Activation of White Phosphorus by Low-Valent Group 5 Complexes: Formation and Reactivity of cyclo-P₄ Inverted Sandwich Compounds

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S Supporting Information

ABSTRACT: We report the synthesis and comprehensive study of the electronic structure of a unique series of dinuclear group 5 cyclo-tetraphosphide inverted sandwich complexes. White phosphorus (P₄) reacts with niobium(III) and tantalum(III) β-diketiminate (BDI) tert-butylimido complexes to produce the bridging cyclo-P₄ phosphate species \((\text{BDI})(\text{NtBu})\text{M}\)₂(µ-η³-P₄) \((1, M = \text{Nb}; 2, M = \text{Ta})\) in fair yields. 1 is alternatively synthesized upon hydroxelolysis of (BDI)Nb(NBu)Me₂ in the presence of P₄. The trinuclear side product \((\text{BDI})\text{NbNtBu}(\text{P}_4)\) (3) is also identified. Protonation of 1 with \([\text{HOEt}_2][\text{B}(\text{C}_6\text{F}_5)_4]\) does not occur at the phosphide ring but rather involves the BDI ligand to yield \((\text{BDI})\text{Nb}(\text{NtBu})\)₂(µ-η³-P₄) \([\text{B}(\text{C}_6\text{F}_5)_4]\)₂ \((4)\). The monocation and dication analogues \(((\text{BDI})(\text{NtBu})\text{Nb})_2(\mu-\eta^3-P_4)\) \((\text{B}(\text{ArF})_4)\) are both synthesized by oxidation of 1 with AgBArF₃. DFT calculations were used in combination with EPR and UV–visible spectroscopies to probe the nature of the metal–phosphorus bonding.

INTRODUCTION

Since its discovery in the middle of the 17th century, elemental phosphorus has fascinated chemists. Even still, novel allotropes of this element continue to be discovered and studied.¹ Among these, white phosphorus (P₄) is readily available as the direct product of reduction of phosphate minerals² and could be used directly as a building block for synthesizing a wide array of phosphorus-containing inorganic and organic products. Currently, most industrial processes involve molecular phosphorus chlorination or oxychlorination to PCl₅ and POCl₃ before.³,⁴ The development of environmentally friendly and atom-efficient strategies for the direct functionalization of P₄ to organo-phosphorus products, polyphosphorus cages, and other P-containing inorganic derivatives is therefore highly desirable.

A classic methodology for activating white phosphorus involves using well-identified or in situ generated reduced metal complexes.⁵–⁷ Depending on the reducing ability, nature, and coordination environment, a wide array of metal–phosphide species can be generated.³⁴,⁸–¹⁰ Despite several recent achievements in the manipulation of these activated metal–phosphorus species,¹¹–¹³ direct incorporation of P atoms from P₄ under mild conditions both stoichiometrically and catalytically remains a great challenge for contemporary main group and transition metal organometallic chemists. This notably requires a deeper understanding of the nature of the metal–phosphide interaction and the reaction processes involved.

To date, the formation of square-planar cyclo-tetraphosphide species from P₄ has only been observed on rare occasions.⁸,²⁹–³³ Examples of compounds containing a cyclo-tetraphosphide motif bridging two metal ions in a symmetrical fashion, also known as cyclo-P₄ inverted sandwiches, remain extremely limited, and their chemical properties are almost unexplored. Reported examples of bimetallic inverted sandwichs are neutral and of general formula \([\text{L}_2\text{M}]_2(\mu-\eta^3-P_4)\). They were obtained either from reduction of P₄ by low-valent metal species (uranium³²,³³ or zirconium⁸) or upon reduction of alkali phosphides.³⁴ and diphosphane by alkali metals dissolved in liquid ammonia (M = K, Rb, Cs). More recently, Cummins et al. also reported the formation of \(((\text{ODipp})\text{Nb})_2(\mu-\eta^3-P_4)\) (Dipp = 2,6- iPr₂C₆H₃)b yP abstraction from a niobium triphosphide precursor.³⁶ Several tetraphosphane organic derivatives were also described.³⁷–³⁹

Recently, we identified new trivalent group 5 imido complexes supported by the bulky 2,6-disopropylphenyl-β-diketiminate (BDI) ligand.⁴⁰,⁴¹ These species exhibit an extensive and rich reduction chemistry, including semihydrogenation of alkynes.⁴² Activation of C=−F bonds,⁴³,⁴⁴ arenes,⁴⁵ and azides⁴⁶ through unusual pathways. In continuation of this work, we targeted the use of the unsaturated “(BDI)Nb=−N'Bu” fragment to achieve early transition metal pnictide complexes. Herein we investigate the reactivity of these Nb and Ta low-valent precursors with white phosphorus. The formation and chemistry of rare dinitrogen and ditantalum cyclo-P₄ inverted sandwich complexes isolable in three different charge states are described. Structural, spectroscopic, and density functional theory (DFT) studies aiming at comparing and determining the precise electronic structure of this series of molecules are also presented.

