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

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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, P3, P2, and P1 units. Using [Ni(IMes)2] ([IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene], electron-deficient NiP3 and NiP4 clusters have been isolated, which can be described as superhypercloso and hypercloso clusters according to the Wade–Mingos rules. Use of the bulkier NHC ligand were identified as additional products. The coordination of white phosphorus (P4) is a barely explored route to binary nickel 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 essential for understanding the structure and bonding in metal phosphides.[3] The use of nickel as a metal for P4 activation may result in radicals are particularly versatile, as the outcome of photolysis or thermolysis reactions of nickel complexes of the type [Cp*Ni(CO)2]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-t-Bu5C5H5), or Cp” (1,2,4-t-Bu5C5H5) lead to the tetranuclear heterocubane clusters [(Cp*NiI)(μ3-η1:1-P4)(μ3-η1:P1)] (Cp* = Cp*, Cp’), whereas a trigonal-prismatic structure [Cp”NiI2(μ3-η1:1:1-P4)] (Cp” = 1,2,3,4-t-tol C5H) 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 μ3-η1:1:P4 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 [(k2-PPP-NP3)Ni(η1:1-P1)] (A, NP3 = tris(2-diphenylphosphinoethyl)amine) containing an intact, end-on coordinated P4 tetrahedron.[10] Moreover, Le Floch and Mézailles reported on the use of [Ni(cod)]2 (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)2)(μ3-η1:1:1-1-P4)] (C, ImPr2 = 1,3-bis(isopropyl)imidazolin-2-ylidene) by reaction of cod-stabilised Ni(ImPr2)2 fragments with P4.[10] While these examples demonstrate both the coordination and degradation of P4 by 14 valence electron (VE) and 18 VE Ni2 compounds, examples of P4 aggregation using Ni0 appear to be unknown.

Figure 1. a) Overview of products resulting from P4 activation using Ni0 sources.[8–10] 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 cyclo-P₄⁻ by Miluykov, Hey-Hawkins and co-workers.⁵¹

