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Di-*tert*-butyldiphosphatetrahedrane: Catalytic Synthesis of the Elusive Phosphaalkyne Dimer

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Abstract: While tetrahedranes as a family are scarce, neutral heteroatomic species are all but unknown, with the only reported example being AsP₃. Herein, we describe the isolation of a neutral heteroatomic X_2Y_2 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] (NHC = 1,3-bis(2,4,6trimethylphenyl)imidazolin-2-ylidene (IMes) and 1,3-bis(2,6diisopropylphenyl)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, (tBuC)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.^[7–13] Some heavier congeners, e.g. $(RE)_4$ (E = Si and Ge, R = SitBu₃) and related group 13 element compounds, are also known,^[14-21] as are the structures adopted by white phosphorus (P_4) and yellow arsenic (As_4) . Undoubtedly, P₄ 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 AsP₃, which was synthesized by reaction of a niobium cyclotriphosphido complex with AsCl₃.^[22]

Diphosphatetrahedranes, $(\text{RCP})_2$, represent a particularly attractive target in this area, potentially providing a hybrid between the two most famous tetrahedral molecules, P₄ and $(t\text{BuC})_4$. 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,

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Regensburg, Germany, E-mail: <u>robert.wolf@ur.de</u> Supporting information for this article is given via a link at the end of the document. while 1,2-diphosphatriafulvene (**IV**) is predicted to be the preferred isomer of (HCP)₂, the diphosphatetrahedrane (**I**) is the most stable isomer of (*t*BuCP)₂ (Figure 1b).^[3,5] Related diphosphacyclobutadienes **II** and **III** are considerably higher in energy in both cases.

We reasoned that the dimerization of phosphaalkynes, R-C≡P, could present an elegant avenue toward elusive diphosphatetrahedranes. Indeed, transition metal-bound phosphaalkyne dimers (most frequently 1.3diphosphacyclobutadienes,^[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)_n (n = 3-6).^[25-30] However, an uncomplexed phosphaalkyne dimer has never been observed.



Figure 1. a) The tetrahedrane (*t*BuC)₄ in equilibrium with the cyclobutadiene isomer and DFT structure of (*t*BuCP)₂;^[6] b) calculated relative electronic energies (Δ E in kcal·mol⁻¹) for (RCP)₂ with R = H (data from ref. [3]) and R = *t*Bu (see the SI).

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 ³¹P{¹H} NMR spectrum of the reaction of [Ni(CO)₄] with an excess of *t*BuCP (50 equivalents) exhibited a high field-shifted singlet at –468.2 ppm in addition to the signal of free *t*BuCP at –68.1 ppm. It was anticipated that such an upfield shift could be consistent with formation of a P₂C₂ tetrahedron (*cf.* P₄, δ = –521 ppm), through dimerization of *t*BuCP. This assumption was later confirmed through isolation of the pure product **1a** (*vide infra*). A subsequent screening of various nickel tricarbonyl complexes [(NHC)Ni(CO)₃] (NHC = IMes, IPr, *i*Pr₂Im^{Me} (= 1,3-di(isopropyl)-4,5-di(methyl)imidazolin-2-ylidene)) for this

dimerization reaction of tBuCP revealed that the bulky NHC ligands IPr and IMes gave optimal results (see the Supporting Information for details), while the use of the smaller isopropylsubstituted ligand *i*Pr₂Im^{Me} resulted in only a low yield of **1a**. Using [(IMes)Ni(CO)₃], 1a can be isolated in up to 55% yield on a 500 mg scale using just 2 mol% of the nickel catalyst in *n*-hexane for 18 h (Figure 2). Fractional condensation of the raw product affords pure 1a as a pyrophoric, yellow oil with a melting point of -32 °C. Above the melting point, neat **1a** dimerizes to the known ladderane-type tetramer tetraphosphatricyclo[4.2.0.0^{2,5}]octadiene (2a, Figure 2) within several hours.^[25] However, 1a is stable at -80 °C for weeks without noticeable decomposition as evidenced by ³¹P{¹H} NMR. Dimerization of **1a** to **2a** is significantly slower in dilute solutions (e.g. 0.2 M in toluene). The use of 1adamantylphosphalkyne under similar conditions results in the analogous formation of diadamantyldiphosphatetrahedrane (1b), as indicated by a resonance at -479.8 ppm in ³¹P{¹H} NMR spectra. However, attempts to isolate 1b in pure form have thus far been hampered by decomposition to higher phosphaalkyne oligomers (e.g. the ladderane (AdCP)₄ (2b) analogous to 2a).



