Phosphaalkyne Complexes

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Homoleptic Phosphaalkyne Complexes of Silver(I)

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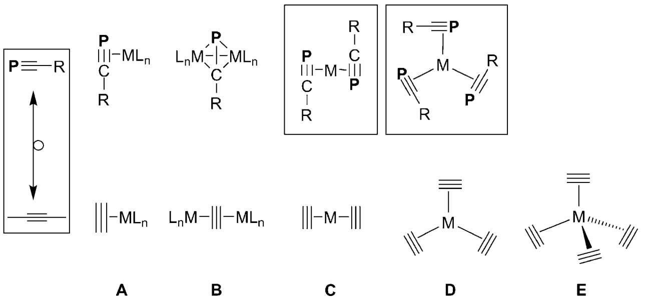
Dedicated to Professor Ullrich Zenneck on the occasion of his 70th birthday

Abstract: *By employing silver salts with a weakly coordinating anion Ag[A] ([A] = [FAl{OC$_{12}$F$_{15}$}$_3$], [Al{OC(CF$_3$)$_3$}$_4$]), two phosphaalkynes could be coordinated side-on to a bare silver(I) center to form the unprecedented homoleptic complexes [Ag(η^2-P≡CtBu)$_2$][FAl{OC$_{12}$F$_{15}$}$_3$] (**1**) and [Ag(η^2-P≡CtBu)$_2$][Al{OC(CF$_3$)$_3$}$_4$] (**2**). DFT calculations show that the perpendicular arrangement in **1** is the minimum energy structure of the coordination of the two phosphaalkynes to a silver atom, whereas for **2** a unique square-planar coordination mode of the phosphaalkynes at Ag$^+$ was found. Reactions with donor molecules yield the trigonally planar coordinated silver salts [((CH$_3$)$_2$CO)Ag(η^2-P≡CtBu)$_2$][FAl{OC$_{12}$F$_{15}$}$_3$] (**3**) and [(C$_7$H$_8$)$_2$Ag(η^2-P≡CtBu)][FAl{OC$_{12}$F$_{15}$}$_3$] (**4**). All of the compounds were comprehensively characterized in solution and in the solid state.*



Scheme 1. Isolobal relationship between phosphaalkynes and alkynes and possible side-on coordination modes.

The lasting interest in alkylidynephosphane (phosphaalkyne) chemistry can be attributed to the diversity of reactions that are possible with this class of compounds. Cycloadditions[1] and the formation of cage-like moieties[2] are possible as well as the coordination to metal fragments via different coordination modes. The first isolated[3] and most widely used representative of this species, *tert*-butylphosphaalkyne, has been shown to exhibit side-on coordination reactivity, just as its isolobal relationship to alkynes suggests (Scheme 1).[4] The side-on coordination (type **A**) of the P≡C triple bond towards metal centers is one of the most common modes.[5] This is based on the electronic nature of the triple bond,[6] because the HOMO represents the π-orbital of the triple bond. Therefore, the largest number of reported complexes shows a side-on coordination of the phosphaalkyne. In bimetallic complexes, this results in a tetrahedrane structure (type **B**).[5a,7] All complexes of the reported types **A** and **B** have in common that they are only known for heteroleptic metal complexes. Homoleptic phosphaalkyne complexes of the types **C** and **D** are not known so far.

Homoleptic silver(I) complexes of the isolobal acetylene have been calculated theoretically in the past,[8] but it was only in 2007 that the Krossing group reported the successful synthesis of [Ag(C$_2$H$_2$)$_3$]$^+$ (type **D**) and [Ag(C$_2$H$_2$)$_4$]$^+$ (type **E**).[9] The formation of these two silver complexes was only possible because of the use of the weakly coordinating anion (WCA) [Al{OC(CF$_3$)$_3$}$_4$]$^-$ (pftb). This very large WCA is able to stabilize cations by considerable separation from them, thus creating "pseudo gas-phase conditions".[10] The type **C** silver cation [Ag(C$_2$H$_2$)$_2$]$^+$ has been calculated and verified by high-pressure mass spectrometry,[11] but there is no evidence yet that it exists in the condensed phase. However, computational analyses of the complex [Ag(η^2-C$_2$H$_2$)$_2$][pftb] predict a complexation energy of -151.5 kJ mol^{-1} (MP2/TZVPP level calculations), indicating that those complexes should be accessible experimentally.[9] In the solid state, the coordinating anion [Al{OC(CH$_3$)(CF$_3$)$_2$}$_4$]$^-$ is able to stabilize [Ag(C$_2$H$_2$)]$^+$ in a complex of type **A**. Therefore, the question arises whether phosphaalkynes are also able to coordinate Ag$^+$ in a similar fashion and if so, how many and in which coordination mode. Herein, we present the first examples of side-on coordinated homoleptic phosphaalkyne complexes.

