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Journal of Organometallic Chemistry 691 (2006) 2859–2862
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Communication

Transformation of an η^1-coordinated phosphaalkyne into a bridging phosphinidene ligand

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Received 14 February 2006; accepted 8 March 2006

Abstract

The tripalladium cluster [Pd$_3$(μ_3-CO)(μ-dppm)$_3$](PF$_6$)$_2$ (**1**) reacts with two equivalents of ^{t}BuCP to give [Pd$_3$(μ-dppm)$_3$(η^1-PCBu^t)$_2$](PF$_6$)$_2$ (**2**). Prolonged storage of acetone solutions of **2** only resulted in the isolation of [Pd$_3$(μ-dppm)$_3$(η^1:μ_3-PCH$_2$Bu^t)(OCMe$_2$)](PF$_6$)$_2$ (**3**). Compound **3** has been characterized by X-ray crystallography.

Keywords: Phosphaalkynes; Palladium; Clusters; Phosphinidene ligands

The kinetically stabilized phosphaalkyne Bu^{t}CP, first prepared by Becker [1], has proven to be one of the most important and versatile building blocks during the recent renaissance in phosphaorganic chemistry [2]. Phosphaalkynes have been shown to be the precursors for a wide range of cyclic and acyclic organophosphorus compounds and the resemblance of these species to their isoelectronic and isostructural organic analogues has coined the "phosphorus-the carbon copy" analogy [3].

The coordination chemistry of phosphaalkynes is dominated by metal-mediated coupling reactions and side on η^2-(PC) coordination where the ligand can act as a 2-electron [3] or a 4-electron [4,5] donor. A further bonding mode that is available for phosphaalkynes when binding to transition metals is via η^1-coordination through the "lone pair" on the phosphorus atom [3,6]. In contrast to the isoelectronic nitrile (RCN) species this interaction is rare and typically only observed in complexes where η^2-binding is sterically disfavoured [6,7]. Side-on coordination of the phosphaalkyne group to metals activates the Lewis basic character of the phosphorus atom and has allowed for the construction of multi-metallic complexes [5].

We now wish to report that reaction of [Pd$_3$(μ_3-CO)(μ-dppm)$_3$](PF$_6$)$_2$ [8] with ^{t}BuCP results in the first example of a metal cluster containing an η^1-phosphaalkyne ligand. Furthermore the coordinated phosphorus atom undergoes a subsequent transformation to give a phosphinidene ligand: a process presumably facilitated by the ability of the three metal atoms of the cluster to accommodate this remarkable change in bonding.

Although some aspects of the interactions of phosphalkynes with metal clusters containing iron [9,10], ruthenium [11], osmium [12], rhenium [13], and iridium [14] clusters have been reported, reactions with late transition metal clusters have received far less attention. These clusters contain fewer valence electrons than those of the mid transition metals, and their reactivities are rather different [15]. There has previously been a single report of a palladium–phosphaalkyne cluster: treatment of [Pt(PPh$_3$)$_2$(^{t}BuCP)] with [Pd(PPh$_3$)$_4$] giving the pentametallic complex [Pd$_2$Pt$_3$(PPh$_3$)$_5$(η^1:η^2-^{t}BuCP)$_3$] [16].

Treatment of [Pd$_3$(μ_3-CO)(μ-dppm)$_3$](PF$_6$)$_2$ (**1**) with two equivalents of ^{t}BuCP in acetone affords [Pd$_3$(μ-dppm)$_3$(η^1-

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doi:10.1016/j.jorganchem.2006.03.014

PCBu^t)$_2$](PF$_6$)$_2$ **2** [17]. The reaction can be monitored by IR spectroscopy, as the appearance of **2** is accompanied by disappearance of the ν(CO) stretch characteristic of **1**. Compound **2** can be isolated as green crystals following recrystallisation from acetone–toluene.