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RESULTS AND DISCUSSION

Reaction of the trivalent [(BDI)(NtBu)M(CO)2] (M = Nb, Ta) dicarbonyl precursors with white phosphorus afforded the dinuclear inverted sandwich complexes [(BDI)(NtBu)M(μ-η1η2P4)] (I, M = Nb; 2, M = Ta) as bright green (1) and blue (2) crystalline materials in fair yields (Scheme 1).

Scheme 1. Synthesis of Complexes 1 and 2 from the Dicarbonyl Precursors [(BDI)(NtBu)M(CO)2] (M = Nb, Ta)

Figure 1. Solid-state molecular structures of 1 (top) and 2 (bottom). Hydrogen atoms and disopropyl aryl groups of the BDI ligands have been removed, and 'Bu moieties have been truncated for clarity. Niobium (light blue), tantalum (green), phosphorus (orange), nitrogen (blue), and carbon (gray) atoms are represented with 50% probability ellipsoids. Selected metrical parameters are reported in Table 1.

reaction, performed in benzene at 60 °C, proceeded faster in the case of niobium (6 vs 24 h, respectively, for M = Nb vs Ta), which can be attributed to a higher dissociation rate of the metal—carbonyl bond in the case of Ta. The reaction proceeded faster under UV illumination, with [(BDI)(NtBu)Ta(CO)2] being converted to 2 in 2 h at room temperature. However, in that case the isolated yield was decreased to 34% due to the formation of several byproducts, as gauged by NMR spectroscopy.

The Nb:P4 ratio had no influence on the reaction, and similar results were obtained when 2:1 to 1:2 Nb:P4 ratios were used. Both species are air-stable and were characterized by ES-MS spectrometry, elemental analysis, UV–vis, and 1H and 13C NMR spectroscopy. The 1H and 13C NMR patterns for 1 and 2 are consistent with highly symmetric diamagnetic species in solution. Despite several attempts performed at various temperatures (−40 to +50 °C), we were unable to locate 31P NMR resonances in the −1000 to +1500 ppm range for either complex in solution. Gratifyingly, the solid-state 31P MAS NMR spectrum recorded at 293 K for I displayed two sets of signals (δiso = +251(2) and +84(2) ppm with large chemical shift anisotropy; see Supporting Information (SI)), corresponding to the two non-equivalent P atoms in the cyclo-P4 ligand, in agreement with the asymmetric μ-η1η2 coordination mode observed by X-ray crystallography (see below). In contrast, the previously reported {[(ODipp)2]Nb2(μ-η1η2P4)} complex featured a sharp singlet resonance at +124 ppm in its solution 31P{1H} NMR spectrum.26 Analysis of the solid-state 31P MAS NMR spectrum for 2 was more difficult because of substantial line-broadening, and we were only able to identify one type of signal at δiso = +208(8) ppm (see SI).

The solid-state molecular structures of 1 and 2, determined by single-crystal X-ray diffraction, are shown in Figure 1, and metrical parameters are presented in Table 1. In both cases, the dimeric [(BDI)(NtBu)M(μ-η1η2P4)] (M = Nb, Ta) unit lies on a crystallographically imposed center of symmetry located in the center of the metal–metal axis. Two independent molecules are found in the asymmetric unit for 1, and the following discussion uses averaged metrical parameters. The P4 core is nearly a perfect square plane with 0° P–P–P–P torsion angles, P–P–P angles of 88.86(3)° and 88.83(2)° for 1 and 2, respectively, and almost identical P–P single bond distances. The average P–P bond distances found for 1 and 2 (2.233(3) and 2.248(5) Å, respectively) compare well with those recently reported for (N2P2Zr)2(P4) (2.240(1) Å)8 and (Dipp- O,Nb)2(P4) (2.233(2) Å),36 formally described as containing cyclo-P4− cores. In contrast, shorter P–P distances are found in formally dianionic cyclo-P4− rings in Cs or U complexes (2.14–2.17 Å, see Results and Discussion below).32,35 The tetraphosphorus ring is sandwiched between the two metal cations in an unsymmetrical fashion, as expressed by the strong disymmetry between the M–P distances, with, for each metal center, one short (Nb1–P1 = 2.511(1) Å in 1; Ta1–P1 = 2.500(7)(1) Å in 2) and two average (Nb1–P2 = 2.700(1) Å; Nb1–P2A = 2.702(2) Å in 1; Ta1–P2 = 2.691(1) Å; Ta1–P2A = 2.674(8) Å in 2) metal–phosphorus bond distances. The remaining M–P interaction, located trans to the metal imido moiety, is considered as non-bonding with much longer M–P separation (2.845(1) and 2.817(1) Å for 1 and 2, respectively), attributed to the trans influence of the imido ligand. Therefore, the coordination mode of the cyclo-P4 ligand is best described as μ-η1η2. Interestingly, the metal···metal separation is shorter in the case of tantalum (4.299(1) Å) compared to niobium (4.3605(1) Å in 1) and reflects a greater covalent interaction of the tantalum metal centers with the cyclo-P4 core. The metrical parameters within the (BDI)M–(NtBu) unit are unremarkable and similar to those found in related complexes.40,41,45,47