To investigate the possible outcome of the reaction of [Ag(P≡C*t*Bu)$_{n-1}$]$^+$ ($n = 1$–3) with *t*BuC≡P, DFT calculations at the B3LYP/def2-TZVP level of theory were conducted for the gas phase. These calculations show that the coordination

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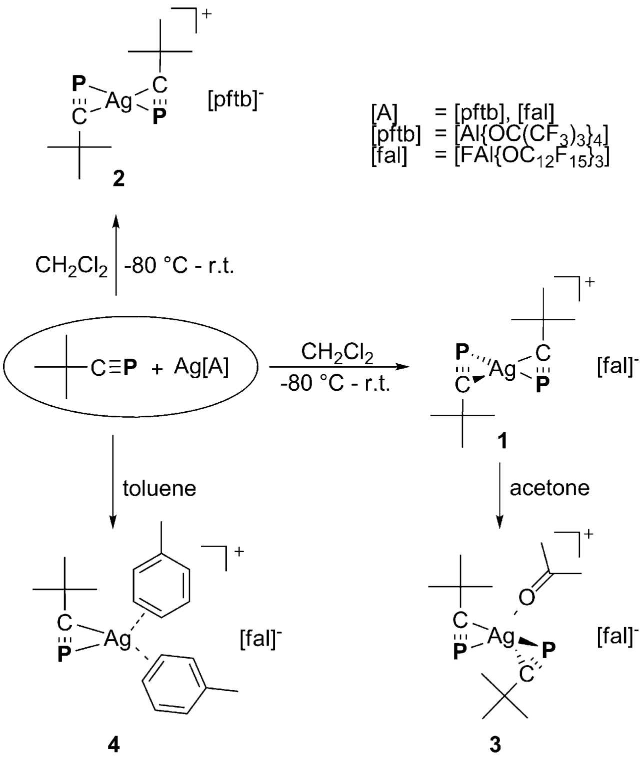
of one molecule of *t*BuC≡P to a hypothetical $[\mathrm{Ag(CH_2Cl_2)_2}]^+$ ion to give $[\mathrm{Ag(P{\equiv}C}t\mathrm{Bu)(CH_2Cl_2)}]^+$ is exothermic ($-55.46\ \mathrm{kJ\,mol^{-1}}$). The substitution of the remaining $\mathrm{CH_2Cl_2}$ ligand in $[\mathrm{Ag(P{\equiv}C}t\mathrm{Bu)(CH_2Cl_2)}]^+$ by a second *t*BuC≡P is exothermic as well by $-48.66\ \mathrm{kJ\,mol^{-1}}$. The resulting complex $[\mathrm{Ag(P{\equiv}C}t\mathrm{Bu)_2}]^+$ (type **C**) should thus be accessible. For this complex, two possible arrangements of the *t*BuC≡P ligands at the silver atom have been considered: a tetrahedral and a square planar arrangement with *trans* geometry of the phosphaalkynes. The former is the minimum energy structure, while the calculated structure with coplanar *t*BuC≡P units lies higher in energy by only $4.26\ \mathrm{kJ\,mol^{-1}}$. The further addition of a third *t*BuC≡P ligand to $[\mathrm{Ag(P{\equiv}C}t\mathrm{Bu)_2}]^+$ forming $[\mathrm{Ag(P{\equiv}C}t\mathrm{Bu)_3}]^+$ is exothermic in the gas phase ($-26.09\ \mathrm{kJ\,mol^{-1}}$) but inhibited by entropy at room temperature: The Gibbs free energy is positive at RT and becomes negative below $T = 233$ K, which indicates that the hypothetical complex $[\mathrm{Ag(P{\equiv}C}t\mathrm{Bu)_3}]^+$ should only be stable below this temperature.

