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Cyaphide ($C{\equiv}P^-$): The Phosphorus Analogue of Cyanide ($C{\equiv}N^-$)

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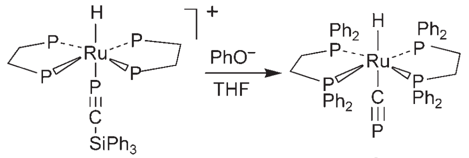
Along with the halide ions, cyanide ($C{\equiv}N^-$) is one of the ions that a first-year chemistry student is required to learn. It is an ion that is fundamental to inorganic chemistry in both its ionic salts and as a ligand in coordination complexes. In organic chemistry, it is an important functional group in alkyl and aryl cyanides ($R{-}C{\equiv}N$) and isocyanides ($R{-}N{\equiv}C$). It is not surprising that many researchers have attempted to prepare phosphorus analogues of these cyanide-containing ions and molecules, where the nitrogen atom is replaced by phosphorus. Several phosphorus analogues of aralkyl cyanides, the phosphaalkynes ($R{-}C{\equiv}P$), have been reported[1] and shown to coordinate through the phosphorus atom or through both the phosphorus and carbon atoms (η^2) in a range of transition-metal complexes.[2] On the other hand, analogues of aryl or alkyl isocyanides ($R{-}P{\equiv}C$), variously named isophosphaalkynes, isophosphacyanides, or aralkyl isocyaphides, are unknown.[3] Attempts to prepare them have often resulted in the $R{-}C{\equiv}P$ isomer. Moreover, the $R{-}P{\equiv}C$ group has not been observed as a terminal ligand in transition-metal complexes (for example, as $M{-}C{\equiv}P{-}R$). However, the $R{-}P{\equiv}C$ ligand has been stabilized as a μ_2-bridging ligand in dinuclear complexes in which the carbon atom is coordinated to two platinum or two iron atoms.[3]

The $C{\equiv}P^-$ ion itself, having never been isolated in form of a salt, is the most elusive of all C≡P-containing species. However, it is the recent synthesis and characterization of a transition-metal complex[4] with a terminal cyaphide ligand that reinvigorates the search for inorganic forms of the $C{\equiv}P^-$ ion. The complex *trans*-$[(dppe)_2Ru(H)(C{\equiv}P)]$ (dppe = bis(1,2-diphenylphosphinoethane)) was prepared in 72 % yield by the reaction of the phosphaalkyne complex $[(dppe)_2Ru(H)(P{\equiv}C\text{-}SiPh_3)]^+$ (**1**) with PhO^- at room temperature or below [Eq. (1)].

Presumably the reaction occurs by nucleophilic attack of the PhO^- ion on the silicon atom to give $PhOSiPh_3$ and the isocyaphide intermediate $[(dppe)_2Ru(H)(P{\equiv}C)]$, which rearranges to the carbon-bonded product $[(dppe)_2Ru(H)(C{\equiv}P)]$ (**2**). An X-ray diffraction study of **2** shows an essentially linear Ru-C≡P unit (177.9(1)°). The C≡P bond (1.573(2) Å) is slightly longer than in $(CF_3)_3B{-}C{\equiv}P^-$ (1.563(10) Å),[5] in which there can be only σ bonding between the C and B atoms. The C≡P bond in **2** is also slightly longer than in tBu−C≡P (1.536(2) Å).[1] This lengthened C≡P bond in **2** may indicate some π back-bonding from the d^6 Ru^{II} center into the π* orbitals of the C≡P ligand. This back-bonding possibility is supported by the relatively low wave number of the ν(C≡P) band (1229 cm^{-1}) in the Raman and IR spectra of **2** as compared with the ν(C≡P) values in $(CF_3)_3B{-}C{\equiv}P^-$ (1468 cm^{-1})[5] and in tBu−C≡P (1533 cm^{-1}).[1]

The only previously reported transition-metal complex proposed to contain a terminal $C{\equiv}P^-$ ligand is *trans*-$[Pt(PEt_3)_2(Cl)(C{\equiv}P)]$ (**4**), which was prepared by the reaction of **3** (Scheme 1) with $[Pd(PEt_3)_4]$.[6] Presumably this reaction proceeds by insertion of the Pd center into the C−Cl bond of **3**, followed by transfer of the 2,4,6-tri-*tert*-butylphenyl group from the phosphorus atom to the Pd center and separation of the Pt and Pd complexes. Complex **5** was isolated in 90 % yield.