The reaction between [(BDI)(NtBu)M(CO)2] (M = Nb, Ta) and P4 was also attempted in the presence of B(C6F5)3 in an effort to trap intermediate species, but similar results were obtained.

A more convenient route to 1 involves the hydrogelenolysis of the easily accessed bis-dimethyl precursor (BDI)Nb(NtBu)-Me2 47 in the presence of P4 (Scheme 2). The product precipitated from n-hexane solvent to afford 1 in moderate yield after filtration and recrystallization from toluene. Our group has
the reaction does not exclusively yield \([(\text{BDI})(\text{NtBu})\text{M}]_2\)− several phosphorus-containing byproducts. However, even if the NMR spectrum exhibited several signals in the 4.8 ppm range, integrating for one proton each at 5.36, 5.30, and 4.96 ppm, it is likely that the formation of \(\text{P}_4\) is the main product of the reaction. This selectivity may be partially driven by the relative inertness of compound 1 (see below), which, together with its poorer solubility, facilitates its isolation.

The moderate yield of 1 is explained by the formation of several phosphorus-containing byproducts. However, even if the reaction does not exclusively yield \([[(\text{BDI})(\text{NtBu})\text{M}]_2\)−\(\mu\)−\(\eta^1-\eta^1\text{P}_4\)], 1 is the main product of the reaction. This selectivity may be partially driven by the relative inertness of compound 1 (see below), which, together with its poorer solubility, facilitates its isolation.

The remaining dark green filtrate contained several byproducts, as gauged by NMR spectroscopy. Notably, the \(^1\text{H}\) NMR spectrum exhibited several signals in the 4.8−5.4 ppm range, corresponding to the HC(C(Me)NAr)_2 protons of several BDI-Nb species. The \(^31\text{P}\) NMR spectrum displayed a complicated pattern of resonances between −162 and +184 ppm, attesting that several phosphorus-containing species are formed. Unfortunately, these species exhibited similar solubility and co-crystallized in common solvents (n-hexane, benzene, toluene, HMDSO, OEt\(_2\)); despite several attempts, their full analysis was unsuccessful, preventing their full analysis.

Even so, fractional recrystallization of the n-hexane reaction mixture at −40 °C produced a microcrystalline material whose analysis by ES-MS spectroscopy indicated the presence of a high-nuclearity species, 3, with a molecular peak at \(m/z = 1698.2800\) corresponding to \([[(\text{BDI})\text{NbNtBu}]_3(\text{P}_{12})\)−BDI]⁺. The formation of a trinuclear species was corroborated by the \(^1\text{H}\) NMR spectrum, which displayed three resonances integrating for one proton each at 5.36, 5.30, and 4.96 ppm and corresponding to three independent BDI ligands within the same molecule.

Analysis by X-ray diffraction revealed a system composed of 12 phosphorus atoms capped by three \((\text{BDI})\text{N}(\text{NtBu})\) fragments (Figure 2) of the general overall formula \(((\text{BDI})\)−\text{MnBu})_3\) (3). The architecture of the \(\text{P}_{12}\) core is unprecedented and can be seen as a \(\text{P}_7\) cage featuring a \(\mu\)−\(\eta^1\)−\(\eta^1\) \(\text{P}_5\) ring. The \(\text{P}\)−\(\text{P}\) bond distances vary from 2.146(1) to 2.290(1) Å. These metric values are comparable to those of other known phosphide cages and are in agreement with simple \(\text{P}\)−\(\text{P}\) bond lengths range between 2.560(1) and 2.648(1) Å and are shorter in the case of \(\text{P}_3\) (mean \(\text{P}−\text{P}\) distance value for \(\text{P}_3 = 2.564(6)\) vs 2.62(2) Å for \(\text{P}_1\) and \(\text{P}_2\), which is expected given a lower coordination number for \(\text{P}_3\) compared to those of \(\text{P}_1\) and \(\text{P}_2\).