The ^{31}P{^{1}H} NMR spectrum of **2** consists of a triplet at δ −6.3 and a septet at δ −121.4, mutually coupled with J_{PP} 22 Hz, together with a second septet for the hexafluorophosphate anions at δ −142.8. The triplet is slightly downfield of the dppm resonance in **1**, but can be assigned to the six equivalent phosphorus nuclei in the three dppm ligands. The coupling pattern demonstrates that the two ^{t}BuCP ligands are equivalent. The value of δ_P for the phosphaalkyne is a good indicator for the coordination mode adopted by the ligand. Generally η^2(2e)-ligands have δ 80–250, η^2(4e)-ligands have δ 400–550 and η^1-ligands have δ −150 to 50. Using this criterion, the phosphaalkyne ligands in **2** are η^1-coordinated. Presumably η^2-^{t}BuCP coordination to the tripalladium centre is disfavoured due to steric clash between the phenyl and *tert*-butyl groups that would result if this binding mode were to occur. Consistent with the proposed η^1-bonding mode, the ^{13}C{^{1}H} NMR spectrum exhibited a virtual triplet resonance due to the sp hybridised carbon atoms of the ^{t}BuCP ligands at δ 214.8 ($^{1+3}J_{CP}$ 60 Hz).

Although these data are fully consistent with an η^1-binding regime, there are a number of possible structures for **2** which are indistinguishable on the basis of the NMR spectra, and two possibilities are shown in Fig. 1. In structure A, the phosphaalkynes adopt the μ_3:η^1-coordination mode. The μ_3 coordination mode is quite common for this class of tripalladium or triplatinum clusters [12], and has been observed previously for halides [18], isocyanides [19] and SnF$_3^-$ [20] in addition to CO [21] in **1**. However, this coordination mode has not been previously observed for a phosphaalkyne. In structure B, the phosphaalkynes are coordinated to a single palladium centre. In order for this to be consistent with the NMR data, a fluxional process would need to occur to make the dppm phosphorus atoms equivalent on the NMR timescale. It has been postulated for other ligands that the mechanism for fluxionality involves intermediates containing μ_2- or μ_3-ligands [20]. Therefore, if structure B is the ground state, it is likely that structure A is an intermediate in the fluxional process. Low temperature NMR studies revealed little change in the spectra on cooling to −80 °C, suggesting if a fluxional process is present, the activation energy is low.

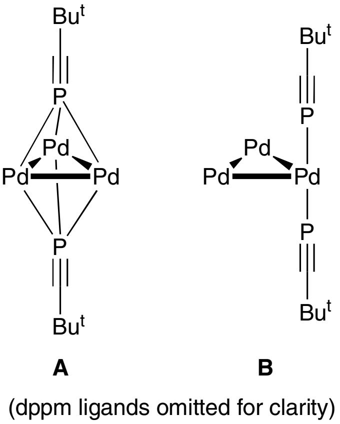

Fig. 1. Possible structures for compound **2**, involving bridging or terminal η^1-phosphaalkyne ligands.

Attempts to crystallise **2** from an acetone–toluene solution led to the formation of red crystals that were suitable for single crystal X-ray crystallography [22]. On analysis, these crystals were shown to be [Pd$_3$(μ-dppm)$_3$(η^1:μ_3-PCH$_2$Bu^t)(OCMe$_2$)](PF$_6$)$_2$ · 1.5Me$_2$CO · PhMe (**3** · 1.5Me$_2$CO · PhMe). The structure of **3** is shown in Fig. 2 together with selected bond lengths and angles. The cation, shown schematically in Fig. 3, is still a tripalladium cluster but now contains a bridging phosphinidene ligand that has inserted into two of the Pd—Pd bonds. The cluster contains one intact metal—metal bond, Pd(2)—Pd(3), which at 2.6977(3) Å is longer than those in **1** [2.576(1)—2.610(2) Å]. The two other Pd···Pd dis-

