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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 P0, P2, P3, and P6 units. Using [Ni(IMes)2] [IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidine], electron-deficient Ni2P6 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 ligand were identified as additional products.

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 P0, P2, P3, and P6 units. Using [Ni(IMes)2] [IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidine], electron-deficient Ni2P6 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 ligand were identified as additional products.

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 [k6-PPP-NP3][Ni(η1-P4)] (A), NP3 = tris(2-diphenylphosphinophenyl)amine containing an intact, end-on coordinated P4 tetrahedron.[9] 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][µ-η3-P4]] (C, ImPr2 = 1,3-bis(isopropyl)imidazolin-2-ylidine) 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 Ni0 compounds, examples of P4 aggregation using Ni0 appear to be unknown.

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Figure 1. a) Overview of products resulting from P4 activation using Ni0 sources.[6,10] b) P4 activation and aggregation products described herein.
Building on our previous work on P₄ activation with N- heterocyclic carbene (NHC) nickel(I) complexes,[7,12] 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 carbene itself, alkenes, and arenes. After synthesising a range of known NHC compounds, including the bis(carbene) complexes [Ni(NHC)₂] (NHC = IMes, IPr),[13] trimethylvinylsilane complexes [(NHC)Ni(η²-H, C=CHSiMe₃)]₃,[14] (NHC = IMes, IPr) and the toluene complex [(IPr)Ni(η²-toluene)] we proceeded to systematically study the reactivity of these compounds toward P₄. Reactions of [(NHC)Ni(η²-H, C=CHSiMe₃)]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 [Ni(IMes)]₂. Gratifyingly, the 31P{1H} NMR spectrum of the pure compound containing a pentaphosphacyclopentadienide ligand cyclo-P₄·P₅ by Miluykov, Hey-Hawkins and co-workers.[11]

Figure 2. Molecular structure of 1 in the solid state. Thermal ellipsoids are set at 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni1-Ni2 2.7533(3), Ni2-Ni3 2.7320(3), Ni3-Ni1 2.6528(3), Ni1-P1 2.1045(4), Ni2-P1 2.1739(4), Ni3-P1 2.1720(4), P2-P3 2.1671(5), P3-P4 2.1754(5); Ni3-Ni2-Ni1 61.815(9), Ni2-Ni3-Ni1 66.177(9), Ni3-Ni1-Ni2 52.009(8), P2-P3-P4 133.21(2), P1-Ni1-P4 99.288(16).

The molecular structure of 1 is reminiscent of the distorted kite-like cyclo-P₄ complex [(C₅FeMe₂)(μ-P₄)] reported by Walter and co-workers.[10] 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: 2.7533(3) Å and Ni1-Ni3: 2.6528(3) Å). Ni₃ triangles are a common structure motif, for example, in carboxyl- or phosphate-stabilised clusters.[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) (P2-P3) and 2.1754(5) (P3-P4), which are in the range commonly observed for P-P single bonds. Notably, the P3 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 the 1H NMR spectra are in good agreement with the calculated 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/Fe²⁺), 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\(^{10}\) configuration for each Ni atom (see the Supporting Information for a depiction). This is consistent with classical electron-counting rules.\(^{[18]}\) Thus, the cluster may be defined as a superhcloso-cluster (12 = 2(n−1), n = 7, number of cluster atoms).

The reaction of [Ni(IMes)]\(_2\) with P\(_4\) is significantly less selective when THF is used as a solvent instead of toluene. Besides 1, two other products formed could be identified by \(^{31}\)P\(^{[1]}\)H NMR spectroscopy and X-ray crystallography. After work-up, brown crystals of the trinuclear cluster [(IMes)\(_3\)Ni\(_3\)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\(_3\)P\(_3\) octahedra sharing a common Ni\(_3\) face). Notably, compounds featuring pnictogen (P, As) prisms with iron or cobalt are usually stabilised by anionic cyclopentadienyl ligands.\(^{[19]}\) Similar to 1, an unsymmetrical Ni\(_3\)-triangle is observed (Ni1–Ni2 2.4835(3) Å, Ni1–Ni3 2.4882(3) Å, Ni2–Ni3 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 \(^{31}\)P\(^{[1]}\)H NMR spectrum in C\(_6\)D\(_6\) 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 multicentre bonds between the cluster atoms were identified (see the Supporting Information for a depiction). Thus, due to its closed deltahedral structure (distorted tricapped trigonal prism) and fulfilment of the 2\(n\) cluster electron rule (\(n = 9\)), 2 can be described as a 9-vertex hypercloso-cluster. Additionally, a 3d\(^{10}\) configuration for each Ni atom in 2 could be derived from the analysis of the IBO (see the Supporting Information for details).