Phosphorus has a proclivity for homoatomic bonding\(^{19−54}\) and activation of \(\text{P}_n\) by transition metal species can lead to various \(\text{P}_n\) \((n > 4)\) species upon aggregation of smaller fragments. However, clusters of nuclearity above \(n = 7\) are obtained only on very rare occasions.\(^{51−58}\) To date, only two other \(\text{P}_{12}\) clusters possessing different topologies have been

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\begin{array}{|c|c|c|c|c|c|}
\hline
\text{compd} & \text{P−P [Å]} & \text{P−P−P [deg]} & \text{M−P [Å]} & \text{M−M [Å]} & \text{Nb−NtBu [Å]} & \text{Nb−N_{12} [Å]} \\
\hline
1 & 2.233(3) & 88.86(3) & 2.51−2.85 & 4.3605(1) & 1.779(2) & 2.192(6) \\
2 & 2.248(5) & 88.83(2) & 2.50−2.82 & 4.2993(1) & 1.7912(1) & 2.1877(7) \\
4 & 2.235(2) & 88.72(8) & 2.52−2.79 & 4.298(1) & 1.7758(8) & 2.2656(6) \\
5 & 2.209(4) & 89.62(6) & 2.59−2.87 & 4.4929(7) & 1.7744(7) & 2.15(2) \\
6 & 2.182(5) & 88.9(2) & 2.69−2.89 & 4.61(4) & 1.7686(6) & 2.10(1) \\
\hline
\end{array}
\]
described. Bertrand reported the high-yield synthesis of a HNC-capped P12 cluster from P₄, and the structure of the trinuclear cobalt \{[(Cp')Co]₂(μ-P₁₂)\} (Cp' = 1,2,4-Bu₃C₆H₂) complex was elucidated from ³¹P NMR spectroscopy by Scherer et al. In the present case, 1 was found unreactive toward P₄ and 3 is therefore not the result of P₄ incorporation into 1. Unfortunately, separation of 3 from the other reaction byproducts failed in our hands, preventing further analysis of this compound.

In an attempt to find a more efficient method for the preparation of compound 2, we investigated the hydrogenolysis of the tantalum dimethyl complex (BDI)Ta(NtBu)Me₂ in the presence of P₄. However, the outcome was quite different from that observed for its Nb counterpart. Indeed, the major product of the reaction was the cyclometalated tantalum hydride species \{ArNC(Me)CHC(Me)N-[2-(CHMeCH₂)-6-Pr-C₆H₃]⁻Ta(NtBu)H\} as assayed by NMR spectroscopy, similar to what we previously reported for the same reaction performed in the absence of white phosphorus.

**Reactivity Studies.** Compound 1 is fairly robust and can be handled in air either in the solid state or in solution. The cyclo-P₄ ring was not hydrogenated in the presence of H₂ and was not displaced by strong π-acidic ligands such as CO.

In order to determine if the coordinated cyclo-P₄ exhibited basic properties, we explored the reaction of 1 with 2 equiv of [HOEt₂][B(C₆F₅)₄]. The reaction produced a new compound formulated as \{[(BDI)Nb(NtBu)]₂(μ-η⁵:η⁶P₄)\}[B(C₆F₅)₄] (4), in which the BDI backbone has been protonated (Scheme 3, BDI⁺ = [ArNC-(Me)₂CH₂]). Compound 4 can be isolated in high yields as pink crystals. Because of its ion-pair formulation, 4 has poor solubility in hydrocarbon solvents, Et₂O, CH₂Cl₂, and CHCl₃, but is fairly soluble and stable in (CH₂Cl)₂. In naphthalene, its 1H NMR spectrum displays two doublets at 5.44 and 4.68 ppm (JHH = 16.7 Hz) that couple in the ¹H COSY NMR spectrum, corresponding to the two diastereotropic CH₂ protons in H₂C(C(Me)NAr)₂.

Further confirmation of the molecular structure of 4 was obtained by single-crystal X-ray crystallography. The structure consists of ion pairs with two BAr⁻ counteranions balancing the charge of the \{[(BDI)⁺(NtBu)Nb]₂(μ-η⁵:η⁶P₄)\}⁺ dicatonic complex shown in Figure 3. Selected metrical parameters are given in Table 1. The CH₂ protons in H₂C(C(Me)NAr)₂ were located from the Fourier difference map and refined isotropically. The H₂C(C(Me)NAr)₂ ligand core is no longer planar, with the sp³-hybridized methylene carbon lying at 0.51(1) Å below the plane defined by the two C=N imino moieties. The C=N bond lengths are short (1.286(6) Å), in agreement with localized double imine bonds. As a consequence of the β-diketiminate protonation, the interaction between the niobium center and the neutral BDI⁺ ligand is weakened compared to that found in 1, with longer Nb--N bond distances in 4 (2.265(6) Å) than in 1 (2.192(6) Å). This results in a stronger Nb-cyclo-P₄ interaction in 4, as shown by the shorter Nb···Nb separation (4.298(1) Å in 5 vs 4.3605(1) Å in 1), while the geometry of the tetraphosphorus core is essentially unchanged, with similar phosphorus−phosphorus bond distances and angles in 1 and 4 (see Table 1). The average Nb=NBu imido bond length in 5 (1.775(8) Å) is similar to that found for 1.

