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Aggregation and Degradation of White Phosphorus Mediated by N-Heterocyclic Carbene Nickel(0) Complexes

Gabriele Hiehlmeier, Peter Coburger, Nicolaas P. van Leest, Bas de Bruin, and Robert Wolf

Abstract: The reaction of zerovalent nickel compounds with white phosphorus (P₄) is a barely explored route to binary nickel phosphide clusters. Here, we show that coordinatively and electronically unsaturated N-heterocyclic carbene (NHC) nickel(0) complexes afford unusual cluster compounds with P₅, P₆, P₇, and P₈ units. Using [Ni(IMes)_2] [IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene] electron-deficient Ni₃P₄ and Ni₃P₆ clusters have been isolated, which can be described as superhypercloso and hypercloso clusters according to the Wade–Mingos rules. Use of the bulkier NHC complexes [Ni(IPr)_2] or [(IPr)(η²-toluenes)] IPR = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene affords a closo-Ni₃P₄ cluster. Inverse-sandwich complexes [(NHC)Ni₃P₅] (NHC = IMes, IPr) with an aromatic cyclo-P₅⁻ ligand were identified as additional products.

Reactions of transition metal complexes with white phosphorus present a powerful strategy to access binary metal phosphide frameworks, and the structural motifs of the resulting compounds are highly diverse.¹⁻² On the one hand, degradation of P₄ to products containing one to four phosphorus atoms is of tremendous industrial relevance, in order to improve the processes used in the production of organophosphorus compounds.³ On the other hand, the aggregation of P₄ to polyphosphorus compounds with five or more phosphorus atoms is essential for understanding the structure and bonding in metal phosphides.⁴

The use of nickel as a metal for P₄ activation may result in unique nickel phosphide clusters. Besides a few reactions of P₄ with Ni⁰ species, for example, the formation of the sandwich compound [(triphos)Ni₃(μ₂,η¹⁻,P₃)](BF₄)₂ (triphos = Me(CH₂CH₂PPh₂)₃),⁵ known examples typically involve Ni in the +1 oxidation state. Cyclopentadienyl-substituted Ni⁻ radicals are particularly versatile, as the outcome of photolysis or thermolysis reactions of nickel complexes of the type [Cp²Ni(CO)₂], with P₄ is highly dependent on the size of the Cp ligand used.⁶ Relatively small cyclopentadienyl ligands such as Cp*, Cp'' (1,3-tBu₂C₅H₃), or Cp''' (1,2,4-tBu₃C₅H₂) lead to the tetranuclear heterocubane clusters [[Cp''²Ni₃(μ₃,η⁻,P₃)(μ₃-P)]₄] (Cp'' = Cp*, Cp''), and the sandwich complex [Cp''²Ni(η⁻,P₃)] (Cp'' = Cp*, Cp'') whereas a trigonal-prismatic structure [[Cp''²Ni₃(μ₃,η⁻,P₃)]₃] (Cp'' = 1,2,3,4-tPr₄C₅H) is accessed by using a superbulky tetraisopropylcyclopentadienyl ligand. Our group recently showed that [CpNi(NHC)] (NHC = IMes, IPr) radicals can selectively activate P₄ to afford μ₂,η⁻⁻,P₃-butterfly complexes.⁷

In contrast to Ni⁰ compounds, only a few examples of P₄ activation using Ni⁰ sources have been reported (Figure 1).⁸⁻¹⁰ In seminal work dating back to 1979, Sacconi and co-workers reported the formation of the complex [(κ²-PPP-NNP⁰)Ni(η⁻⁻,P₃)] (A, N⁰ = tris(2,3-diphenylphosphinoethyl)amine) containing an intact, end-on coordinated P₄ tetrahedron.¹¹ Moreover, Le Floch and Mézailles reported on the use of [Ni(cod)] (cod = 1,4-cycloocta-1,5-diene) for the synthesis of nickel phosphide nanoparticles.⁶ More recently, the group of Radius reported the synthesis of the butterfly compound [(Ni(IMes)₂)_2][μ₂,η⁻⁻,P₃] (C, IMesPr₂ = 1,3-bis(isopropyl)imidazolin-2-ylidene) by reaction of cod-stabilised Ni(IMes)₂ fragments with P₄.¹⁰ While these examples demonstrate both the coordination and degradation of P₄ by 14 valence electron (VE) and 18 VE Ni⁰ compounds, examples of P₄ aggregation using Ni⁰ appear to be unknown.

