



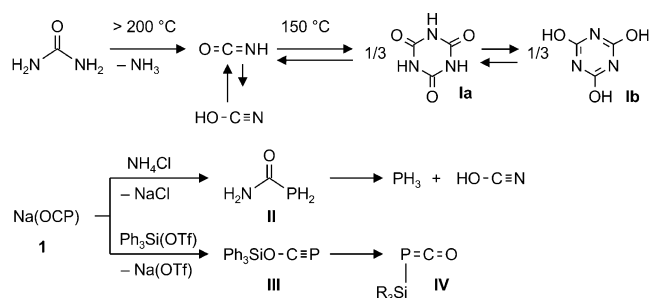
2,4,6-Tri(hydroxy)-1,3,5-triphosphinine, $P_3C_3(OH)_3$: The Phosphorus Analogue of Cyanuric Acid

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Abstract: Cyanuric acid ($C_3H_3N_3O_3$) is widely used as cross-linker in basic polymers (often in combination with other crosslinking agents like melamine) but also finds application in more sophisticated materials such as in supramolecular assemblies and molecular sheets. The unknown phosphorus analogue of cyanuric acid, $P_3C_3(OH)_3$, may become an equally useful building block for phosphorus-based polymers or materials which have unique properties.^[1] Herein we describe a straightforward synthesis of 2,4,6-tri(hydroxy)-1,3,5-triphosphinine and its derivatives $P_3C_3(OR)_3$ which have been applied as strong π -acceptor η^6 -ligands in piano stool $Mo(CO)_3$ complexes.

Cyanuric acid **I** was discovered by Wöhler^[2] nearly two centuries ago and became a useful basic chemical. Its industrial production on a million kilogram scale is still based on the pyrolysis of urea (Scheme 1). In this reaction ammonia is released and isocyanic acid (HNCO) is formed which has been identified as the key intermediate.^[3] Derivatives of the cyanuric acid^[4] are employed in the synthesis of herbicides,^[5] dyes,^[6] flame retardants^[7] and are employed as components in supramolecular assemblies.^[8] The keto form **Ia** is thermodynamically preferred over the tautomeric form **Ib**.

To the best of our knowledge, the phosphorus analogues of cyanuric and isocyanuric acid have neither been synthesized nor observed by spectroscopic methods. The six-membered P_3C_3 ring is known from 1,3,5-triphosphinines which are isolated with sterically demanding alkyl substituents to achieve kinetical stability (e.g. $R = \textit{tert}$ -butyl, 1,1-dimethylpropyl, 1-methylcyclohexyl, 1-methylcyclopentyl, adamantyl).^[9] Although the aromatic stabilization in the parent 1,3,5-triphosphinine is similar to that in benzene, even the heavily substituted analogues undergo easily chemical transformations in which the low-coordinate phosphorus



Scheme 1. Classic synthesis of cyanuric acid **I** and relevant reactions of $Na(OCP)$.

centers change to ones with a higher coordination number. For example, $P_3C_3^tBu_3$ reacts reversibly with dihydrogen or forms inorganic cage compounds when reacted with pnictogen trihalides.^[10] 1,3,5-Triphosphinines are excellent ligands to bind metals in both η^1 and η^6 coordination modes.^[11] Very recently the first aromatic pnictogen–silicon congeners of benzene $E_3Si_3R_3$ [$E = P, As$; $R = (PhC(N^tBu)_2)_3$] have been isolated.^[12]

A straightforward approach to $P_3C_3(OH)_3$ would be the trimerization of $HO-C\equiv P$. But attempts to produce any of the HPCO isomers in solution by protonation of phosphaethylenolate salts, $M^+(OCP)^-$ ($M = Na, K$) failed so far.^[13] The phosphaketene $HP=C=O$ is by 20.3 kcal mol⁻¹^[14] more stable than the tautomer $HO-C\equiv P$ and was only detected by IR and microwave spectroscopy in the gas phase as product of the photolysis of PH_3 and CO .^[15] An alternative synthesis of $P_3C_3(OH)_3$ could consist in the thermolysis of the phosphorus analogue of urea, namely $H_2P(CO)NH_2$ **II** (Scheme 1), which however, decomposes to PH_3 and isocyanic acid upon heating.^[10a] It is known that phosphaketenes, $R-P=C=O$, dimerize to cyclic 1,3-diketones $(RP)_2(CO)_2$ ^[16] which are reluctant to undergo a ring expansion to the desired trimers. We therefore reasoned that a suitable oxyphosphaalkyne ($RO-C\equiv P$) is needed which in the first step may dimerize to a 1,3-diphosphabutadiene. Because this species is still a reactive diene component, it may further react with a third equivalent of $RO-C\equiv P$ to give $P_3C_3(OR)_3$ in analogy to the few known examples of transition metal promoted trimerization of alkyl-substituted phosphaealkynes to triphosphinines.^[17] The stability of $R-O-C\equiv P$ versus $R-P=C=O$ is mainly dictated by the $R-O$ versus $R-P$ and $C\equiv P$ versus $C=O$ bond dissociation energies.^[18] To date only lanthanide complexes were found in which the OCP unit binds via the oxygen center^[19] while all tetrel-substituted oxyphosphaalkynes R_3E-OCP with $E = C, Si, Ge, Sn, Pb$ are thermodynamically less