To probe possible nucleophilicity, 1 was treated with acyl chlorides but did not react and was not affected by the strong Lewis acid B(C₆F₅)₃. Overall, the lack of reactivity of the cyclo-P₄ unit with Bronsted and Lewis acids might reflect the poor basicity/nucleophilicity of the tetraphosphide in 1, but this may as well be a kinetic effect due to the steric protection provided by the bulky BDI ligands; note that we previously reported analogous behavior with the arenedi inverted sandwich complex \{[(BDI)⁺N(C₆H₅)]₂(μ-η⁵:η⁶C₆H₆)\}⁺. Although the niobium centers in 1 can formally be described as d⁰ metal centers, the overall molecule should be considered electron-rich and can therefore be easily oxidized.

The reaction between 1 and 1 equiv of Ag[B(C₆F₅)₃] proceeded quickly at room temperature in toluene and afforded...
an insoluble dark green material. Complex \{[(BDI)(N'Bu)-Nb]_2(\mu-\eta^2:\eta^3P_4)\} [B(C_6F_5)_4] (S) was isolated in 77% yield upon extraction of the solid residue with \(\alpha,\alpha,\alpha\)-trifluorotoluene and crystallization by \(n\)-hexane layering. In return, S could be quantitatively reduced back to 1 using 1 equiv of bis-(cyclopentadienyl)cobalt(II) (as assayed by \(^1\)H NMR spectroscopy, Scheme 4). The \(^1\)H NMR spectrum for S displays several broad, unassignable features from −0.8 to +8.9 ppm that remain broad over the −50 to +60 °C temperature range, and no \(^{31}\)P NMR signals could be located. This is attributed to the paramagnetic nature of this \(S = \frac{1}{2}\) radical species (see EPR study below).

The two-electron oxidation product, \{[(BDI)(N'Bu)Nb]_2(\mu-\eta^2:\eta^3P_4)\} [B(C_6F_5)_4] (6), was isolated in 64% yield from an analogous reaction performed with greater than 2 equiv of the silver oxidizing agent. This ion-pair compound is insoluble in most conventional solvents. 6 is either poorly soluble or reactive with most solvents, but it is sufficiently stable in \(\alpha,\alpha,\alpha\)-trifluorotoluene to obtain \(^1\)H and \(^{31}\)P NMR spectra. The \(^1\)H NMR spectrum for 6 features the expected BDI resonances for a symmetric diamagnetic species in solution. Contrary to 1, 6 displays a sharp singlet resonance in its \(^{31}\)P NMR spectrum at +516 ppm, which indicates that all the phosphorus atoms of the cyclo-P_4^{2−} moiety are equivalent on the NMR time scale. This resonance is shifted significantly downfield compared to that of the previously reported M_2P_4 species (\(\delta = +331-348\) ppm for \(M = K, Rb, Cs\)).

Interestingly, the choice of the counteranion of the Ag(I) salt turned out to be crucial: use of Ag[BF_4] in place of Ag[B(C_6F_5)_4] resulted in a complex mixture of products, as gauged by \(^1\)H NMR spectroscopy. Analysis of the reaction mixture by \(^{19}\)F NMR showed a broad resonance centered at +83 ppm which corresponds to the previously reported Nb(V) difluoride species \{[(BDI)(N'Bu)Nb]_2(F_2)\} \(^{47}\). This likely arises from fluoride abstraction from tetrafluoroborate by a cationic Nb species. Alternatively, when triflate was used in place of the non-coordinating tris-pentafluoroborate anion, the pentavalent niobium triflate species \{[(BDI)(N'Bu)Nb](OTf)_2\} (7) was isolated as yellow crystals in 24% yield. Compound 7 was fully characterized by multinuclear NMR spectroscopy, elemental analysis, IR, and X-ray diffraction (see SI). The formation of 7 most likely involves a reactive intermediate which undergoes ligand exchange in the presence of coordinating triflate anions. However, attempts to isolate or characterize by \(^{31}\)P NMR the byproduct(s) were unsuccessful.