Figure 1. a) Overview of products resulting from P₄ activation using Ni⁰ sources; b) P₄ activation and aggregation products described herein.
Despite an unsuccessful attempt to synthesise a sandwich complex containing a pentaphosphacyclopentadienide ligand \textit{cyclo-P}_5 by Miluykov, Hey-Hawkins and co-workers.\cite{11}

Building on our previous work on P₄ activation with N-heterocyclic carbene (NHC) nickel(I) complexes,\cite{12,13} we recently became interested in studying the reactivity of related Ni₃ complexes. NHC complexes seemed promising because they can be stabilised by various labile ligands, for example, the carbenes themselves, alkenes, and arenes. After synthesising a range of known NHC compounds, including the bis(carbene) complexes \([\text{Ni(IMes)}]_2\) (NHC = IMes, IPr),\cite{13} trimethylvinylsilane complexes \([\text{NHC}][\text{Ni(η}^2-\text{H}_3\text{C}=\text{CHSiMe}_3)]\)\cite{14} (NHC = IMes, IPr) and the toluene complex \([\text{IPr(Ni(η}^2\text{-toluene})]}\)\cite{15} we proceeded to systematically study the reactivity of these compounds toward P₄. Reactions of \([\text{NHC}][\text{Ni(η}^2-\text{H}_3\text{C}=\text{CHSiMe}_3)]\) (NHC = IMes, IPr) with different amounts of P₄ afforded black, insoluble material that was not characterised any further. We next turned our attention from nickel complexes comprising labile alkene ligands to the less reactive \([\text{Ni-(IMes)}]_2\). Gratifyingly, the \(^{31}\text{P}[^{1}\text{H}]\) NMR spectrum of the reaction of \([\text{Ni(IMes)}]_2\) with P₄ (0.5 equivalents) in toluene suggested formation of a major product, characterised by two main signals in a 1:1 ratio (Scheme 1). A single-crystal X-ray diffraction (XRD) study of large block-shaped crystals grown from toluene revealed the formation of the trinickel phosphorus cluster \([\text{IMes}_2\text{Ni}_3\text{P}_4]\) (1) (Figure 2).

The molecular structure of 1 is reminiscent of the distorted kite-like \textit{cyclo-P}_5 complex \([\text{CP}_2\text{Fe}_2(\mu-P_2)]\) reported by Walter and co-workers.\cite{16} However, 1 can be described as a bicapped trigonal bipyramid featuring a Ni₃ triangle with one short Ni₂–Ni₃ bond (2.3720(3) Å) and two long nickel–nickel bonds (Ni₁–Ni₂: 2.753(3) Å and Ni₁–Ni₃: 2.6528(3) Å). Ni₃ triangles are a common structure motif, for example, in carbonyl- or phosphine-stabilised clusters.\cite{17} The Ni₃ triangle is capped by two phosphorus atoms P₁ and P₄. The P₄ atom is part of a P₄ chain with P–P bond lengths of 2.1671(5) Å (P₂–P₃) and 2.1754(5) Å (P₃–P₄), which are in the range commonly observed for P–P single bonds. Notably, the P₁ plane and the Ni₃ plane are almost perpendicular with a plane twist angle of 89.6°.

Compound 1 can be isolated in pure form as a black crystalline solid in 20% yield. As expected from analysis of the initial reaction mixture, \(^{31}\text{P}[^{1}\text{H}]\) NMR measurements of pure 1 dissolved in CD₂Cl₂ revealed two signals at chemical shifts of 463.1 ppm (P₁/P₄) and 105.6 ppm (P₂/P₃, averaged \(J_{PP} = 67.0\) Hz), which are assigned to 1. Notably, the observation of just two \(^{31}\text{P}[^{1}\text{H}]\) NMR resonances is in apparent contrast with the presence of four distinct P atom positions in the solid-state XRD structure of 1. An additional minor signal is observed at 134.0 ppm. This signal is assigned to an unidentified species, which may be an isomer of 1. A variable temperature (VT) NMR study showed that the integral ratio of signal P₁/P₄ to P₂/P₃ remains constant at 1:1 whereas the intensity of the signal at 134.0 ppm increases with higher temperatures and disappears upon cooling the solution to 283 K (see the Supporting Information for spectra). In order to understand this dynamic behaviour, DFT calculations were performed on a truncated model compound, where the mesityl substituents at the NHC moieties were replaced by phenyl groups. The calculations reproduce the asymmetric molecular structure of 1, but also reveal an isoenergetic isomer (\(\Delta E = -0.3\) kcal mol⁻¹) with a more symmetrical Ni₃P₄ core (see the Supporting Information for details). The fluxional behaviour observed by NMR spectroscopy can presumably be attributed to an exchange process between P₁/P₄ and P₂/P₃, which proceeds via this symmetrical isomer or a symmetrical transition state with a low energy (\(\Delta E = 2.6\) kcal mol⁻¹). The \(^{1}H\) NMR spectra are in good agreement with these findings, exhibiting three different signal sets for the IMes ligand and similar thermal dependence of the integral ratios.