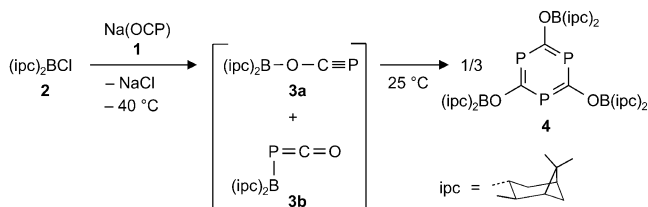
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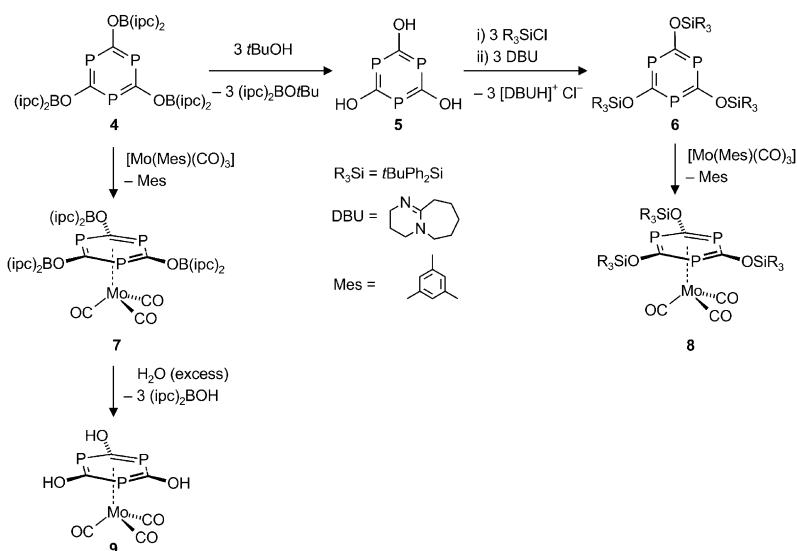
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stable than the corresponding phosphaketene $R_3E\text{-PCO}$ isomers. Only the siloxy phosphalkyne **III** has been observed as transient product in a kinetically controlled reaction before it isomerized to the thermodynamically preferred isomer **IV**. Boron is more oxophilic than silicon (bond dissociation energies: B–O: 809 kJ mol⁻¹, Si–O: 799.6 ± 13.4 kJ mol⁻¹) while the B–P dissociation energy is smaller in comparison with that of the Si–P bond (B–P: 347 ± 16.7 kJ mol⁻¹, Si–P 363.6 kJ mol⁻¹).^[20] Composite calculations at the CBS-QB3 level show that $Me_2B\text{-O-C}\equiv P$ is only slightly more stable (by 1.4 kcal mol⁻¹) than its isomer $Me_2B\text{-P=C=O}$ (for details and substituent effects see Table S1 in the Supporting Information) which means that the formation of either constitutional isomer can be expected. An equimolar solution of the readily available (–)-B-chlorodiisopinocampheylborane (ipc)₂B–Cl **2** [(–)-DIP-Chloride] and Na(OCP)(dioxane)_{2.5} **1** has been analyzed by ³¹P-NMR spectroscopy at –40 °C and shows, beside the signal of unreacted Na(OCP) (δ = –391.2 ppm), three new resonances at δ = –298.0 ppm, δ = –321.2 ppm, and δ = –317.4 ppm. We tentatively assign the resonance at δ = –298.0 ppm to (ipc)₂B–O–C≡P [**3a**] and the other two to isomers of (ipc)₂B–P=C=O [**3b**] (Scheme 2).^[18,21] When the solution was warmed to room temperature, a new singlet in the ³¹P-NMR spectrum at δ = 182.7 ppm appeared, which is in the range of triphosphinines such as $P_3C_3(Bu)_3$ [$\delta(^{31}P)$ = 211.8 ppm], along with several persistent resonances indicating side products.