Moreover, we were able to identify [(IMes)\(_2\)Ni\(_3\)P\(_3\)](3a) as a side product. This compound co-crystallises with 2 from the mother liquor of the reaction mixture of [Ni(IMes)]\(_2\) with P\(_4\). Structural analysis of crystals of the composition [(IMes)\(_3\)Ni\(_3\)P\(_6\)]·[(IMes)\(_3\)Ni\(_2\)P\(_3\)](2.3a) revealed that compound 3a features a dinuclear inverse sandwich structure in the solid state with a bridging cyclo-P\(_3\)-ligand (Figure 3). The Ni1–Ni2 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\(_3\)-ligands.\(^{[20,21]}\) The pentaphosphacyclopentadienyl ligand is frequently observed in transition metal mediated P\(_4\) activation.\(^{[1]}\) However, most complexes comprising such a cyclo-P\(_3\)-ligand feature group 8 metals and there are only a few examples of other transition metal complexes.\(^{[21]}\) Furthermore, all known cyclo-P\(_3\)-complexes additionally contain cyclopentadienyl ligands, while complex 3a is stabilised by an L-type ligand.

Having established the ability of [Ni(IMes)]\(_2\) to act as a precursor to interesting Ni/P clusters, we proceeded with performing the analogous reactions using the bulkier carbene complex [Ni(IPr)]\(_2\) in order to examine if there is any difference in product distribution (Scheme 2). And, indeed, in contrast to observations made using [Ni(IMes)]\(_2\), \(^{31}\)P\(^{[1]}\)H NMR spectroscopy revealed no resonances. Nevertheless, the \(^1\)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 [(IPr)\(_2\)Ni\(_3\)P\(_3\)](4), an 11-vertex closo-cluster with 24 cluster electrons, adopting an octadecahedral geometry similar to the undecaborate anion [B\(_{11}\)H\(_{11}\)]\(^−\) (Figure 4).\(^{[22]}\) The homoquadracyclic-like P\(_4\) framework is reminiscent of the P\(_4\) 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.\(^{[23]}\) Nevertheless, to the best of our knowledge, this is the first example of such a P\(_4\) framework in an isolated molecular compound.\(^{[4]}\) The structure of compound 4 again comprises three Ni atoms, but the Ni–Ni distances are significantly longer than in complexes 1 and 2 [Ni1–Ni2 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’).

**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 P\(_3\) 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 2.2155(5), P4–P5 2.2116(5), P5–P6 2.2822(5), P4–P6 2.2049(5), Ni1–Ni2-Ni3 57.974(9), Ni1-Ni3-Ni2 57.791(9), Ni1-P1-P3 61.729(16), Ni1-P1-P5 59.285(16), Ni1-P3-P5 58.985(16), P6-P4-P5 62.226(16), P4-P5-P6 58.744(16), P4-P6-P5 59.030(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)]\(_2\) and [(IPr)Ni(h\(^n\)-toluene)] toward P\(_4\).
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/[nBu4N][PF6, Figure S20) shows one reversible oxidation wave at E_on = -0.76 V (vs. Fe/ Fe^+). Analysis of the IBO reveals 12 orbitals that involve bonding between the cluster atoms again being 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 d^8-configuration for the NiI atom and d^10-configurations for Ni2/Ni2'.

Apart from 4, the reaction of [(IPr)Ni(η^3-toluene)] with P₄ also affords green crystals of [(IPr)Ni_i(P3)] (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)Ni_i(P4)]) was calculated at the TPSSH/IGLO-III (CP(PPP) on Ni) level of theory. 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), A^IP = 30.0 MHz (27.5 MHz, averaged value, DFT-calculated values of 3^b in parentheses; see the
obviously complex, and the details of the initial P4 activation
However, the mechanism of formation of these products is
fragments observed in the molecular structures of
P8 framework. Bulky substituents on the NHC ligands
complexes with Ni3P4 (3a)
3Ni3P8 (4) closo-cluster with a novel homoquadricyclane-like
P8 framework. Bulkily substituted 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 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.

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Conflict of interest

The authors declare no conflict of interest.

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