Building on our previous work on P₄ activation with N-heterocyclic carbene (NHC) nickel(I) complexes,⁶,²¹ we recently became interested in studying the reactivity of related Ni⁰ complexes. NHC complexes seemed promising because they can be stabilised by various labile ligands, for example, the carbеныes themselves, alkenes, and arenes. After synthesising a range of known NHC compounds, including the bis(carbene) complexes [Ni(NHC)₂], (NHC = IMes, IPr), we proceeded to systematically study the reactivity of these complexes toward P₄. Reactions of [Ni(IMes)₂] with P₄ (0.5 equivalents) in toluene revealed the formation of the trinuclear nickel phosphorus cluster [(IMes)₃Ni₃P₄](CH₂SiMe₃)₂ reported by Miluykov, Hey-Hawkins and co-workers.⁶¹ However, the 3¹P{¹H} NMR spectrum of the 31P{1H} NMR spectrum of the trinuclear nickel phosphorus cluster [(IMes)₃Ni₃P₄] is reminiscent of the distorted kike cyclo-P₄ complex [(CyFe)(μ-P₄)] reported by Walter and co-workers.⁶³ However, I 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: 2.7533(3) Å and Ni1–Ni3: 2.6528(3) Å). Ni₃ triangles are a common structure motif, for example, in carbonyl- or phosphine-stabilised clusters.⁶³ The Ni₃ triangle is capped by two phosphorus atoms P1 and P4. The P4 atom is part of a P₃-chain with P–P bond lengths of 2.1671(5) P2–P3 and 2.1754(5) 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, 3¹P{¹H} NMR measurements of pure 1 dissolved in C₆D₆ revealed two signals at chemical shifts of 463.1 ppm (P1/P4) and 105.6 ppm (P2/P3, averaged JPP = 67.0 Hz), which are assigned to 1. Notably, the observation of just two 3¹P{¹H} 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 (ΔE = −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 (ΔE = 2.6 kcal mol⁻¹). The ¹H 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 E₁/₂ = −1.07 and −2.76 V (vs. Fe/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 waveform. 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 3\textsuperscript{d}\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, \text{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 1, two other products formed could be identified by \(^{31}\text{P}\{^1\text{H}\} \text{NMR spectroscopy and X-ray crystallography. After work-up, brown crystals of the trinuclear cluster } [(\text{IMes})\textsubscript{3}Ni\textsubscript{3}P\textsubscript{6}] \text{ were obtained from } n\text{-hexane} (\text{Figure 3}). \text{Structural analysis of 2 reveals a distorted tricapped trigonal prism (or, equivalently, two facial Ni}_2P\text{octahedra sharing a common Ni}_3 \text{ face). Notably, compounds featuring pincerligands (P, As) prisms with iron or cobalt are usually stabilised by anionic cyclopentadienyl ligands.}\textsuperscript{[19]} \text{Similar to 1, an unsymmetrical Ni}_3\text{triangle is observed (Ni}_1−Ni}_2\text{ 2.4835(3) Å, Ni}_1−Ni}_3\text{ 2.4882(3) Å, Ni}_2−Ni}_3\text{ 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 } \(^{31}\text{P}\{^1\text{H}\} \text{NMR spectrum in C}_6\text{D}_6 \text{shows a broad resonance at } −8.6 \text{ 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 the 3\text{d}\textsuperscript{10} cluster. Addition of H\textsubscript{2} is more effective for the \text{Ni} in one of the P}\textsubscript{5}\text{ ligands.}\textsuperscript{[21]} \text{The homoquadricyclane-like } P\text{ framework is reminiscent of the } P\textsubscript{5} \text{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]} \text{Nevertheless, the } ^1\text{H} \text{NMR spectrum clearly showed the formation of free } IPr \text{ and one new distinct diamagnetic } IPr \text{ environment.}

Furthermore, a single-crystal X-ray diffraction study on crystals grown from toluene revealed the formation of \([(IPr)_2Ni(P_5)] \text{ (4), an 11-vertex } \text{closo-cluster with 24 cluster electrons}, adopting an octadecahedral geometry similar to the undecaborate anion [B\textsubscript{11}H\textsubscript{11}]\textsuperscript{2−} \text{ (Figure 4).}\textsuperscript{[22]} \text{The homoquadricyclane-like } P\text{ framework is reminiscent of the } P\textsubscript{5} \text{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]} \text{Nevertheless, to the best of our knowledge, this is the first example of such a } P\text{ framework in an isolated molecular compound.}\textsuperscript{[4]} \text{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}_1−Ni}_2\text{ 3.3246(18) Å and Ni}_2−Ni}_3\text{ 3.636(2) Å). Ni}_1 \text{is coordinated by six } P \text{atoms (P}_1, P'_1, P}_2, P'_2, P}_3, P'_3 \text{ and Ni2Ni2'} \text{are coordinated by five } P \text{atoms (P}_1, P}_2, P}_3, P}_4, P'_4 \text{for Ni2 and P1', P2', P3', P4', P4' for P2 and P3' and N2Ni2'.}

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**Figure 3.** Molecular structure of 2 (left) and 3a (right) in the solid state. Thermal ellipsoids are set at 50% probability level. Hydrogen atoms, solvent molecules and disorder in the Pt ring (3a) are omitted for clarity. Selected bond lengths [Å] and angles [°] for 2: Ni1−Ni2 2.4834(3), Ni1−Ni3 2.4883(3), Ni2−Ni3 2.6432(3), P1−P2 2.2087(5), P2−P3 2.2698(5), P1−P3 2.2156(5), P4−P5 2.2116(5), P5−P6 2.2822(5), P4−P6 2.2049(5), Ni2−Ni1-Ni3 64.223(10), Ni1−Ni2-Ni3 57.974(9), Ni1−Ni3-Ni2 57.793(9), P2−P1-P3 61.729(16), P1−P2−P3 59.285(16), P1−P3−P2 58.985(16), P6−P4−P5 62.226(16), P4−P5−P6 58.744(16), P4−P6−P5 59.010(16); 3a: Ni1−Ni1’ 2.6339(13), P1−P2 2.182(8), P2−P3 2.194(7), P3−P4 2.205(8) P4−P5 2.211(9), P5−P1 2.207(7), P2−P1−P5 108.2(2), P1−P2−P3 108.7(2), P2−P3−P4 107.6(3), P3−P4−P5 108.1(3), P1−P5−P4 107.4(3).