Scheme 2. The formation of [**3a**], [**3b**] and **4** from the reaction of Na(OCP) **1** with (ipc)₂B–Cl **2**.

When a solution of one equivalent of Na(OCP)-(dioxane)_{2.5} in THF was added at room temperature to a solution of **2**, a very clean reaction occurs and only the signal at δ = 182.7 ppm is observed in the ³¹P-NMR spectrum of the reaction mixture. Note that inverting the sense of addition—that is, adding **2** to **1**—leads to a mixture of several products which have not been identified. Characterization by single-crystal X-ray crystallography shows that the product with $\delta(^{31}P)$ = 182.7 ppm is the desired $P_3C_3[OB(ipc)_2]_3$ (**4**). We assume that **4** is formed by trimerization of the borinic ester functionalized phosphalkyne (ipc)₂B–O–C≡P [**3b**] although we could not detect any intermediates. The ¹³C-NMR resonance for the aromatic carbon atoms could be observed at δ = 226.6 ppm which is similar to the one of $P_3C_3(tBu)_3$ (δ =



Scheme 3. Deprotection of **4** to give **5**. Protection with ^tBuPh₂SiCl formed the silyl ether functionalized compound **6**. Syntheses of complexes **7**, **8**, and **9**.

227 ppm) using a triple resonance broad-band (TBI) probe with ¹H/²D/³¹P/BB channels. The three O–BR₂ functionalities in **4** can be easily cleaved when an excess of alcohol like methanol or *tert*-butanol is added to a solution of **4** in [D₈]THF (Scheme 3). The quantitative formation of $P_3C_3\text{-(OH)}_3$ (**5**) is indicated by a new singlet in the ³¹P-NMR spectrum at δ = 133.7 ppm (without observable J_{P-H} coupling). The presence of a higher order multiplet in the ¹³C-NMR spectrum at δ = 231.3 ppm verified the existence of a P_3C_3 core with magnetically inequivalent carbon atoms. The resonance for the OH groups in the ¹H-NMR spectrum could not be unambiguously identified but after reaction of **4** with [D₁]methanol one singlet resonance in the ²H-NMR spectrum at δ = 10.0 ppm indicates the presence of three deuterioxy (O–D) groups of the triol [D₃]**5**. We have no spectroscopic evidence for the presence of other tautomers of $P_3C_3(OH)_3$ although CBS-QB3 calculations in the gas phase indicate that the 1,3,5-*H*-2,4,6-trione, (PH)₃(CO)₃ lies practically at the same energy as the triol tautomer (energy difference: 0.6 kcal mol⁻¹, which can be considered in the range of the computational error). This is in marked contrast to the mono-hydroxy derivative, phosphinin-2-ol, which is significantly more stable by 18.1 kcal mol⁻¹ than the keto form.^[22] These calculations refer to isolated molecules. In order to explain why only the triol tautomer is observed in solution, we assume that this isomer may be stabilized in THF solution via O⋯H⋯O hydrogen bonds (note that the PH group is a poor hydrogen donor). This assumption is supported by the fact that 1,3,5-triphosphinine-2,4,6-triol **5** is stable in THF solution for several days but decomposes in benzene over hours to form PH₃ and further unidentified products. Also upon removal of the solvent compound **5** decomposes. The aromaticity was evaluated by NICS calculations at the B3LYP/6-311+G** level of theory which show that $P_3C_3(OH)_3$ [NICS(1): –8.1 ppm] is best described as an aromatic compound comparable to benzene [NICS(1):

−10.2 ppm] or 1,3,5-triphenylphosphine $P_3C_3H_3$ [NICS(1): −8.6 ppm].

The reaction between **5** and $t\text{BuPh}_2\text{SiCl}$ in presence of 1,8-diazabicycloundec-7-ene (DBU) cleanly leads to the silylated compound $P_3C_3(\text{OSi}^t\text{BuPh}_2)_3$ **6** as indicated by one singlet in the ^{31}P spectrum ($\delta = 177.5$ ppm). Similarly to the triol **5**, compound **6** could not be isolated due to its sensitivity and was only observed in solution.