Although the proposed cyaphide complex **4** was too unstable to be isolated, a ^{31}P NMR signal at $\delta = 68.0$ ppm was assigned to the $C{\equiv}P^-$ ligand. This signal was split into a triplet ($J_{PP} = 9.2$ Hz) by coupling to the two equivalent phosphorus atoms of the PEt_3 ligands. There were also satellite peaks resulting from coupling with ^{195}Pt ($J_{PtP} = 303$ Hz). The ^{31}P NMR chemical shift at $\delta = 68.0$ ppm is very different from that in the recently characterized ruthenium complex **2** ($\delta = 165.0$ ppm); this difference is not surprising because $\delta(^{31}P)$ values in $R{-}C{\equiv}P$ compounds, where the R group is a nonmetal, range from approximately 96 to −384 ppm.[5,7]



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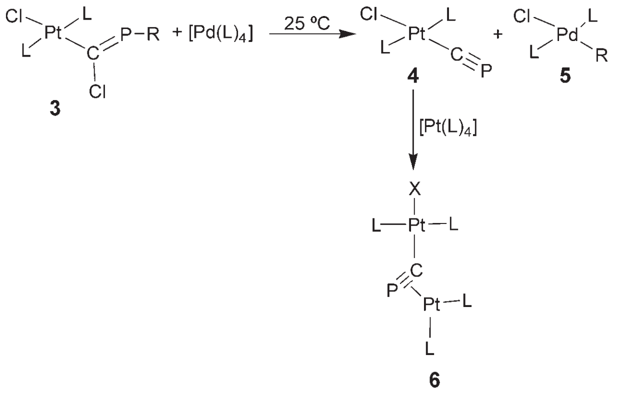
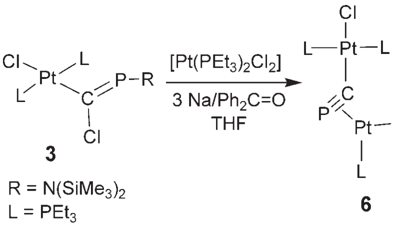


Scheme 1. Synthesis of Pt complexes with terminal and bridging CP$^-$ ligands; L = PEt$_3$, R = 2,4,6-tri-*tert*-butylphenyl.

The unstable **4** was trapped as a stable compound by treating the mixture of **4** and **5** with $[\mathrm{Pt(PEt_3)_4}]$ (Scheme 1). The product **6** of this reaction was isolated in 80% yield and characterized by an X-ray diffraction study. Its structure contains a bridging $\mathrm{C{\equiv}P^-}$ ligand that is carbon-bonded to the metal center in the $\{\mathrm{Pt(PEt_3)_2Cl}\}$ unit and η^2-bonded to the Pt center in the $\{\mathrm{Pt(PEt_3)_2}\}$ unit. Both Pt atoms, the C≡P atoms, the Cl atom, and the P atoms in the $\{\mathrm{Pt(PEt_3)_2}\}$ unit lie essentially in the same plane; only the PEt$_3$ ligands in the $\{\mathrm{Pt(PEt_3)_2Cl}\}$ unit lie out of the plane. Thus, the coordination geometry around both Pt atoms is essentially planar. The C≡P bond (1.666(6) Å) is longer than the triple bonds in phosphaalkynes R−C≡P (1.536(2) Å for R = *tert*-butyl,[1] 1.52(1) Å for R = 2,4,6-tri-*tert*-butylphenyl) and the C≡P bond in $[\mathrm{(dppe)_2Ru(H)(C{\equiv}P)}]$ (**2**; 1.573(2) Å).[4] The lengthening effect of η^2 coordination on the C≡P bond is also observed in $[\mathrm{(Ph_3P)_2Pt(\eta^2\text{-}\mathit{t}BuC{\equiv}P)}]$, where the C≡P bond (1.67(2) Å) is longer than in uncoordinated *t*Bu−C≡P (1.536(2) Å). Thus, the C≡P bond in **6** corresponds closely to a double bond as in (mesityl)P=CPh$_2$ (1.692(3) Å) and Ph(H)C=P−R (1.67 Å for R = 2,4,6-tri-*tert*-butylphenyl).[1,6] The presence of the *trans*-$\{\mathrm{Pt(PEt_3)_2(Cl)(C{\equiv}P)}\}$ unit in **6** also supports the formulation of **4** as a complex with a terminal cyaphide ligand. The reaction of **4** with $[\mathrm{Pt(PEt_3)_4}]$ to form an η^2 complex of the $\mathrm{C{\equiv}P^-}$ ligand is not surprising because of the well-known tendency of other triple-bonded compounds such as phosphaalkynes and alkynes to form analogous η^2 complexes.[2]

