Abstract: While tetrahedranes as a family are scarce, neutral heteroatomic species are all but unknown, with the only reported example being AsP$_3$. Herein, we describe the isolation of a neutral heteroatomic X$_2$Y$_4$ molecular tetrahedron (X, Y = p-block elements), which also is the long-sought-after free phosphaalkyne dimer. Di-tert-butyldiphosphatetrahedrane, (tBuCP)$_2$, is formed from the monomer tBuCP in a nickel-catalyzed dimerization reaction using [(NHC)Ni(CO)$_3$]$_2$ (NHC = 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene (IMes) and 1,3-bis(2,6-disopropylphenyl)imidazolin-2-ylidene (IPr)). Single-crystal X-ray structure determination of a silver(I) complex confirms the structure of (tBuCP)$_2$. The influence of the N-heterocyclic carbene ligand on the catalytic reaction was investigated, and a mechanism was elucidated using a combination of synthetic and kinetic studies and quantum chemical calculations.

Tetrahedranes (tricyclo[1.1.0.0$^{2,4}$]butanes) have considerable practical and theoretical significance because of their high energy content, large bond strain and ensuing high reactivity.$^{[1]}$ While theoretical chemists have endeavored to determine the electronic structure and the thermodynamic stability of tetrahedranes with ever increasing accuracy,$^{[2–5]}$ synthetic chemists have striven to develop effective protocols for their preparation. The isolation by Maier and co-workers of the first organic tetrahedrane, (BuC)$_4$, was a milestone in organic synthesis (Figure 1a).$^{[6]}$ Nevertheless, the number of well-characterized tetrahedranes remains small, even more than four decades later.$^{[7–10]}$ Some heavier congeners, for example, (RE)$_4$ (E = Si and Ge, R = SiBu$_3$) and related group 13 element compounds, are also known,$^{[11–13]}$ as are the structures adopted by white phosphorus (P$_4$) and yellow arsenic (As$_4$). Undoubtedly, P$_4$ is the most industrially significant tetrahedrane. Moreover, neutral tetrahedranes containing two different heteroatoms in their skeleton are almost unknown, the only example to have been isolated so far being AsP$_3$, which was synthesized by reaction of an iobium cyclotriphosphido with a dibutylphosphinidene.$^{[14–20]}$

Diphosphatetrahedranes, (RCP)$_2$, represent a particularly attractive target in this area, potentially providing a hybrid between the two most famous tetrahedral molecules, P$_4$ and (tBuC)$_4$. However, high level quantum chemical studies indicate that, similar to pure carbon-based tetrahedranes, such a species must be stabilized by bulky alkyl substituents (Figure 1b). Thus, while 1,2-diphosphatriafulvene (IV) is predicted to be the preferred isomer of (HCP)$_2$, the diphosphatetrahedrane (I) is the most stable isomer of (tBuC)$_2$. Figure 1b) Related diphosphacyclobutadienes II and III are considerably higher in energy in both cases.

We reasoned that the dimerization of phosphaalkynes, R-C=\(\text{P}\), could present an elegant avenue toward elusive diphosphatetrahedranes. Indeed, transition metal-bound phosphaalkyne dimers (most frequently 1,3-diphosphacyclobutadienes,$^{[23]}$ but also other isomers) commonly result from transition metal-mediated phosphaalkyne oligomerization reactions.$^{[24]}$ Free diphosphatetrahedranes have also been proposed as key intermediates in thermal and photochemical oligomerization reactions of phosphaalkynes, which typically lead to higher phosphaalkyne oligomers (RCP)$_3$ ($n = 3$–6).$^{[28–30]}$ However, an uncomplexed phosphaalkyne dimer has never been observed.

Building on previous work on iron(-I) and cobalt(-I)-mediated phosphaalkyne dimerizations,$^{[31–33]}$ we recently began studying the analogous reactivity of phosphaalkynes with nickel(0) species. Unexpectedly, the $^{[31]}$P$^{[1]}$H NMR spectrum of the reaction of [Ni(CO)$_3$]$_2$ with an excess of tBuCP (50 equivalents) exhibited a high-field-shifted singlet at $-468.2$ ppm in addition to the signal of free tBuCP at $-68.1$ ppm. It was anticipated that such an upfield shift could be consistent with formation of a P$_2$C$_3$ tetrahedron (cf.
displays as singlet resonance at −468.2 ppm similar to other tetrahedral phosphorus compounds, for example, \( P_1 (\Delta P) = −520 \) ppm and As\( P_1 (\Delta P) = −584 \) ppm.\(^\text{34–36}\) The \( ^1H \) NMR spectrum shows a singlet resonance at 1.07 ppm for the \( tBu \) group. In the \( ^{13}C[\text{H}] \) spectrum, a singlet resonance is observed for the methyl groups, whereas the two other carbon signals split into triplets with \( J_{FC} = 46.7 \) Hz and \( J_{FC} = 5.7 \) Hz (Figure 2). \( 1 \alpha \) was further characterized by elemental analysis, IR, UV/VIS spectroscopy and mass spectrometry. The UV/VIS spectrum reveals a weak absorption band at 275 nm \( (\epsilon_{\text{max}} = 1200 \text{ Lmol}^{-1}\text{cm}^{-1}) \) tailing into the visible region with a shoulder at 350 nm accounting for the yellow color. Analysis of \( 1 \alpha \) by EI-MS mass spectrometry revealed a molecular ion peak at \( m/z = 200.0879 \) in good agreement with the calculated molecular ion peak \( (m/z = 200.0878) \) and additionally showed fragmentation pathways via loss of \( \text{P} \) units (e.g. \( M^+ - \text{CH}_2 - \text{P}_2: \ 123,1172, \text{calcd} 123,1173) \).