Here we consider it appropriate to draw a parallel between the present cyclo-P_4 inverted sandwich species and the related benzene inverted sandwich species \{[(BDI)Nb(N'Bu)]_2(\mu-\eta^2:\eta^3-C_6H_6)\}, which is best described as a diniobium(III) complex with strong Nb–arene back-donation.\(^{45}\) In the latter case, and contrary to what is observed for 2, we observed that the two-electron oxidation is irreversible and the arene-bridged complex decomposes.\(^{37}\) This difference in reactivity can be ascribed to a stronger interaction and stronger orbital overlap with the cyclo-P_4 ring vs \(C_6H_6\). This is also consistent with the fact that benzene does not displace CO in the dicarbonyls \{[(BDI)(N'Bu)M(CO)_2] \(M = Nb, Ta\)\}, while P_4 does.

**Structural Comparisons.** The isolation of a family of closely related systems in several charge states provides a rare opportunity for comparing their structures and physicochemical properties. Both 5 and 6 were structurally characterized by single-crystal X-ray diffraction (Figure 3). As in the structure of 1, each niobium atom in 5 and 6 is coordinated by a bidentate (BDI) ligand, a (N'Bu) imido fragment bound in a terminal fashion, and a planar \(\eta^3\)-bridging cyclo-P_4 ring perpendicular to the Nb–Nb axis. The three structures differ in their charge state, resulting in the presence of one and two Ba^3\(^{\text{+}}\) counterions in the structures of complexes 5 and 6, respectively.

In Table 1, the most relevant structural parameters for the cyclo-P_4 species 1, 2, and 4–6 are reported. The geometry of the P_4 motif is an almost perfect square plane across the series, with P–P–P angles close to 90 °C (see Table 1). The P–P bond lengths within each P_4 core show very little deviation, and therefore the discussion is based on an averaged value for each species. Comparison of the P–P distances shows very significant differences: specifically, the average P–P bond length is almost identical (within esd’s) in 1 and 4 (2.234 Å), both containing a formally cyclo-P_4^{2−} core, but is shortened by around 0.03 Å in 5 (2.209(4) Å) and by another 0.03 Å in 6 (2.182(5) Å). Such distances compare well to those found in other systems containing the reduced cyclo-P_4 motif and seem diagnostic of its formal charge state, with values ranging from 2.22 to 2.25 Å for tetraanionic rings,\(^{5,64}\) and from 2.14 to 2.20 Å for diaionic rings.\(^{52,53,35}\) The degree of interaction between the metal center and the bridging tetraphosphide is also very dependent on the oxidation state. Overall, shorter Nb–P bond distances are found in the reduced species 1 compared to 6, although these span an extended range because of the asymmetric coordination mode of the P_4 core. This is best seen when comparing the Nb···Nb separation, which increases significantly from 4.3605(1) Å in 1 to 4.4929(7) Å in 5 and 4.611(4) Å in 6. This is compensated by a stronger donation from the BDI backbone and, to a lesser extent, from the imido ligand to the d^0 metal centers, as expressed by a shortening of the Nb–N_{BDI} distances (2.192(6) Å in 1 vs 2.10(1) Å in 6). Hence, as expected, the data show that increasing the charge on the central cyclo-P_4 ring results in a more contracted [Nb,P_4] core.

**Computational Analysis.** Although it is convenient to refer to formal charges when describing these systems, the nature of metal–phosphorus bonding is essentially covalent. We thus turned to DFT calculations to get a better comprehension of their electronic structure.

Geometry optimizations were carried out without any symmetry constraints on complexes 1, 2, 4–6 using the B3PW91 functional (see SI for computational details). This functional is found to correctly account for the structural features of the five investigated complexes (see SI for metric comparison with X-ray data). The maximum deviation of the P–P bonds is around 0.04 Å, whereas the P–P–P angles are...
perfectly reproduced. The unsymmetrical coordination of P₄ to the two metal centers is also reproduced computationally. Thus, these computational methods appear to be well suited to further study the electronic and spectroscopic properties of these complexes (see below). Since an unsymmetrical coordination of P₄ to the two Nb centers is found in 1, any attempt to analyze atomic charges is questionable. Thus, a NBO analysis was carried out. Analysis of the Wiberg bond indexes (WBO) points in the direction of formally Nb(V) metal centers and a P₄⁺ ligand. Indeed, for one Nb center, two interactions with the BDI ligand (WBO = 0.57), and the one with the imido (WBO = 1.95) are equivalent (even slightly stronger) to those in complex 1, but the four interactions with the four phosphorus (WBO = 0.71, 0.52, 0.52, and 0.36) as well as the Nb–P₄ interaction (WBO = 0.12) are weakened.

The analysis of the molecular orbitals in 1, 2, and 4 shows that the HOMO is a δ-bonding orbital involved in the covalent bonding between the metal centers and the P₄ ring, while the electron density in the non-bonding LUMO is essentially localized on metal d-orbitals. (See Figure 4 for a representation of the HOMO and LUMO orbitals in 1.)