Complex **6** can be prepared by another method in one step in good yield (79%) by reducing **3** with Na/Ph$_2$C=O in the presence of $[\mathrm{Pt(PEt_3)_2Cl_2}]$ [Eq. (2)].[8] Although the course of this reaction is not clear, three equivalents of Na are required, presumably for the purpose of reducing the complexes and removing three Cl$^-$ ions as NaCl. The fate of the N(SiMe$_3$)$_2$ group is not known.

Despite its coordination to two Pt atoms in **6**, the $\mathrm{C{\equiv}P^-}$ ligand is able to coordinate to a third metal center as illustrated in Scheme 2.[8] An X-ray diffraction study of **7** shows that the addition of the $\{\mathrm{W(CO)_5}\}$ group to the phosphorus atom changes the geometry and bond lengths from those in **6** very little. Besides the $\{\mathrm{W(CO)_5}\}$ group, a $\{\mathrm{PtCl_2(PEt_3)}\}$ unit was also added to **6**, presumably giving a compound analogous to **7** in which the $\{\mathrm{W(CO)_5}\}$ fragment is replaced by $\{\mathrm{PtCl_2(PEt_3)}\}$. It is evident from these results that the $\mathrm{C{\equiv}P^-}$ ligand is capable of coordinating to one, two, or three metal centers.

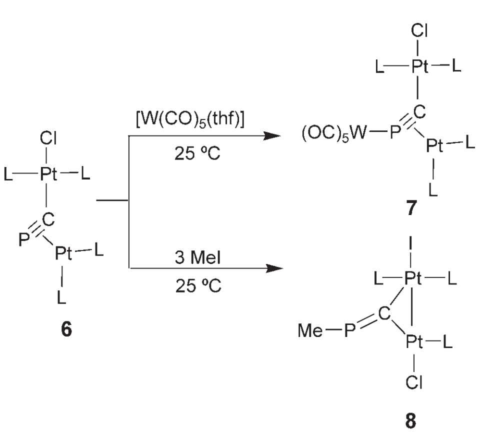


(2)

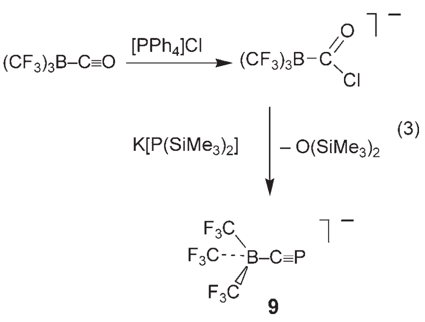
The organic electrophile CH$_3$I also reacts with **6** to put a methyl group on the phosphorus atom (Scheme 2). Subsequent loss of a PEt$_3$ group and formation of a Pt−Pt bond leads to **8**, whose structure was assigned on the basis of key ^{31}P and ^{13}C NMR features that are similar to those of an isostructural compound whose structure was established by X-ray studies.[6]

Besides the transition-metal complexes noted above, the only other Lewis acid adduct of the $\mathrm{C{\equiv}P^-}$ ion is $\mathrm{(CF_3)_3B{-}C{\equiv}P^-}$ (**9**).[5] It was prepared from $\mathrm{(CF_3)_3B{-}C{\equiv}O}$ as shown in Equation (3).