Attempts to grow single crystals of \( 1 \alpha \) suitable for X-ray crystallography have so far been unsuccessful. For this reason, the preparation of a metal complex was attempted with \([\text{Ag(CH}_3\text{Cl}_2](\text{pftb})] \) \( (\text{pftb} = \text{Al(OC}(\text{CF}_3)\text{)}_3)\)\(^\text{37,38}\). A clean reaction was observed in toluene using two equivalents of \( 1 \alpha \) per silver atom, and a species with a significantly downfield shifted \( ^{31}P[\text{H}] \) NMR signal \( (−446.8 \) ppm, cf. −468.2 ppm for \( 1 \alpha \)) was detected. Further NMR monitoring also showed the slow formation of the tetramer \( 2 \alpha \). A single-crystal X-ray diffraction study on crystals grown from \( \text{CH}_3\text{Cl}_2 \) revealed the formation of \([\text{Ag}(1 \alpha)(2 \alpha)]_2[\text{pftb}] \) \( (3) \), where both \( 1 \alpha \) and \( 2 \alpha \) are incorporated in the same complex (Figure 3).\(^\text{39}\) Crucially, the X-ray diffraction experiment confirms the tetrahedral structure of \( 1 \alpha \). The \( \text{P}_5 \text{C}_5 \) tetrahedron is bound to the Ag atom in an \( \eta^3 \) fashion via the \( \text{P} \)–\( \text{P} \) bond \( (\text{P}_1 – \text{P}_2 = 2.308(3) \text{ Å}) \). The four \( \text{P} – \text{C} \) bond lengths in the tetrahedron range 1.821(9)–1.836(9) \( \text{ Å} \), while the \( \text{C} – \text{C} \) bond length \( (\text{C}_1 – \text{C}_2 = 1.462(12) \text{ Å}) \) is similar to that of \( \text{tBuC}_3 \) (average: 1.485 \text{ Å}).\(^\text{40}\) Broadened singlet resonances are observed in the \( ^{31}P[\text{H}] \) NMR spectrum at −19.8 and −446.8 ppm when crystals of \( 3 \) are dissolved in...
CD2Cl2, and the 1H NMR data are also consistent with the molecular structure obtained by X-ray crystallography.[41]

In an attempt to identify possible intermediates in the formation of 1a, the nickel tricarbonyl complexes [(NHC)Ni(CO)]2 (NHC = IMes, IPr, IPrImMe) were reacted with one equivalent of phosphalkyne RCP (R = tBu, Ad) in n-hexane at ambient temperature. Each of these reactions led to an instant color change from colorless to bright yellow and concomitant gas evolution (liberation of CO gas). For the sterically more demanding NHC ligands IPr and IMes, the phosphalkyne complexes [(NHC)Ni(CO)PC(Pr)] (NHC = IMes, R = tBu (4a), Ad (4b), NHC = IPr; R = tBu (4c), Ad (4d)) featuring η1-bound phosphalkyne ligands were the sole P-containing products of these reactions (Figure 4a). Complexes 4a–4d can be isolated as crystalline solids in yields from 34% to 87%, and were characterized by single crystal X-ray diffraction, multinuclear NMR spectroscopy, IR spectroscopy and elemental analysis (see Supporting Information for details). The structural and spectroscopic data compare well to the related, isostructural complexes [(IPrImMe)Ni(PC(Bu))] and [(IPrIm=1.3-di(isopropyl)imidazol-2-ylidene) and [(trop|NMe)(PCPMe)] (trop = 5H-dibenzo-[a,d]cyclohepten-5-yl).[42,43]

Conversely, the reaction of tBuCP with [(IPrImMe)Ni(CO)] afforded a mixture of the mononuclear 1,3-diphosphacyclobutadiene complex [(IPrImMe)Ni(CO)(η1-P{PCCPMe})] (5), the dinuclear complex [(IPrImMe)Ni(CO)]2(μ1,η1-η1-tBuCP)] (6) and a tetranuclear cluster [(IPrImMe)Ni2(CO)3(tBuCP)2] (7). Figure 4b). The three different species were identified in the 31P[1H] NMR spectrum and structurally authenticated by X-ray diffraction experiments after fractional crystallization. Treatment of [(IPrImMe)Ni(CO)] with just 0.5 or two equivalents of tBuCP resulted in similar mixtures. Upon addition of tBuCP to one equivalent of [Ni(CO)]3, more than ten different species were detected by 31P[1H] NMR spectroscopy. The unselective nature of these reactions is in contrast to the selective formation of the η1-bound phosphalkyne complexes 4a–d and presumably accounts for the lower yields in the catalytic formation of 1a.