Because of their increased π -accepting properties, π -conjugated heterocycles with sp^2 -hybridized phosphorus centers are remarkable ligands often leading to very stable complexes.^[23] Therefore the reactions between the borylated and silylated tri(oxy)triphosphinines **4** or **6** and $[\text{Mo}(\text{Mes})(\text{CO})_3]$ were investigated. In both cases, a clean displacement of the mesitylene (Mes) group occurs, leading to products **7** or **8** which show singlet resonances at $\delta = 8.1$ ppm or $\delta = 16.1$ ppm in the ^{31}P -NMR spectrum, respectively. The chemical shift of the related complex $[\text{Mo}(P_3C_3^t\text{Bu}_3)(\text{CO})_3]$ is observed at $\delta = 56.7$ ppm.^[11d] Reaction of the borylated complex **7** in THF with an excess of water leads to **9** which was characterized in solution (^{31}P NMR: $\delta = -4.9$ ppm). ATR-IR spectra were obtained from the crystalline products of **7** and **8** and the one of $[\text{Mo}(\text{Mes})(\text{CO})_3]$ was measured under the same conditions for comparison.^[24] The IR spectrum of **9** was measured in solution. The two stretching frequencies of the carbonyl groups decrease in the order **7**

(ν_{CO} [cm^{-1}] = 2022.4, 1971.6), **8** (ν_{CO} [cm^{-1}] = 1992.8 (s), 1941.4), **9** (ν_{CO} [cm^{-1}] = 1988.4 (s), 1924.7), $[\text{Mo}(\text{Mes})(\text{CO})_3]$ (ν_{CO} [cm^{-1}] = 1941.1 (s), 1869.9). The data are not available for $[\text{Mo}(P_3C_3^t\text{Bu}_3)(\text{CO})_3]$ but for $[\text{Cr}(P_3C_3^t\text{Bu}_3)(\text{CO})_3]$ the stretching absorptions in a cyclohexane solution are observed at ν_{CO} [cm^{-1}] = 1979 (s), 1926 (s).^[25] These data indicate the strong electron-accepting properties of the phosphacyanuric acid derivatives, especially for the borylated complex **7**, which diminishes the donation of electron density from Mo to CO. This effect leads to a low Mo–C bond order close to one and consequently a high C≡O bond order causing elevated ν_{CO} stretching frequencies. In line with this assumption are the resonances in the ^{95}Mo -NMR spectrum which are significantly deshielded for **7** and **8** ($\delta = -1567$ ppm; $\delta = -1578$ ppm) in comparison to $[\text{Mo}(\text{Mes})(\text{CO})_3]$ ($\delta = -1903$ ppm).^[26]

Single crystals of the uncoordinated borylated trioxy-phosphinine $P_3C_3[\text{OB}(\text{ipc})_2]_3$ **4** (light yellow) and the dark yellow complexes $[\text{Mo}(P_3C_3(\text{OX})_3)(\text{CO})_3]$ **7** [$\text{X} = \text{B}(\text{ipc})_2$] and **8** [$\text{X} = \text{Si}^t\text{BuPh}_2$] were subjected to X-ray diffraction analyses in order to determine the structures which are displayed in Figure 1 a–c. The P_3C_3 ring in **4** is planar with an average P–C bond length of 1.736 Å. The averaged bond angles C–P–C 104.0° and P–C–P 136.0° are very similar to the ones in $P_3C_3^t\text{Bu}_3$.