![Figure 4. HOMO (left) and LUMO (right) orbitals of complex 1.](image)

In 5, the coordination is slightly less strong, in line with longer Nb–P bond distances. Indeed, for one Nb center, the two interactions with the BDI ligand (WBO = 0.57) and the one with the imido (WBO = 1.95) are equivalent (even slightly stronger) to those in complex 1, but the four interactions with the four phosphorus (WBO = 0.71, 0.52, 0.52, and 0.36) as well as the Nb–Nb interaction (WBO = 0.12) are weakened.

**EPR Spectroscopy.** The room-temperature X-band EPR spectrum of 5 was nicely resolved and could be satisfactorily simulated: both experimental and simulated spectra are presented in Figure 5. The spectrum is isotropic and is defined by a single g value, giso = 2.041. The 19 equally spaced lines and splitting pattern suggest that the spin is delocalized onto two equivalent Nb centers. Accordingly, the spectrum was modeled with a hyperfine interaction of 41.5 G, with two equivalent ⁹³Nb nuclei (100% natural abundance, I = ⁹/₂). No evidence for superhyperfine couplings with the I = ⁷/₂ ³¹P nuclei could be detected.

Using DFT methods, it has been possible to derive the spin density of complex 5, which was computed as a doublet spin state, yielding an extra α spin. The spin density is found to be mainly located on the two Nb centers (more than 0.6 electron), with the remaining 0.4 electron delocalized over the different ligands. The spin density is symmetrically distributed over the two Nb centers, in agreement with the EPR experiment. This observation is in stark contrast to that of {[(BDI)(N'Bu)Nb]₂-[μ-C₆H₄]}₂{Ba²⁺}, where the single electron is not delocalized equally onto both niobiums, resulting in a more complex EPR signal.⁵⁷ The more isotropic and equal distribution of the spin density in 5 suggests better orbital overlap.

**Optical Spectra.** The optical spectra of the formally cyclo-P₄⁺ species 1, 2 (recorded in toluene solution), and 4 (recorded in dichloroethane) feature two types of intense absorptions (Figure 6). High-intensity (20 000 < ε < 37 000 L·cm⁻¹·mol⁻¹) bands are observed in the UV region around 320 nm that we attribute to intraligand π→π* transitions. Additionally, 1, 2, and 4 display strong absorption bands (29 000 < ε < 42 000 L·cm⁻¹·mol⁻¹) in the visible region (λ = 645, 603, and 694 nm for 1, 2, and 4, respectively) responsible for the bright colors of these molecules. Given their high intensities, it is unlikely that these correspond to Laporte-forbidden d→d transitions. Instead, we attribute these processes to phosphorus-to-metal charge-transfer transitions. The energy for this transition is strongly affected both by the nature of the metal center (Ta vs Nb) and by the supporting ligand (BDI vs BDI²⁺) and is therefore a useful tool to probe the nature of the metal–cyclo-P₄ interaction.

Time-dependent density functional theory (TD-DFT) calculations were carried out to further probe the nature of these transitions. The calculated λₘₐₓ Values (see table in SI) are in good agreement with the experimental values and
correspond to a HOMO—LUMO excitation. Upon analysis of the nature of the HOMO and LUMO orbitals involved in the excitation, it appears that the transition can be described as a pseudo-charge transfer between the cyclo-P₄ ligand (HOMO) and the metal centers (LUMO). While 1 and 2 exhibit similar electron configurations, this transition for 2 is radically blue-shifted in comparison with that for 1. DFT shows an increased stabilization of the HOMO δ-bonding orbital in the case of tantalum due to increased covalency, resulting in a larger HOMO—LUMO gap in 2, as observed by UV—visible spectroscopy. This is also in agreement with the X-ray structural data, which show shorter Ta–P bonds in 2 than Nb–P bonds in 1 (see above).

The optical spectrum for the radical cation species 5 features ligand π→π* transitions in the UV region as well as a broad and intense (ε = 22 750 L·cm⁻¹·mol⁻¹) absorption band at low energy (λ = 921 nm, Figure 6). The nature of the frontier orbitals involved in this transition indicates that there is an electronic rearrangement between the SOMO (mainly based on a bonding Nb–P–P–Nb interaction) and the LUMO (non-bonding interaction between the two Nb centers). As a consequence of the depopulation of the Nb–P₄–Nb δ-bonding orbital, no such intense transition is observed in the symmetric fully oxidized dication complex 6. Instead, the absorption spectrum for 6 shows a broad feature centered at λ = 522 nm (ε = 6 160 L·cm⁻¹·mol⁻¹), corresponding to a transition from BDI-Nb bonding orbitals (HOMO—10, HOMO—8) to the LUMO (non-bonding interaction between one d-orbital located on each Nb).