Conducting the reaction of *t*BuC≡P with Ag[A] (A = $[\mathrm{AlF\{OC_{12}F_{15}\}_3}]$ (fal), $[\mathrm{Al\{OC(CF_3)_3\}_4}]$ (pftb)) in $\mathrm{CH_2Cl_2}$ leads to the formation of homoleptic complexes of the general formula $[\mathrm{Ag(P{\equiv}C}t\mathrm{Bu)_2}]^+[\mathrm{A}]^-$ (A = fal (**1**); pftb (**2**)) (Scheme 2). In both complexes, the *t*BuC≡P ligands are coordinating in a side-on fashion to $\mathrm{Ag^+}$. Interestingly, while in **1** a tetrahedral coordination is accomplished, the two *t*BuC≡P ligands in **2** coordinate to the silver cation in a square-planar *trans*-fashion, which reflects the calculated low energy difference between both arrangements.

The presence of weakly coordinating anions is crucial for the successful reaction, as no other $\mathrm{Ag^+}$ salt with other anions ($\mathrm{BF_4^-}$, $\mathrm{PF_6^-}$, or $\mathrm{SbF_6^-}$) reacted with *t*BuC≡P in a similar fashion. Those reactions lead to the formation of a silver mirror and a mixture of oxidation products of *t*BuC≡P that could not be separated or characterized despite numerous attempts.[12] Ag[pftb], on the other hand, is known to stabilize reactive molecules such as $\mathrm{P_4}$[13] and $\mathrm{As_4}$,[14] making it possible to store the resulting complexes over long periods in the solid state and make them available for subsequent reactions.[15] In a subsequent reaction, by adding a donor to **1**, a change of geometry occurs on the metal center and trigonal planar heteroleptic complexes of $\mathrm{Ag^I}$ can be isolated. Exemplified for the donor acetone, the complex $[\mathrm{((CH_3)_2CO)Ag(P{\equiv}C}t\mathrm{Bu)_2}]^+[\mathrm{fal}]^-$ (**3**) is formed. Furthermore, conducting the reaction in toluene yields the trigonal planar complexes $[\mathrm{(C_7H_8)_2Ag(P{\equiv}C}t\mathrm{Bu)}]^+[\mathrm{fal}]^-$ (**4**) and $[\mathrm{Ag(C_7H_8)_3}]^+[\mathrm{fal}]^-$. All of the compounds could be crystallized from diffusion of *n*-hexane into a $\mathrm{CH_2Cl_2}$ solution. The compounds **1** and **2** form colorless crystals, which can be stored at RT under argon without losing crystallinity. Exposure to light, however, leads to the decomposition and formation of a silver mirror. X-ray structure analysis of **1** and **2** shows the phosphaalkynes coordinated to the silver(I) center in a side-on fashion (Figure 1).



Scheme 2. Syntheses of phosphaalkyne complexes of silver(I).

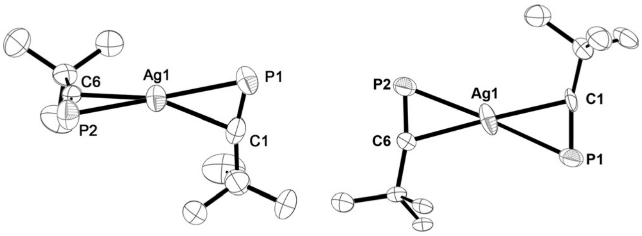


Figure 1. Molecular structures of cations of **1** (left) and **2** (right) in the solid state.[22] Hydrogen atoms, disorder, and anion are omitted for clarity. Ellipsoids are set at 50% probability. Selected bond distances [Å] and angles [°]: **1**: Ag1–P1 2.501(3), P1–C1 1.549(11), P2–C6 1.561(6); P1-C1-C2 166.9(7), $\mathrm{(P1\text{-}C1)_{cent}\text{-}Ag1\text{-}(P2\text{-}C6)_{cent}}$ 164.46. **2**: Ag1–P1 2.523(6), Ag1–P2 2.501(6), P1–C1 1.58(2), P2–C6 1.513(19); $\mathrm{(P1\text{-}C1)_{cent}\text{-}Ag1\text{-}(P2\text{-}C6)_{cent}}$ 176.9.