**Scheme 2.** Reactivity of [Ni(IPr)]\textsubscript{2} and [(IPr)Ni(h\textsuperscript{+}-toluene)] toward P\textsubscript{4}.

Figure 4. Molecular structure of [(IPr)Ni₂P₈] 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' 56.83(3), P₃-P₁-P₂ 103.21(11), P₃'-P₂-P₄ 61.57(8), P₂'-P₃-P₄' 62.67(9), P₃'-P₄-P₅ 55.77(8).

Figure 5. VT ³¹P{¹H} NMR spectra of [(IPr)Ni₃P₈] in D₈-toluene.[²⁴]

Figure 6. Left: Experimental and simulated X-band EPR spectrum of 3b in a toluene glass at 20 K. Freq. 9.6508 GHz, 0.6325 mW, 20 K, mod. 4.000 Gauss; g-tensor parameters obtained from simulations and DFT calculations for 3b' are: g₁ = 2.186 (2.11), g₂ = 1.987 (2.01), A¹°P₂ = 30.0 MHz (27.5 MHz, averaged value, DFT-calculated values of 3° in parentheses; see the Supporting Information for further details).

Unfortunately, separation of free IPr from compound 4 proved to be challenging. The use of [(IPr)Ni(n°-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/[nBu₄N]PF₆, Figure S20) shows one reversible oxidation wave at E₁/₂ = −0.76 V (vs. Fc/Fc⁺). 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 d⁰-configuration for Ni₂/Ni₂'.

Apart from 4, the reaction of [(IPr)Ni(n°-toluene)] with P₄ also affords green crystals of [(IPr)Ni₁(n°-P₄)] (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 electronic structure of a slightly truncated model complex 3° ([IPh]Ni₁(n°-P₄)]·IPh = 1,3-diphenylimidazolin-2-ylidene) was calculated at the TPSSh/IGLO-III (CP(PPP)) on Ni level of theory.[²⁵] This method was chosen since it has proven to yield reliable results for the calculation of magnetic properties. Significant interactions between the Ni atoms (Mayer bond order: 0.8) as well as the Ni atoms and the aromatic P₄ ring were found (Mayer bond order: 0.5). The X-band EPR spectrum of 3b (Figure 6) recorded in a toluene glass at 20 K reveals an axial 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 (g₁ = g₂ = 2.186 (2.11), g₃ = 1.987 (2.01), A¹°P₂ = 30.0 MHz (27.5 MHz, averaged value, DFT-calculated values of 3° in parentheses; see the Supporting Information for further details).

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However, the mechanism of formation of these products is the steric demand from I of the NHC ligand on the products obtained. Upon increasing the steric demand from IP$_2$ to IMes, di- and trinuclear complexes with Ni$_2$P$_4$(1), Ni$_2$P$_5$(2) cores as well as Ni$_2$P$_6$(3a) were obtained. Notably, 3a represents the first nickel pentaphosphacyclopentadienyl complex. The bulky NHC IP$_2$ again changes the outcome of the reaction to afford a Ni$_2$P$_4$(4) closo-cluster with a novel homocycladicycle-like P$_8$ 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 P$_2$ 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 [D$_2$]tulene to temperatures above 313 K led to decomposition to unidentified products.


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