Figure 2. a) Synthesis of 1a by [(NHC)Ni(CO)₃] (NHC = IMes, IPr) catalyzed dimerization of *t*BuCP, b) ³¹P{¹H} and ¹³C{¹H} NMR spectra for 1a at 300 K in C₆D₆. The asterisk marks a trace of the tetramer (*t*BuCP)₄ (2a, i.e. the dimerization product of 1a).

Multinuclear NMR spectra of **1a** are in agreement with the tetrahedral structure with localized $C_{2\nu}$ symmetry. The ³¹P{¹H} NMR spectrum of **1a** in C₆D₆ displays a singlet resonance at -468.2 ppm similar to other tetrahedral phosphorus compounds, e.g. P₄ (δ (³¹P) = -520 ppm) and AsP₃ (δ (³¹P) = -484 ppm).^[34-36] The ¹H NMR spectrum shows a singlet resonance at 1.07 ppm for the *t*Bu group. In the ¹³C{¹H} spectrum, a singlet resonance is observed for the methyl groups, whereas the two other carbon signals split into triplets with ¹J_{P-C} = 46.7 Hz and ²J_{P-C} = 5.7 Hz (Figure 2). **1a** 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

(ε_{max} =1200 L·mol⁻¹·cm⁻¹) tailing into the visible region with a shoulder at 350 nm accounting for the yellow color. Analysis of **1a** 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 P₂ units (e.g. M⁺-CH₃-P₂: 123.1172, calcd. 123.1173).

Attempts to grow single crystals of 1a suitable for X-ray crystallography have so far been unsuccessful. For this reason, the preparation of a metal complex was attempted with $[Ag(CH_2Cl_2)_2(pftb)] (pftb = AI\{OC(CF_3)_3\}_4).^{[37,38]} A clean reaction$ was observed in toluene using two equivalents of 1a per silver atom, and a species with a significantly downfield shifted ³¹P{¹H} NMR signal (-446.8 ppm, cf. -468.2 ppm for 1a) was detected. Further NMR monitoring also showed the slow formation of the tetramer 2a. A single-crystal X-ray diffraction study on crystals grown from CH₂Cl₂ revealed the formation of [{Ag(1a)(2a)}₂][pftb]₂ (3), where both 1a and 2a are incorporated in the same complex (Figure 3).^[39] Crucially, the X-ray diffraction experiment confirms the tetrahedral structure of 1a. The P₂C₂ tetrahedron is bound to the Ag atom in an η² fashion via the P-P bond (P1-P2 2.308(3) Å). The four P-C bond lengths in the tetrahedron range 1.821(9)-1.836(9)Å, while the C-C bond length (C1-C2 1.462(12) Å) is similar to that of (tBuC)4 (average: 1.485 Å).[40] Broadened singlet resonances are observed in the ³¹P{¹H} NMR spectrum at -19.8 and -446.8 ppm when crystals of ${\bf 3}$ are dissolved in CD₂Cl₂, and the ¹H NMR data are also consistent with the molecular structure obtained by X-ray crystallography.[41]



Figure 3. Molecular structure of **3** in the solid state. Thermal ellipsoids are set at 50% probability level. Hydrogen atoms and the [pftb]⁻ counterions are omitted for clarity. Selected bond lengths [Å] and angles [^o]: P1-P2 2.308(3), P1-C1 1.836(9), P1-C2 1.835(9), P2-C1 1.821(9), P2-C2 1.820(8), C1-C2 1.462(12), C1-P2-P1 51.2(3), C1-P2-C2 47.4(4), C2-P2-P1 51.1(3), C1-P1-P2 50.6(3), C2-P1-P2 50.5(3), C2-P1-C1 46.9(4), P2-C1-P1 78.3(3), C2-C1-P2 66.3(5), C2-C1-P1 78.3(3), C1-C2-P2 66.4(5), C1-C2-P1 66.6(5).

In an attempt to identify possible intermediates in the formation of **1a**, the nickel tricarbonyl complexes [(NHC)Ni(CO)₃] (NHC = IMes, IPr, *i*Pr₂Im^{Me}) were reacted with one equivalent of phosphaalkyne RCP (R = *t*Bu, 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 phosphaalkyne complexes [(NHC)Ni(CO)(PCR)] (NHC = IMes, R = *t*Bu (**4a**), Ad (**4b**), NHC = IPr; R = *t*Bu (**4c**), Ad (**4d**)) featuring η^2 -bound phosphaalkyne 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 the Supporting Information for details). The structural and spectroscopic data compare well to related, isoelectronic complexes $[(iPr_2Im)_2Ni(PCtBu)]$ $(iPr_2Im = 1,3$ di(isopropyl)imidazolin-2-ylidene) and $[(trop_2NMe)Ni-(PCPh_3)]$ (trop = 5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl).^[42,43]