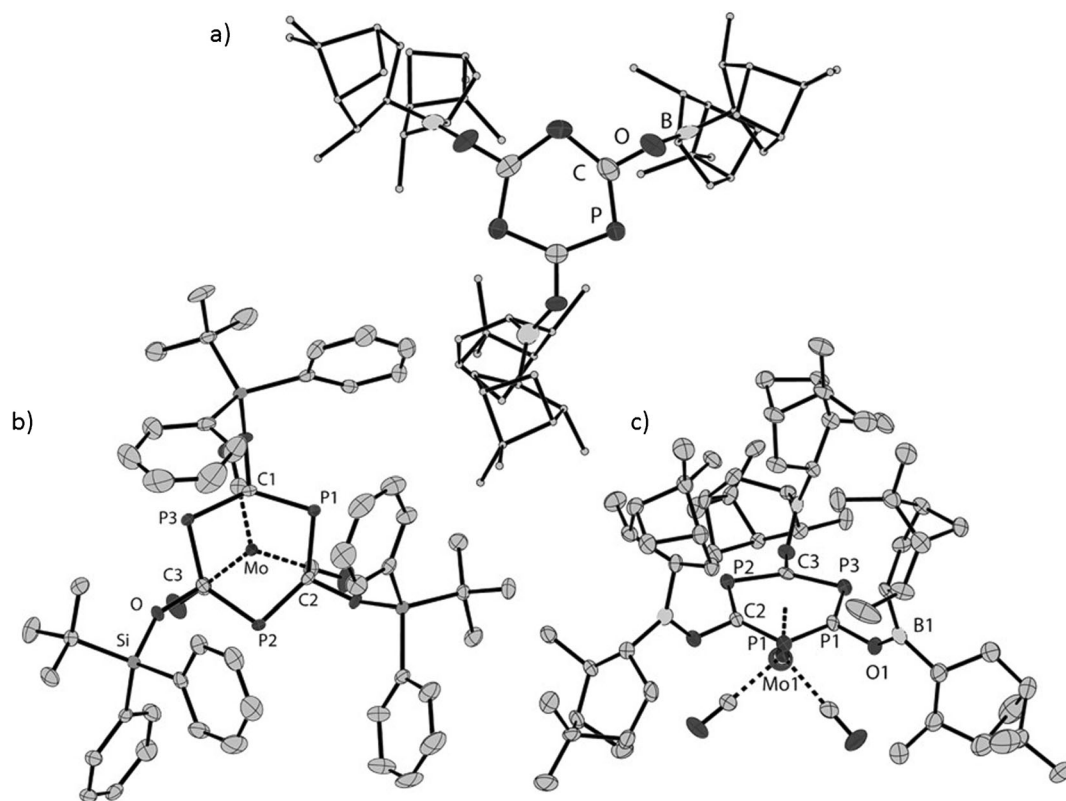


Figure 1. a) Structure of **4**. Thermal ellipsoids are shown at a 50% probability level. For clarity, hydrogen atoms and solvent molecules are omitted and the camphor groups in **4** are only shown as ball-and-stick models. Ct = centroid of the P_3C_3 ring. Interatomic distances [Å] and angles [°]: P–C_{average} 1.736; P–C–P_{average} 136.0; C–P–C_{average} 104.0. b) Structure of **7**. P–C_{average} 1.765, Mo–C_{ring}_{average} 2.342, Mo–P_{ring}_{average} 2.602, Mo–Ct 1.733; P–C–P_{average} 138.7, C–P–C_{average} 101.18. c) Structure of **8**. P–C_{average} 1.768, Mo–C_{ring}_{average} 2.364, Mo–P_{ring}_{average} 2.623, Mo–Ct 1.753; P–C–P_{average} 137.86, C–P–C_{average} 101.92.

The P_3C_3 unit in **7** and **8** is again planar and binds to the molybdenum center in a η^6 -coordination mode. The average P–C bond distances (1.765 and 1.768 Å) are slightly but significantly elongated compared to those in **4** also with respect to the $Mo(CO)_3$ -coordinated $P_3C_3(Bu)_3$ (1.753 Å).^[11e] The endocyclic P–C–P angles in **7** and **8** are somewhat widened and the C–P–C angles slightly narrowed with respect to **4**. The distance between the Mo center and the centroid of the P_3C_3 ring, Ct, decreases in the order $[Mo(P_3C_3'Bu_3)(CO)_3]$ (1.800 Å)^[24] > **8** (1.753 Å) > **7** (1.733 Å) which again can be interpreted as an increase in the metal-to- P_3C_3 ring electron donation and strengthening of the metal triphosphinine interaction in this order.

In summary a remarkably simple synthesis of 2,4,6-oxy functionalized 1,3,5-triphosphinines on a multi-gram scale has been found which does not require the use of transition metals. These $P_3C_3(OX)_3$ (X = H, BR_2 , SiR_3) compounds are analogues to (iso)cyanuric acid but in stark contrast are rather labile compounds. However, they may be η^6 -coordinated via the aromatic P_3C_3 unit to transition metal fragments which results in stable molecules and opens possibilities to use complexes of $P_3C_3(OX)_3$ as building block or cross-linkers for polymeric materials. The interaction between the metal center and the triphosphinine ring can be influenced by the substituents X bound to the oxygen centers of the $P_3C_3(OX)_3$ ring by which the properties of triphosphinine complexes may be fine-tuned which may be of interest in coordination chemistry and catalysis.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: coordination compounds · cyanuric acid · heterocycles · phosphinines · phosphorus

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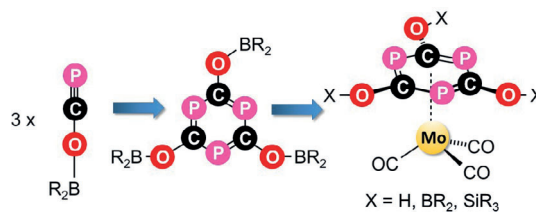


Phosphorus Heterocycles

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2,4,6-Tri(hydroxy)-1,3,5-triposphinine,
 $P_3C_3(OH)_3$: The Phosphorus Analogue of
 Cyanuric Acid



Done in three ticks: The trimerization of boryl-substituted phosphalkynes allows the straightforward synthesis of triphosphabenzene derivatives on a multi-gram scale.

These compounds give stable metal complexes and can be further functionalized at the oxygen centers.