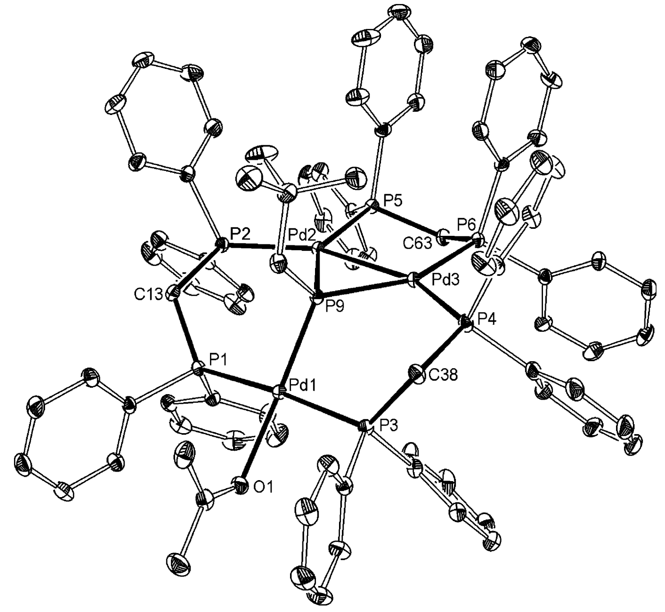

Fig. 2. The structure of [Pd$_3$(μ-dppm)$_3$(η^1:μ_3-PCH$_2$Bu^t)(OCMe$_2$)](PF$_6$)$_2$ (**3**) with the counteranions, hydrogen atoms and solvent moiety are omitted for clarity. Selected bond lengths (Å) and angles (°): Pd(2)—Pd(3) 2.6977(3), Pd(1)—P(9) 2.2748(7), Pd(2)—P(9) 2.2435(7), Pd(3)—P(9) 2.2541(7), P(9)—C(76) 1.865(3), Pd(1)—P(9)—C(76) 97.24(10), Pd(2)—P(9)—C(76) 121.28(11), Pd(3)—P(9)—C(76) 122.16(10), P(9)—C(76)—C(77) 119.9(2).

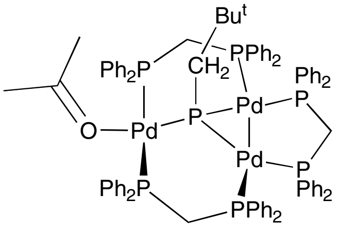

Fig. 3. The structure of [Pd$_3$(μ-dppm)$_3$(η^1:μ_3-PCH$_2$Bu^t)(OCMe$_2$)]$^{2+}$.

tances are 3.953(3) and 3.965(3) Å, too long to be regarded as bonding. All the palladium centers are 4-coordinate, with Pd(2) and Pd(3) coordinated to two dppm phosphorus atoms and the phosphinidene phosphorus atom P(9) in addition to each other, and Pd(1) coordinated to two dppm phosphorus atoms, P(9) and an acetone ligand. Pd(1) has a distorted square planar geometry, with *cis* angles ranging from 87.44(6)° to 102.01(3)°. **3** is formally a 46-electron cluster, with the phosphinidene ligand acting as a 4-electron donor.

In support of our identification of the group PCH_2Bu^t group as a phosphinidene ligand, P(9)—C(76), previously the triple bond of a phosphaalkyne ligand, has a bond length of 1.865(3) Å in $\mathbf{3} \cdot 1.5Me_2CO \cdot PhMe$, which is typical of a P—C single bond. The two hydrogen atoms on C(76) were located in the difference map during the structure solution, but in the final structure have been placed into calculated positions. Compound **3** was the only isolated product from the decomposition of **2**. Although, formally, a molecule of ^tBuCP is displaced during the formation of **3**, this was not observed in NMR studies of the supernatant solution. Instead, multiple products were observed which proved to be intractable. It is likely that a trace amount of water in the acetone is the source of the two phosphinidene methylene hydrogen atoms. The water oxygen atom is presumably in one of the other unidentified decomposition products, together with the displaced ^tBuCP molecule.

Attempts to obtain ^1H and $^{31}P\{^1H\}$ NMR spectra of **3** were hampered by the low solubility of the complex. In the ^1H NMR spectra, peaks assigned to the phenyl and *tert*-butyl groups were observed as a multiplet at δ 7.75–6.74 and a singlet at δ 1.96, respectively. These integrated to the ratio 60:9 as expected from the structure.

The reduction of η^1-bound phosphaalkynes to give phosphine ligands has been reported [24] and it has been shown that trace quantities of water react with *trans*-$[ReCl(\eta^1\text{-}P{\equiv}CBu^t)(dppe)_2]$ to give the remarkable phosphinidene oxide *trans*-$[ReCl\{P(O)CH_2Bu^t\}(dppe)_2]$ [25]. We believe, however, that this is the first example of the conversion of an η^1-bound phosphaalkyne into a phosphinidene ligand and clearly the additional flexibility of having three metal centers in **3** may promote this process.