In both cations, the P–C bonds are triple bonds (P1–C1 and P2–C6 of **1**: 1.549(11)/ 1.561(6) Å, of **2**: 1.58(2)/1.513(19) Å). These are in good agreement with the triple bond distances in free *t*BuC≡P (photoelectron spectra: 1.536(2) Å,[5b] X-ray structure: 1.542(2) Å[16]). The P-C-C angles in both compounds are near 180°, confirming sp-hybridized C atoms. The cation in **1** is disordered; Figure 1 shows molecule **A** with the major occupation.[17] As the tetrahedrally coordinated $\mathrm{Ag^+}$ in **1** is the calculated minimum structure, Hirshfeld surface plots were generated[18] to receive information about possible contacts between the anions and cations in **1** and **2**.[17] In **1**, the bigger $[\mathrm{fal}]^-$ anions provide a suitable cavity for a tetrahedral arrangement of the *t*BuC≡P ligands, which also display contacts between the hydrogen atoms of the cation and fluorine atoms of the anion in the solid state. Although the nearly spherical $[\mathrm{pftb}]^-$ anions in **2** provide enough space for the *t*BuC≡P ligand to coordinate $\mathrm{Ag^+}$ in a square planar fashion, no contacts between the Hirshfeld surface of the [pftb] anion and the cation could be observed. The size of the anion thus has a direct influence on the geometry of the cation. Interestingly, the silver cations are shifted slightly towards the more electronegative carbon atoms within the PC triple bond. In **1**, the perpendicular from Ag onto the C≡P bond cuts the bond at 0.52 Å (d(PC) = 1.549(11) Å) and in **2** at 0.53 Å (d(PC) = 1.58(2) Å). A similar behavior has recently been found for heteroleptic Au$^+$ complexes of different phosphaalkynes.[5h]

The ^{31}P{^{1}H} NMR spectrum of complex **1** in CD_2Cl_2 at 293 K showed a singlet at δ −68.5. Variable-temperature ^{31}P{^{1}H} NMR experiments in CD_2Cl_2 revealed a slight downfield shift and a broadening of the signal as the temperature drops.[17] This behavior can be assigned to a low-energy dynamic process, as the signal at 203 K is still far from coalescence. Several dynamic processes are possible: 1) interconversion between tetrahedral and square planar form; 2) hindered rotation of the coordinated phosphaalkyne; and 3) dissociation-reassociation of the phosphaalkyne onto Ag$^+$.

To determine which of these processes plays a major role, VT ^{31}P{^{1}H} NMR spectra of **1** were recorded in CD_2Cl_2 containing two equivalents of free *t*BuC≡P (see Figure 2 b).

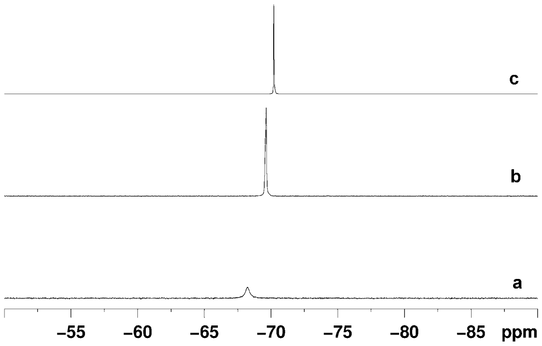


Figure 2. ^{31}P{^{1}H} NMR spectra in CD_2Cl_2 at 253 K of: a) complex **1** as dissolved; b) **1** with two additional equiv of free *t*BuC≡P; c) pure *t*BuC≡P.

At each temperature, the spectrum showed only one signal at chemical shifts intermediate between those observed for pure **1** and those of free *t*BuC≡P. For instance, at 253 K the CD_2Cl_2 solution containing only **1** showed a signal at δ −67.2 ($\Delta\nu_{1/2}$ = 26 Hz) while the sample containing **1** and deliberately added *t*BuC≡P showed a signal at δ −69.6 ($\Delta\nu_{1/2}$ = 10 Hz) (pure *t*BuC≡P: δ −70.2; Figure 2). Moreover, the signals of **1** in the presence of free *t*BuC≡P were sharper than those of pure **1**. All these circumstances support the existence of a fast dissociation equilibrium occurring when **1** is dissolved, resulting in an averaged signal at chemical shifts between that of the undissociated complex **1** and that of free *t*BuC≡P. At lower temperatures, the dissociation is slowed down, as indicated by the broadening of the signals, but not blocked even at 203 K. In the presence of free *t*BuC≡P, the equilibrium is shifted towards the undissociated complex. These results point out the lability with which the *t*BuC≡P molecules are bound to Ag$^+$, as anticipated by X-ray analysis and confirmed by DFT studies. The ^{13}C{^{1}H} NMR spectra of **1** at 273 K show the same behavior: pure **1** shows a broad signal at δ 197.4 (P≡C carbon), while **1** with added *t*BuC≡P resolves into a doublet at δ 189.9.[17] The ^{1}H–^{31}P CP/MAS NMR spectrum of **1** (Figure 3), shows two doublets ($^2J_{P,P}$ = 65 Hz) with equal intensities at δ_{iso} −51.0, and δ_{iso} −51.8 in accordance with the presence of two crystallographically inequivalent phosphorus nuclei within **1**.

