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Phosphorus Activation

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

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

Dedicated to Professor Maurizio Peruzzini on the occasion of his 65th birthday

Abstract: The reaction of zerovalent nickel compounds with white phosphorus (P4) is a rarely 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 P4, P5, P6 and P8 units. Using [Ni(IMes)2] [IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene], electronically deficient NiP8 and Ni5P6 clusters have been isolated, which can be described as superhyperclos and hypercloso clusters according to the Wade–Mingos rules. Use of the bulkier NHC radical allowed affords a closo-Ni3P8 cluster. Inverse-sandwich complexes with NiII species, for example, the formation of the sandwich compound [{(triphos)Ni}2(P4)] 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene affords a closo-Ni3P8 cluster. Inverse-sandwich complexes [{(NHC)2Ni2P5}] (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 P2 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.[4–5]

The use of nickel as a metal for P4 activation may result in unique nickel phosphide clusters. Besides a few reactions of P4 with NiII species, for example, the formation of the sandwich compound [{(triphos)Ni2(μ1,η3:η1-cyclo-P3)}2(BF4)2] (triphos = Me(CH2CH2PPh2)3),[10–11] known examples typically involve Ni in the +1 oxidation state. Cyclopentadienyl-substituted NiII radicals are particularly versatile, as the outcome of photolysis or thermolysis reactions of nickel complexes of the type [Cp*Ni(CO)2], with P2 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*Ni2(μ1,η3:η1-cyclo-P3)(μ1-η3:η1-cyclo-P3)]2] (Cp* = Cp*, Cp´), whereas a trigonal-prismatic structure [{Cp*2Ni3(μ1,η3:η1-cyclo-P3)}2] (Cp* = 1,2,3,4-tBu3C5H2) is accessed by using a superbulky tetraisopropylcyclopentadienyl ligand. Our group recently showed that [CpNi(NHC)] (NHC = IMes, IPr) radicals can selectively activate P2 to afford μ1,η3:η1-P4 butterfly complexes.[7]

In contrast to NiII compounds, only a few examples of P4 activation using NiII 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 [{(κ3-PPP-NNP)Ni(η1:η3-P3)}] (A, NP = tris(2-diphenylphosphinomethyl)amine) containing an intact, end-on coordinated P4 tetrahedron.[8] 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.[9] More recently, the group of Radius reported the synthesis of the butterfly compound [{Ni(ImPr2)3(μ1,η3:η1-cyclo-P3)}2] (C, ImPr2 = 1,3-bis(isopropyl)imidazolin-2-ylidene) by reaction of cod-stabilised Ni(ImPr2)3 fragments with P4.[10] While these examples demonstrate both the coordination and degradation of P4 by 14 valence electron (VE) and 18 VE NiII compounds, examples of P4 aggregation using NiII appear to be unknown.

Figure 1. a) Overview of products resulting from P4 activation using NiII sources;[8–9] b) P4 activation and aggregation products described herein.

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Despite an unsuccessful attempt to synthesise a sandwich complex containing a pentaphosphacyclopentadienide ligand \( \text{cyclo-P}_5 \) by Miluykov, Hey-Hawkins and co-workers.\[^{[31]}\]

Building on our previous work on \( P_4 \) activation with N-heterocyclic carbene (NHC) nickel(I) complexes,\[^{[7,12]}\] we recently became interested in studying the reactivity of related Ni\(^\text{II} \) 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 \([\text{Ni}(\text{IMes})_2] \) (NHC = IMes, IPr), \[^{[13]}\] trimethylvinylsilane complexes \([\text{NHC}][\text{Ni}(\eta^2-\text{H}_2\text{C}=	ext{CHSiMe}_3)_2] \) \[^{[14]}\] (NHC = IMes, IPr) and the toluene complex \([\text{(IPr)Ni(\eta^2-toluene)}] \) \[^{[15]}\] we proceeded to systematically study the reactivity of these compounds toward \( P_4 \). Reactions of \([\text{NHC}][\text{Ni}(\eta^2-\text{H}_2\text{C}=	ext{CHSiMe}_3)_2] \) (NHC = IMes, IPr) with different amounts of \( P_4 \) 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 \([\text{Ni}-(\text{IMes})_2] \). Gratifyingly, the \[^{31}\text{P}[^1\text{H}]] \) NMR spectrum of the reaction of \([\text{Ni}(\text{IMes})_2] \) with \( P_4 \) (0.5 equivalents) in toluene dissolved in \( \text{C}_6\text{D}_6 \) revealed two signals at chemical shifts of 463.1 ppm (P1/P4) and 105.6 ppm (P2/P3), averaged \( J_{\text{PP}} = 67.0 \text{ Hz} \), which are assigned to \( \text{I} \). 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 \( \text{I} \). An additional minor signal is observed at 134.0 ppm. This signal is assigned to an unidentified species, which may be an isomer of \( \text{I} \). 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 \( \text{I} \), but also reveal an isoenergetic isomer (\( \Delta E = -0.3 \text{ kcal mol}^{-1} \)) with a more symmetrical \( \text{Ni}_3 \text{P}_4 \) 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 (\( \Delta E = 2.6 \text{ kcal mol}^{-1} \)). The \(^{1}\text{H} \) 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 \( \text{I} \) 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 \( \text{I} \) (THF/[nBuN][PF6], Figure S18, Supporting Information) features two reversible redox events at \( E_{1/2} = -1.07 \) and \( -2.76 \text{ V (vs. Fe/Fe}^+ \) ) which may be assigned to the reversible oxidation and reduction of the complex, respectively.