Analysis of 1 by liquid field ionisation desorption mass spectrometry (LIFDI-MS) revealed a molecular ion peak at \(m/z = 1212.2952\) in good agreement with the calculated molecular ion peak (1212.2784). The cyclic voltammogram of 1 (THF/[nBu₄N][PF₆], Figure S18, Supporting Information) features two reversible redox events at \(E_{1/2} = -1.07\) and \(-2.76\) V (vs. Fe(II)/Fe⁺), which may be assigned to the reversible oxidation and reduction of the complex, respectively.

The bonding situation in 1 was analysed by means of localised orbitals. In particular, intrinsic bond orbitals (IBO)
were constructed starting from a BP86/def2-TZVP wavefunction. Looking at the composition of those orbitals, six filled orbitals involving multicentre bonds between the Ni and P atoms could be identified along with a 3d\textsuperscript{10} configuration for each Ni atom (see the Supporting Information for a depiction). This is consistent with classical electron-counting rules.\textsuperscript{[18]} Thus, the cluster may be defined as a superhypercloso-cluster (12 = 2(n−1), n = 7, number of cluster atoms).

The reaction of [Ni(IMes)]\textsubscript{2} with P\textsubscript{4} is significantly less selective when THF is used as a solvent instead of toluene. Besides I, two other products formed could be identified by \textsuperscript{31}P\{1H\} NMR spectroscopy and X-ray crystallography. After work-up, brown crystals of the trinuclear cluster [(IMes)\textsubscript{3}Ni\textsubscript{3}P\textsubscript{6}] (2) were obtained from n-hexane (Figure 3).

Structural analysis of 2 reveals a distorted tricapped trigonal prism (or, equivalently, two facial Ni\textsubscript{3}P\textsubscript{3} octahedra sharing a common Ni\textsubscript{i} face). Notably, compounds featuring picotogen (P, As) prisms with iron or cobalt are usually stabilised by closo-P\textsubscript{8} ligands.\textsuperscript{[21]} Moreover, all known closo-P\textsubscript{8} complexes additionally contain cyclopentadienyl ligands, while complex 3a is stabilised by an L-type ligand.

Having established the ability of [Ni(IMes)\textsubscript{2}] to act as a precursor to interesting Ni/P clusters, we proceeded with performing the analogous reactions using the bulkier carbene complex [Ni(IPr)\textsubscript{2}] in order to examine if there is any difference in product distribution (Scheme 2). And, indeed, in contrast to observations made using [Ni(IMes)\textsubscript{2}], \textsuperscript{31}P\{1H\} NMR spectroscopy revealed no resonances. Nevertheless, the 1H NMR spectrum clearly showed the formation of free IPr and one new distinct diamagnetic IPr environment.