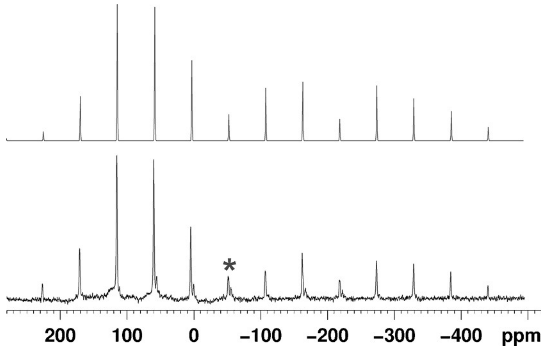


Figure 3. ^{1}H–^{31}P CP/MAS NMR spectrum of **1** obtained at a MAS rate of 9.0 kHz, 6.0 s recycle delay (bottom); spectral simulation (top). The asterisk denotes the isotropic ^{31}P chemical shift.

From the principal components of the ^{31}P chemical shift tensors of **1** obtained from the Herzfeld–Berger (HB) analysis of the sideband patterns,[19] it is apparent that the chemical shielding of the ^{31}P nucleus exhibits considerable anisotropy (Ω = 606 ppm).[17] This can be compared with that of 2,4,6-*t*-$Bu_3C_6H_2$C≡P (Ω = 503 ppm).[20] The ^{1}H–^{13}C CP/MAS NMR spectrum of **1** showed two weak signals with equal intensities, at δ_{iso} 198.3 and δ_{iso} 200.3, for the crystallographically inequivalent C≡P carbon atoms.[17] The NMR behavior of **2** parallels that of **1**, as severe ligand dissociation could also be observed by VT ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR experiments in CD_2Cl_2.[17]

Despite several attempts, the formation of complexes with three equivalents of *t*BuC≡P could not be observed by NMR or X-ray crystallography. In the HR ESI-MS spectra, the molecular ion peaks of **1** and **2** could be detected as methanol adducts.[17] Additionally, IR spectra were recorded in the solid state. However, the expected C≡P absorption bands are superimposed by the C−F vibrations of the anions. This is confirmed by DFT calculations. Furthermore these calculations indicate that the ν_{CP} stretching band is considerably coupled with the δ_C vibrations of the *t*Bu group. For example, for **2**, the vibrations at 1481 cm^{-1} and 1528 cm^{-1} contain the major $\nu_{P\equiv C}$ contribution.[17]

The reaction of **1** with acetone results in the trigonal planar complex **3**. As proof of principle, the reaction of Ag[fal] with *t*BuC≡P has also been conducted in a CH_2Cl_2/toluene mixture leading to the formation of trigonal planar **4** as well as $[Ag(C_7H_8)_3]^+[fal]^-$, which co-crystallize as a solid solution (superimposed on the same crystallographic site). Because of this, anisotropic refinement on the phosphaalkyne moiety of **4** has not been possible.[17] The P−C bonds in **3** represent P≡C triple bonds with bond lengths of 1.556(5) and 1.564(5) Å, respectively. These results show that a trigonal-planar coordination of the silver atom by one or more phosphaalkyne ligands can be achieved and that the space should be large enough for a third molecule of tBuC$\equiv$P (Figure 4).