The bonding situation in \( \text{I} \) was analysed by means of localised orbitals. In particular, intrinsic bond orbitals (IBO)
were constructed starting from a BP86/def2-TZVP wave-function. 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{3}] with P\textsubscript{4} is significantly less selective when THF is used as a solvent instead of toluene. Besides 1, two other products formed could be identified by \textsuperscript{31}P\{\textsuperscript{1}H\} NMR spectroscopy and X-ray crystallography. After work-up, brown crystals of the trinuclear cluster \((\text{IMes})\textsubscript{3}\text{Ni}_{3}\text{P}_6\) (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{3} face). Notably, compounds featuring nictogen (P, As) prisms with iron or cobalt are usually stabilised by anionic cyclopentadienyl ligands.\textsuperscript{[19]} Similar to 1, an unsymmetrical Ni\textsubscript{3}-triangle is observed (Ni\textsubscript{1}–Ni\textsubscript{2} 2.4835(3) Å, Ni\textsubscript{1}–Ni\textsubscript{3} 2.4882(3) Å, Ni\textsubscript{2}–Ni\textsubscript{3} 2.6429(3) Å). The P–P bond lengths range from 2.205(4) to 2.270(4) Å consistent with P–P single bonds. The \textsuperscript{31}P\{\textsuperscript{1}H\} NMR spectrum in C\textsubscript{6}D\textsubscript{6} shows a broad resonance at −8.6 ppm. The bonding situation in 2 was analysed similarly to that in cluster 1. In accordance with electron-counting rules, nine doubly occupied orbitals of Ni\textsubscript{3}P\textsubscript{6} were constructed starting from a BP86/def2-TZVP wave-function. 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). Thus, due to multicentre bonds between the cluster atoms were identified (see the Supporting Information for a depiction). Due to its closed deltahedral structure (distorted tricapped trigonal prism) and fulfilment of the 2\textsuperscript{n} electron-counting rules,\textsuperscript{[18]} thus, the cluster may be defined as a closo-\textsubscript{9}vertex prism) and fulfilment of the 2\textsuperscript{n} 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).

Moreover, we were able to identify \([(\text{IMes})\textsubscript{3}\text{Ni}_{3}\text{P}_6]\) (3a) as a side product. This compound co-crystallises with 2 from the mother liquor of the reaction mixture of [Ni(IMes)\textsubscript{3}] with P\textsubscript{4}. Structural analysis of crystals of the composition \([(\text{IMes})\textsubscript{3}\text{Ni}_{3}\text{P}_6]·[(\text{IMes})\textsubscript{2}\text{Ni}_{2}\text{P}_5]\) revealed that compound 3a features a dinuclear inverse sandwich structure in the solid state with a bridging cyclo-P\textsubscript{5} ligand (Figure 3). The Ni1–Ni1’ distance is 2.6339(13) Å and the P–P bond lengths range from 2.182(8) to 2.211(9) Å, which is in the common range observed for dinuclear 3d transition metal complexes with bridging cyclo-P\textsubscript{5} ligands.\textsuperscript{[20,21]} The pentaphosphacyclopentadienyl ligand is frequently observed in transition metal mediated P\textsubscript{5} activation.\textsuperscript{[1]} However, most complexes comprising such a cyclo-P\textsubscript{5} ligand feature group 8 metals and there are only a few examples of other transition metal complexes.\textsuperscript{[21]} Furthermore, all known cyclo-P\textsubscript{5} complexes additionally contain cyclopentadienyl ligands, while complex 3a is stabilised by an L-type ligand.

