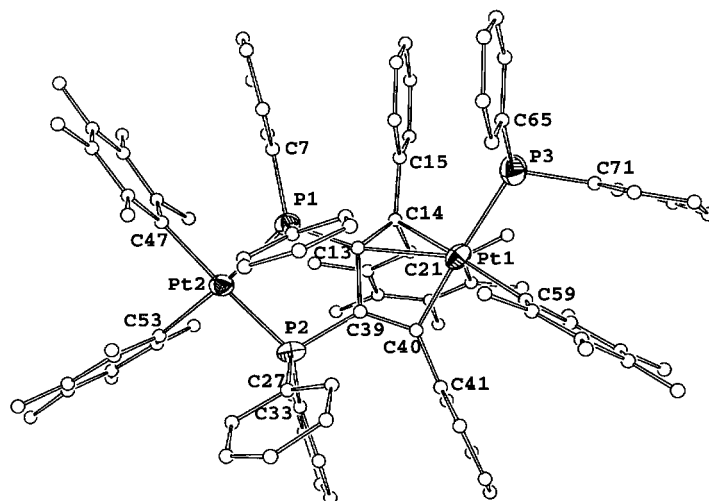


Figure 1. Molecular structure of **8**. Hydrogen atoms have been omitted for clarity. Selected bond lengths [\AA] and angles [$^\circ$]: Pt1–C40 2.022(9), Pt1–C14 2.322(9), Pt1–C13 2.396(9), Pt2–P1 2.300(3), Pt2–P2 2.279(3), C13–C14 1.430(13), C13–C39 1.516(12), C39–C40 1.369(15); C14–C13–C39 118.2(9), C14–C13–P1 130.5(7), C39–C13–P1 108.1(7), C13–C14–Pt1 75.2(5), C40–C39–C13 111.1(9), C40–C39–P2 129.8(7), C13–C39–P2 118.7(7), C39–C40–Pt1 101.0(7).

that the reaction between **1** and **2a** results in the formation of a butadienyldiphosphane ligand which coordinates to the $\text{Pt}2(\text{C}_6\text{F}_5)_2$ unit as a typical diphosphane ligand and to the $\text{Pt}1(\text{C}_6\text{F}_5)\text{PPh}_2\text{H}$ fragment as a vinyl-olefin ligand ($\sigma:\eta^2$). The interatomic distances and angles about the butadienyl chain are within the expected range.^[10,11] The phenyl and PPh_2 groups are mutually *cis* not only in the vinyl unit but also in the η^2 -alkene fragment, indicating that the overall insertion process is probably highly regioselective. A *trans* arrangement about the η^2 -alkene bond is usually displayed in related butadienyl backbones formed by double insertion of alkynes into cyclopalladate complexes.^[11]

In summary these results confirm previous indications of the enhanced reactivity of uncoordinated $\text{C}\equiv\text{C}$ bonds held in the proximity of a metal in phosphanylacetylene complexes. Work to extend these reactions to other $\text{PPh}_{3-x}(\text{C}\equiv\text{CR})_x$ phosphanes ($x=1-3$) and to study the chemical reactivity of the final species is in progress.

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Exploiting the Self-Assembly Strategy for the Design of Selective Cu^{II} Ion Chemosensors**

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Chemosensors, small abiotic molecules that signal the presence of analytes, typically combine two components: a recognition site that binds the target substrate and a readout system that signals binding.^[1] In the case of metal ion sensors the recognition site is a metal-chelating molecule designed to bind the target ion selectively and the readout system is very often a fluorophore. The two components are usually covalently linked through a spacer and the complexation of the metal ion results in a variation of the position and/or intensity of the emission band of the fluorophore. With this set-up a large number of molecular sensors has been devised for the detection of alkali and transition metal ions in solution.^[1] Among the latter group, Cu^{II} has attracted

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