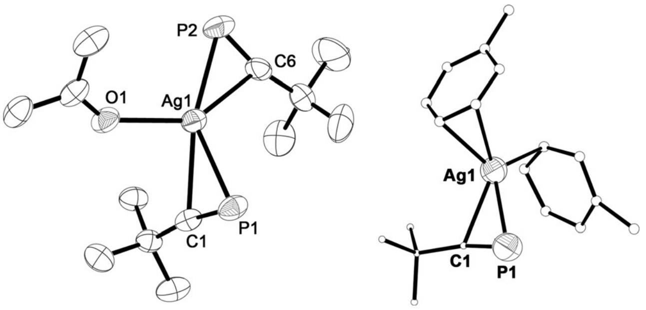


Figure 4. Left: Molecular structure of the cation of **3** in the solid state.[22] H atoms, anions are omitted for clarity. Ellipsoids are set at 50% probability. Selected bond lengths [Å] and angles [°]: Ag1–P1 2.5724(12), Ag1–P2 2.4879(14), Ag1–O1 2.323(3), P1–C1 1.556(5), P2–C6 1.564(5); P1-C1-C2 170.1(3), P2-C6-C7 165.2(4). Right: Representation of the molecular structure of the cation of **4** in the solid state.

DFT calculations in the gas phase reveal that the reaction energy between $[Ag(P\equiv CtBu)_2]^+$ and acetone is negative ($-48.73\ kJ\,mol^{-1}$), forming $[((CH_3)_2CO)Ag(P\equiv CtBu)_2]^+$. Moreover, the Gibbs free energy of the reaction at RT is negative ($\Delta G^{300} = -2.66\ kJ\,mol^{-1}$), pointing to the complex forming spontaneously at RT. Furthermore, the substitution of a toluene ligand in $[Ag(C_7H_8)_3]^+$ to form $[Ag(C_7H_8)_2(P\equiv CtBu)]^+$ is exothermic and the Gibbs free energy is negative.[17]

The $^{31}P\{^1H\}$ NMR spectrum in CD_2Cl_2 of complex **3** at 293 K showed a singlet at $\delta -69.9$. In the solid state, powdered **3** showed two broad signals at $\delta -64.7$ and $\delta -72.3$, beside a weak signal at $\delta -51.5$ for complex **1**.[21] The ^1H–^{13}C CP/MAS NMR spectrum of **3** showed two signals at δ 200 and δ 198 for the C$\equiv$P carbon atoms. In the presence of 2 equivalents tBuC$\equiv$P the $^{13}C\{^1H\}$ NMR spectrum in [D$_6$]acetone of complex **3** at 253 K showed a doublet at δ 186.4 ($^1J_{C,P} = 23$ Hz, C$\equiv$P carbon atoms) indicating that a fast ligand exchange is involved. Thus, the same dissociation behavior as for **1** and **2** can be observed.

In summary, we could isolate the first homoleptic complexes of phosphaalkynes bound to a bare metal center without any additional ligands. The two phosphaalkynes bind in a side-on coordination to form $[Ag(P\equiv CtBu)_2]^+[fal]^-$ (**1**) and $[Ag(P\equiv CtBu)_2]^+[pftb]^-$ (**2**). The use of the WCAs [pftb] and [fal] has been crucial as no similar compounds could be isolated in the reactions of tBuC$\equiv$P and Ag^I salts of smaller anions. The difference between the cations in **1** and **2** is the orientation of the phosphaalkyne ligands in the solid state: while Ag$^+$ is coordinated tetrahedrally in **1**, in **2**, it is coordinated by the two tBuC$\equiv$P ligands in a square-planar fashion. The cation in **1** is the minimum-energy structure as revealed by DFT calculations. ^{31}P and ^{13}C NMR spectroscopic investigations of **1** and **2** in solution and in the solid state show a severe dissociation of the tBuC$\equiv$P ligands from the silver cation in solution. By adding donor ligands to **1**, the trigonally planar complexes $[((CH_3)_2CO)Ag(P\equiv CtBu)_2]^+[fal]^-$ (**3**) and $[(C_7H_8)_2Ag(P\equiv CtBu)]^+[fal]^-$ (**4**) could be isolated, showing that an increase of the coordination sphere of Ag$^+$ coordinated by two phosphaalkynes is possible.

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Keywords: homoleptic compounds · phosphaalkynes · side-on complexes · silver · weakly coordinating anions

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[22] CCDC 1497711 (**1**), 1497712 (**2**), 1497713 (**3**), and 1497714 (**4**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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