Having established the ability of [Ni(IMes)\textsubscript{3}] 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{3}] 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{3}], \textsuperscript{31}P\{\textsuperscript{1}H\} NMR spectroscopy revealed no resonances. Nevertheless, the \textsuperscript{1}H 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 \([(\text{IPr})\textsubscript{3}\text{Ni}_{3}\text{P}_8]\) (4), an 11-vertex closo-cluster with 24 cluster electrons, adopting an octadecahedral geometry similar to the undecaborate anion \([\text{B}_{11}\text{H}_{12}]^{-}\) (Figure 4).\textsuperscript{[22]} The homoquadracyclane-like P\textsubscript{5} framework is reminiscent of the P\textsubscript{5} 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{5} 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 than in complexes 1 and 2 [Ni–Ni 3.3246(18) Å and Ni2–Ni2’ 3.636(2) Å]. Ni1 is coordinated by six P atoms (P1, P1’, P2, P2’, P3, P3’) and Ni2/Ni2’ are coordinated by five P atoms (P1, P2, P3, P4, P4’ for Ni2 and P1’, P2’, P3’, P4’ for Ni2’, P1’).
The molecular structure of 4 in the solid state. Thermal ellipsoids are set at 50% probability level. Hydrogen atoms, solvent molecules and disorder in the IPr ligand are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni1–Ni2 3.3246(18), Ni2–Ni2’ 3.636(2), P1–P2 2.205(3), P1–P3 2.201(3), P2–P3 2.288(3), P2–P4 2.459(3), P3–P4’ 2.434(3), P4–P4’ 2.349(4); Ni2-Ni1-Ni1’ 66.31(5), Ni1-Ni2-Ni2’ 56.85(3), P3-P1-P2 103.21(11), P3’-P2-P4 61.57(8), P2’-P3-P4’ 62.67(9), P3’-P4-P2 55.77(8).

Ni2’. The P4-framework contains short P–P bonds ranging from 2.201(3) to 2.288(3) Å (P1–P3, P1–P2, P2–P3), and long P–P bonds with bond lengths from 2.349(4) to 2.459(3) Å (P4–P4’, P3–P4’, P2–P4).

1H and 13C{1H} NMR spectra of crystals of 4 dissolved in C6D6 showed only one set of IPr signals despite the presence of two distinct IPr environments in the solid-state structure. This evidence for fluxionality in solution was further confirmed by variable-temperature 31P{1H} NMR spectroscopy (Figure 5). Coincidentally, the spectrum recorded at room temperature exhibits an extremely broad signal that could not be resolved. However, heating up the solution results in one broad resonance, whereas cooling the solution to 193 K reveals a signal pattern for an S = 1/2 system showing hyperfine interactions with all five phosphorus atoms. A satisfactory simulation of the experimental spectrum was obtained assuming hyperfine interactions with five equivalent phosphorus atoms (gS = 2.186 (2.11), gL = 1.987 (2.01), A13P = 30.0 MHz (27.5 MHz, averaged value, DFT-calculated values of 3’ in parentheses; see the

The electronic structure of a slightly truncated model complex 3’ (([IPh]Ni(P3-toluene)) with P4 also affords green crystals of [[IPr]Ni2(P3-toluene)] (3b), which were obtained from the h-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 4 (THF/[nBu4N]PF6, Figure S20) shows one reversible oxidation wave at E1/2 = −0.76 V (vs. Fe/ 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) (n = 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 d8-configuration for the NiI atom and d10-configurations for Ni2/Ni2’.

Apart from 4, the reaction of [[IPr]Ni(η4-toluene)] with P4 also suggests by the crystallographic study. Even at 193 K, the couplings could not be resolved completely.
However, the mechanism of formation of these products is the steric demand from Ir clusters. These reactions clearly show an impact of the size presumably facilitate the formation of monocarbene nickel complexes with Ni₃P₈ (1), Ni₃P₄ (2) cores as well as Ni₃P₂ (3a) were obtained. Notably, 3a represents the first nickel pentaphosphacyclodienyl complex. The bulky NHC IPr again changes the outcome of the reaction to afford a Ni₃P₂ (4) closo-cluster with a novel homocycladycyclane-like P₈ framework. Bulky substituents on the NHC ligands presumably facilitate the formation of monocarbene nickel 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 P₉ 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.

Keywords: cluster compounds · nickel · P₉ activation · phosphorus · polyphosphides

[22] Heating up the solution of [D₈]toluene to temperatures above 313 K led to decomposition to unidentified products.


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