Compound **3** is closely related to the compound $[Pt_3(\mu\text{-}dppm)_3(\eta^1{:}\mu_3\text{-}PPh)(CO)]^{2+}$ which Puddephatt has shown results from the oxidative addition reaction of $[Pt_3(\mu_3\text{-}CO)(\mu\text{-}dppm)_3]^{2+}$ with $PhPH_2$ [15]. Puddephatt has also reported analogous reactivity with H_2S [26] to give $[Pt(\mu\text{-}dppm)_3(\mu_3\text{-}S)H]^+$ and with HCCH to give $[Pt_3(CO)(\mu_3{:}\eta^2\text{-}HCCH)(\mu\text{-}dppm)_3]^{2+}$ [27].

In conclusion, we have shown that ^tBuCP coordinates to a tripalladium cluster in a η^1-coordination mode to form the cluster $[Pd_3(\mu\text{-}dppm)_3(\eta^1\text{-}PCBu^t)_2](PF_6)_2$ (**2**). Storage of acetone solution of **2** for prolonged periods affords $[Pd_3(\mu\text{-}dppm)_3(\eta^1{:}\mu_3\text{-}PCH_2Bu^t)(OCMe_2)](PF_6)_2$ (**3**) in which one of the ^tBuCP ligands has been displaced and the other converted to a bridging phosphinidene.

Acknowledgements

We thank the EPSRC for funding and Professor Cameron Jones (Cardiff University) for the supply of *t*-butylphosphaalkyne.

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[17] *Synthesis of* **2**: *tert*-butylphosphaalkyne (20 μl, 0.132 mmol) was added to a solution of **1** (0.100 g, 0.056 mmol) in acetone (15 cm^3). The mixture was stirred for 36 h, then the solvents were removed under reduced pressure. The resulting oil was crystallized from acetone–toluene to give **2** as a green crystalline material. All attempts to grow crystals of **2** suitable for study by X-ray crystallography resulted in failure and/or the formation of **3**. Yield 0.105 g (95%). ^1H NMR (400 MHz, d_6-acetone): δ 7.49–6.91 (m, 60H, Ph), 4.62 (m, 6H, CH_2), 1.77 (s, 18 H, Bu^t). $^{13}C\{^1H\}$ NMR (100 MHz, d_6-acetone): δ 214.8 (vt, $^{1+3}J_{CP}$ 60 Hz, C≡P), 133.3–129.0 (Ph), 32.5 (s, Me), 31.4 (t, $^1J_{CP}$ 117 Hz, CH_2). $^{31}P\{^1H\}$ NMR (109 MHz, d_6-acetone): δ −6.3 (t, $^2J_{PP}$ 22 Hz, 6P, dppm), −121.4 (sept., $^2J_{PP}$ 22 Hz, 2P, P≡C), −142.8 (sept., $^1J_{PF}$ 711 Hz, 2P, PF_6^-).

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[22] Single crystals of **3** · $1.5Me_2CO \cdot PhMe$ were analysed at 150(2) K using graphite monochromated Mo Kα radiation ($\lambda = 0.71070$ Å) and a Nonius Kappa CCD diffractometer. $C_{94.5}H_{100}F_{12}O_{2.5}P_9Pd_3$, $M = 2101.68$, monoclinic, space group *Cc*, $a = 23.4970(1)$, $b = 14.4460(1)$, $c = 28.0660(2)$, $\beta = 99.7450(3)°$, $U = 9389.19(10)$ Å^3, $Z = 4$, $\rho_{calc} = 1.487$ g cm^{-3}, $\mu = 0.793$ mm^{-1}, 61 533 reflections collected, of which 20 114 were independent [$R_{int} = 0.0322$] and 19 190 observed with $>2\sigma$. Final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0281$, $wR_2 = 0.0651$. R indices (all data): $R_1 = 0.0309$, $wR_2 = 0.0667$. The structure was solved using SHELXS-97 and refined using full-matrix least squares in SHELXL-97 [23]. The asymmetric unit was seen to contain one molecule of the palladium complex, two hexafluorophosphate anions, one molecule of toluene and 1.5 molecules of acetone. The anion based on P(7) was seen to exhibit 70:30 disorder with respect to atoms F(2)–F(5). Crystallographic data for compound **3** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 298107. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033, e-mail: deposit@ccdc.cam.ac.uk).

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