With a high-yielding protocol for the preparation of 4a in hand, the reactivity of this species was investigated. 4a is the most potent catalyst for the dimerization of tBuCP among all nickel complexes investigated. Thus, a significantly shorter reaction time for full conversion of the phosphalkyne is required with 4a than with [(IMes)Ni(CO)]3. High temperature 31P[1H] NMR spectroscopic monitoring of this catalytic dimerization reaction revealed the presence of 4a at a constant concentration throughout the whole reaction (see Supporting Information for further details). These observations suggest that 4a is the resting state for the catalytic cycle. Further reaction intermediates were not detected by 31P[1H] NMR spectroscopy even upon monitoring the reaction at –80°C. Also noteworthy is that treatment of 4a with one equivalent AdCP affords the mixed-substituted diphosphaheptahexane (P5C3AdBu, 1c), which can be identified by a 31P[1H] NMR singlet at –473.8 ppm.

Kinetic analysis with 0.5 to 4 mol% of 4a indicates a first-order dependence of the dimerization reaction in both catalyst and phosphalkyne. The proposed rate law is therefore [Eq. (1)]:

\[
\frac{dr}{dt} = k \cdot |4a| \cdot |tBuCP|
\]

These results are in good agreement with DFT calculations performed on the TPSS-D3BJ/def2-TZVP level, which suggest that the reaction between the truncated model complex [(IXy)Ni(CO)(tBuCP)] (4'), IXy = 1,3-bis(2,6-dimethylphenyl)imidazol-2-ylidene) and a molecule of tBuCP initially affords the 1,3-diphosphacyclobutadiene complex A (Figure 5, cf. complex 5, which differs only in the identity of NHC ligand; see Supporting Information for more details).[44] However, A is not the global minimum of the potential hypersurface and transforms into an intermediate B showing an isomerized (tBuCP), ligand. In the next step, a diphosphaheptahexane complex C is formed. The formation of C has a calculated activation barrier of 26.9 kcal mol−1 with respect to A. This is well in line with the reaction temperature of +60°C required for the reaction to proceed at an appreciable rate (vide supra). Subsequent replacement of the diphosphaheptahexane 1a by another phosphalkyne molecule is a downhill process and re-forms the resting state 4' (cf. complex 4, which is the only species we could identify by NMR spectroscopy in solution). Notably, a different scenario...
has been calculated for a further truncated model system consisting of Me-C/P and [(IPh)Ni(PCMe)], (IPh = 1,3-diphenylimidazolin-2-ylidene, see Supporting Information for further details). In this case, significant stabilization of the analogous 1,3-diphosphacyclobutadiene complex (A') is observed. The high activation barrier calculated for the transformation A' → C' (49.8 kcal mol⁻¹) precludes the formation of the diphosphatetrahedrane. It appears that the steric repulsion between bulky substituents on the NHC such as Mes and Dipp and the tBu groups has a destabilizing effect on A, and this destabilization of the 1,3-diphosphacyclobutadiene complex, which is usually a thermodynamic sink in other reactions, enables catalytic turnover in this particular case.

In conclusion, diphosphatetrahedranes (RCP)₂ (R = tBu, Ad) have been synthesized by an unprecedented nickel(0)-catalyzed dimerization reaction of the corresponding phosphaalkynes RCP. The tert-butyl-derivative (tBuCP) (1a) is stable enough to be isolated and thoroughly characterized. The molecular structure of the silver(I) complex 3 confirms the tetrahedral structure of the molecule. 1a is a very rare “mixed” tetrahedrane, which, moreover, represents the hitherto elusive free phosphaalkyne dimer. Its synthesis therefore closes a significant gap in phosphaalkyne oligomer chemistry. 1a is a metastable compound that slowly converts to the ladderane 2a. This reaction shows that such dimers are indeed intermediates in phosphaalkyne tetramerizations as proposed previously.²⁵,²⁶ Synthetic, kinetic and computational investigations suggest that a 1,3-diphosphacyclobutadiene complex is a key intermediate and that destabilization of this complex by steric repulsion is a crucial factor in achieving catalysis. We are currently exploring the further reactivity of the remarkable small molecule 1a.

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Conflict of interest

The authors declare no conflict of interest.

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