The reaction is similar to that described by Wannagat and Seyffert,[9] who treated metal carbonyl complexes $[\mathrm{L_\mathit{x}M{-}C{\equiv}O}]$ with $^-\mathrm{N(SiMe_3)_2}$ to give the corresponding cyanide complex $[\mathrm{L_\mathit{x}M{-}C{\equiv}N}]^-$ and O(SiMe$_3$)$_2$; reactions of metal carbonyl complexes with K[P(SiMe$_3$)$_2$] may be a useful route to CP$^-$ complexes. The PPh$_4$ salt of **9** was isolated in 91% yield. An X-ray diffraction investigation of the compound showed an approximately tetrahedral



Scheme 2. Reactions of the bridging CP$^-$ ligand in **6** with electrophiles; L = PEt$_3$.



arrangement of the four groups around the boron atom and a C≡P bond length of 1.563(10) Å, which is similar to that in *t*Bu−C≡P (1.536(2) Å).[1] The ^{31}P NMR spectrum of **9** contains a multiplet for the CP phosphorus atom at $\delta = 39.6$ ppm; this compares with a value of $\delta = 165.0$ ppm for **2** and $\delta = 68.0$ ppm for *trans*-[Pt(PEt$_3$)$_2$(Cl)(C≡P)]. As with phosphaalkynes,[5,7] a broad range of ^{31}P chemical shifts is observed in inorganic CP$^-$ compounds.

Since CP$^-$ has only been identified in the gas phase, our knowledge of this ion is primarily based on computational studies.[10,11] These yield a C−P bond length of 1.606 Å, which is longer than the triple bond in *t*Bu−C≡P (1.536(2) Å) but not as long as a typical P=C bond as in (mesityl)P=CPh$_2$ (1.692(3) Å). The −1 charge on CP$^-$ is more concentrated on the C atom (−0.65) than the P atom (−0.35), as indicated by calculated Mulliken charges.[11] The high negative charge on the carbon atom may account for the relatively high basicity of CP$^-$ toward protonation in the gas phase to give HCP, a compound that has been isolated but decomposes above −100 °C.[10] The high basicity of CP$^-$, compared with CN$^-$,[10] would lead to the conclusion that it should coordinate strongly in transition-metal complexes. On the other hand, one expects the π bonds in CP$^-$ to be significantly weaker[12] than those in CN$^-$ and therefore to be more reactive. As in the synthesis of isolable phosphaalkynes R−C≡P, where bulky R groups prevent oligomerization of the C≡P bond, it may be the bulkiness of the dppe ligands in [(dppe)$_2$Ru(H)(C≡P)] (**2**) that permit this compound to be isolated. The CP$^-$ ligand may also be stabilized by π back-bonding from the relatively electron-rich Ru^{II} center into the π* orbitals of the CP$^-$ ligand.

In some respects, the comparison of CP$^-$ and CN$^-$ is similar to that of CS and CO. Both CP$^-$ and CS are too reactive to be isolated as stable compounds at room temperature. On the other hand, CS has been stabilized in many transition-metal complexes,[13] and there is a rich chemistry of CS in its complexes.[14] For the CP$^-$ ligand, we know from the investigations described above that it can bind to several metals by coordinating through the carbon atom, the phosphorus atom, and the C≡P π system. Its ability to bridge metal atoms will undoubtedly surpass that of CN$^-$.[15] Like the CS ligand, the CP$^-$ ligand is likely to react with electrophiles at the phosphorus atom and with nucleophiles at the C or P atom. For the present, we can be excited about the fact that one of the fundamental ions (CN$^-$) in inorganic chemistry now has an up-and-coming sibling (CP$^-$).

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