Conversely, the reaction of tBuCP with $[(iPr_2Im^{Me})Ni(CO)_3]$ the afforded а mixture of mononuclear 1.3complex [(*i*Pr₂Im^{Me})Ni(CO)(n⁴diphosphacyclobutadiene $P_2C_2tBu_2$] (5), the dinuclear complex [{(iPr_2Im^{Me})Ni(CO)}₂(μ , η^2 : η^2 -(BuCP) and tetranuclear (6)а cluster [{(*i*Pr₂Im^{Me})Ni₂(CO)₂(*t*BuCP)}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 [(*i*Pr₂Im^{Me})Ni(CO)₃] with just 0.5 or two equivalents of tBuCP resulted in similar mixtures. Upon addition of tBuCP to one equivalent of [Ni(CO)₄], 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 η^2 -bound phosphaalkyne complexes 4a-d and presumably accounts for the lower yields in the catalytic formation of 1a.



Figure 4. Synthesis of 4a-d, 5, 6 and 7; and structures of 4a and 5 in the solid state. Thermal ellipsoids are set at 50% probability level. Hydrogen atoms and the second crystallographically independent molecule (in case of 4a) are omitted for clarity. Selected bond lengths [Å] and angles [°] for 4a: Ni1-C1 1.777(3), Ni1-C7 1.931(2), Ni1-P1 2.1793(9), Ni1-C2 1.898(3), C1-O1 1.137(4), P1-C2 1.636(3), C3-C2-P1 144.2(2), C7-Ni1-P1 102.89(7), C2-Ni1-P1 46.67(8), C2-Ni1-C7 149.56(11), C2-P1-Ni1 57.59(10), O1-C1-Ni1 171.4(4); 5: Ni1-P1 2.3114(3), Ni1-P2 2.3113(3), Ni1-C2 2.0898(11), Ni1-C3 2.0637(11), P1-C2 1.7966(11), P1-C3 1.8143(11), P2-C2 1.8121(11), P2-C3 1.7992(11), Ni1-C1 1.7538(13), C1-O1 1.1458(17), Ni1-C1 2.19421(11), C1-Ni1-C12 94.29(5), O1-C1-Ni1 176.74(12), C2-P1-C3 78.74(5), C3-P2-C2 78.73(5), P1-C2-P2 100.90(6), P2-C3-P1 100.71(6).

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 *t*BuCP among all nickel complexes investigated. Thus, a significantly shorter reaction time for full conversion of the phosphaalkyne 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 the SI 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 diphosphatetrahedrane (P₂C₂Ad*t*Bu, **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 phosphaalkyne. The proposed rate law is therefore

$$r = \frac{d[\mathbf{1}\mathbf{a}]}{dt} = k \cdot [\mathbf{4}\mathbf{a}] \cdot [tBuCP].$$

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)imidazolin-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 the SI 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)2 ligand. In the next step, a diphosphatetrahedrane 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 diphosphatetrahedrane 1a by another phosphaalkyne 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(CO)(PCMe)], (IPh = 1,3diphenylimidazolin-2-ylidene, see the SI for further details). In this case, significant stabilization of the analogous 1,3diphosphacyclobutadiene complex (A') is observed. The high activation barrier calculated for the transformation A' \rightarrow 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-diposphacyclobutadiene complex, which is usually a thermodynamic sink in other reactions,^[33] 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 $(tBuCP)_2$ (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 is 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.^[25,28] Synthetic, kinetic and computational investigations suggest that a 1,3diphosphacyclobutadiene 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**. fellowship for G. H.) is gratefully acknowledged. We thank the group of Prof. Manfred Scheer (Luis Dütsch and Martin Piesch) for the donation of $[Ni(CO)_4)$] and $[Ag(CH_2CI_2)_2(pftb)]$. We also thank Jonas Strohmaier and Georgine Stühler for assistance, and Dr. Daniel Scott and Dr. Sebastian Bestgen for helpful comments on the manuscript.

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Keywords: phosphorus • nickel • phosphaalkynes • dimerization • homogeneous catalysis



Figure 5. Reaction profile calculated with DFT at the TPSS-D3BJ/def2-TZVP level for the dimerization of *t*Bu-C=P catalyzed by [(IXy)Ni(PCtBu)] (IXy = 1,3-bis(2,6-dimethylphenyl)imidazolin-2-ylidene) (4'). Calculated Gibbs energies (in kcal·mol⁻¹at 298 K) and schematic drawings of intermediates and transition states are given.

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Free dimer at last: Di-*tert*butyldiphosphatetrahedrane is accessible by the facile nickelcatalyzed dimerization of *tert*-butyl phosphaalkyne. This compound not only represents an uncomplexed phosphaalkyne dimer, but also is the first example of a tetrahedral molecule with carbon and phosphorus atoms in its scaffold.



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