Furthermore, a single-crystal X-ray diffraction study on crystals grown from toluene revealed the formation of [(IPr)\textsubscript{2}Ni\textsubscript{2}P\textsubscript{5}] (4), an 11-vertex closo-cluster with 24 cluster electrons, adopting an octadecahedral geometry similar to the undecaborate anion [B\textsubscript{11}H\textsubscript{11}]\textsuperscript{2−} (Figure 4).\textsuperscript{[22]} The homoquadricyclane-like P\textsubscript{i} framework is reminiscent of the P\textsubscript{i} subunits in Hittorf’s phosphorus and can be seen as a formal insertion product of Ni in one of the P-P bonds of such a subunit.\textsuperscript{[23]} Nevertheless, to the best of our knowledge, this is the first example of such a P\textsubscript{i} framework in an isolated molecular compound.\textsuperscript{[4]} The structure of compound 4 again comprises three Ni atoms, but the Ni–Ni distances are significantly longer in complexes 1 and 2 [Ni1−Ni2 3.3246(18) Å and Ni2−Ni1 3.363(2) Å]. Ni1 is coordinated by six P atoms (P1, P1\textquotesingle, P2, P2\textquotesingle, P3, P3\textquotesingle) and Ni2/Ni2\textquotesingle are coordinated by five P atoms (P1, P2, P3, P4, P4\textquotesingle) for Ni2 and P1\textquotesingle, P2\textquotesingle, P3\textquotesingle, P4\textquotesingle for Ni1.
The electronic structure of a slightly truncated model complex $3'$ ([(IPh)$_3$Ni$_3$(P$_4$)$_2$]) with $P_4$ also affords green crystals of [(IPr)$_2$Ni$_2$(P$_4$)$_2$] (3b), which were obtained from the $n$-hexane washing solution and identified by X-ray crystallography. Complex 3b is isostructural with 3a and features similar Ni–Ni and P–P bond lengths (see the Supporting Information for further details).

The cyclic voltammogram of [(IPr)Ni(P$_3$)$_3$]$^+$ in [D$_8$]toluene shows one reversible oxidation wave at $E_{1/2} = -0.76$ V (vs. Fc/Fe$^+$). Analysis of the IBO reveals 12 orbitals that involve bonding between the cluster atoms again in accordance with established electron-counting rules. Thus 4 obeys the $2(n + 1) = 11$ electron count rule of a 11-vertex closo-cluster (see the Supporting Information for a depiction of the IBO). The same analysis additionally allows for the assignment of a $d^9$-configuration for the NiI atom and $d^{10}$-configurations for NiII/NiII.

Unfortunately, separation of free IPr from compound 4 proved to be challenging. The use of [(IPr)Ni(η$^3$-toluene)] as an attractive precursor was therefore pursued and led to the isolation of pure 4 as a dark green powder in 41% yield. The cyclic voltammogram of 4 (THF/[nBu$_4$N]PF$_6$, Figure S20) shows one reversible oxidation wave at $E_{1/2} = -0.76$ V (vs. Fc/Fe$^+$). Analysis of the IBO reveals 12 orbitals that involve bonding between the cluster atoms again in accordance with established electron-counting rules. Thus 4 obeys the $2(n + 1) = 11$ electron count rule of a 11-vertex closo-cluster (see the Supporting Information for a depiction of the IBO). The same analysis additionally allows for the assignment of a $d^9$-configuration for the NiI atom and $d^{10}$-configurations for NiII/NiII.

Apart from 4, the reaction of [(IPr)Ni(η$^3$-toluene)] with $P_4$ also affords green crystals of [(IPr)$_2$Ni$_2$(P$_4$)$_2$] (3b), which were obtained from the $n$-hexane washing solution and identified by X-ray crystallography. Complex 3b is isostructural with 3a and features similar Ni–Ni and P–P bond lengths (see the Supporting Information for further details).

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obviously complex, and the details of the initial P4 activation of the NHC ligand on the products obtained. Upon increasing the steric demand from IPr to IMes, di- and trinuclear complexes with NiP4 (1), Ni3P4 (2) cores as well as NiP6 (3a) were obtained. Notably, 3a represents the first nickel pentaphosphacyclopentadienyl complex. The bulky NHC IPr again changes the outcome of the reaction to afford a Ni4P6 (4) closo-cluster with a novel homoquaracyclane-like P8 framework. Bulky substituents on the NHC ligands presumably facilitate the formation of monocarbene nickel phosphorus fragments observed in the molecular structures of 1–4. However, the mechanism of formation of these products is obviously complex, and the details of the initial P2 activation process and the subsequent transformations of the resulting intermediates must be revealed by further studies. Moreover, we are currently investigating the use of 1–4 as single-source precursors for the preparation of nickel phosphides as electrocatalysts for hydrogen evolution.[26]

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**Conflict of interest**

The authors declare no conflict of interest.

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[24] Heating up the solution of 4 in D2O to temperatures above 313 K led to decomposition to unidentified products.


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