**CONCLUSIONS**

We have shown that low-coordinate d² Nb and Ta complexes supported by a combination of imido and β-diketiminate ligands result in a strong activation of P₄ to yield unusual cyclo-tetraphosphide-bridged inverted sandwich complexes. The structure of an unprecedented P₂ cluster byproduct was also determined. Interestingly, the reaction of [{(BDI)Nb(Nb(NBu))}₃(μ-η¹-η⁴-P₄)] with [HOEt₃]₂[B(C₆F₅)₄] was found to result in the protonation of the BDI ligand rather than the phosphide ring.

We have demonstrated for the first time that the cyclo-P₄ motif can exist in various oxidation states within the same system. Specifically, salts of the {[(BDI)(Nbu)Nb]·(μ-η¹-η⁴-P₄)} (n = 1, 2) mono- and dication were isolated. This offered us the rare opportunity to compare the photochemical properties of a family of structurally related compounds. The combined chemical, structural, spectroscopic, and density functional theory analyses suggest that the best description for these complexes is as high-valent Nb centers with substantial covalent bonding with the cyclo-P₄ core. They also revealed that the metal—phosphorus interaction was stronger for Ta than for Nb, and that it was weakened upon oxidation. An increased reactivity is thus expected for the cationic species reported in this work; studies aimed at determining the full scope of reactivity of these species are currently being pursued. In addition, future work will be directed toward the expansion of these studies to encompass niobium imido systems supported by sterically modified BDI as well as other bidentate ligands in order to elucidate the role played by steric and electronic factors in the formation and the kinetic stability of these species.

**EXPERIMENTAL SECTION**

**General Considerations.** Unless otherwise noted, all reactions were performed either using standard Schlenk line techniques or in an MBraun inert atmosphere glovebox under an atmosphere of purified nitrogen (<1 ppm of O₂/H₂O). Glassware and cannulae were stored in an oven at ~160 °C for at least 12 h prior to use. Toluene, n-hexane, THF, and benzene were purified by passage through a column of activated alumina, stored over 3 or 4 Å molecular sieves, and degassed prior to use. a,a,a-Trifluoroacetone and dichloroethane were dried over P₂O₅ distilled under reduced pressure, degassed, and stored over 4 Å molecular sieves. C₆D₆ was dried over sodium/benzophene, and CDCl₃ was dried over CaH₂. The deuterated solvents were then vacuum-transferred to a storage flask and degassed before being stored over activated molecular sieves in a drybox. (BDI)(CO)₂Nb(NBu)₄, (BDI)₂Ta(NBu)₄, and (BDI)Me₂Nb(NBu)₄ were prepared using literature procedures. White phosphorus (P₄) was prepared from activated alumina under nitrogen gas. Elemental analyses were performed at the School of Human Sciences, Science Center, London Metropolitan University, or at the College of Chemistry, University of California, Berkeley. The X-ray structural determinations were performed at CHEXRAY, University of California, Berkeley, on a Bruker SMART APEX II QUAZAR diffractometer. Solution EPR spectra were collected at 9.251 GHz (X-band) frequency at room temperature in CF₃CH₂, using a Varian E-109 spectrometer equipped with an E-102 microwave bridge. The EPR spectra were simulated and optimized using WinSim. Mass spectra were acquired on a Finnigan LTQ FT mass spectrometer equipped with an ESI source. THF and n-hexane solutions were prepared and filtered in the glovebox and maintained under a nitrogen atmosphere until injection in the spectrometer through a syringe pump. Mass spectra were recorded over a mass range (m/z) of 400–2000 on a Fourier transform ion cyclotron resonance (FT-ICR) MS detector, while MS/MS data were obtained with a linear ion trap (LTQ) analyzer. The exact mass and experimental isotopic profiles were compared in each case to the theoretical ones. Details concerning X-ray diffraction analyses and DFT computational studies are provided in the SI.

**Synthetic Methods.** (1) Method A: From [BDI](CO)₉Nb(NBu)₄. A 0.5 mL benzene solution of [(BDI)-(CO)₉(NBu)₄] (29.9 mg, 0.047 mmol, 1 equiv) and P₄ (5.8 mg, 3.6 mg, 0.047 mmol, 1 equiv) was heated to 60 °C (LTQ) analyzer. The exact mass and experimental isotopic prop
6H, CHMe2, $\delta_{\text{HH}} = 6.7$ Hz. 0.61 (d, 6H, CHMe2, $\delta_{\text{HH}} = 6.7$ Hz).

13C{[H] NMR (125.8 MHz, CDC13, 293 K): $\delta = 175.2$ (C, HC(C(Me)Nar2)), 140.0 (C, Ar), 132.5 (CH, Ar), 124.8 (CH, Ar), 123.5 (CH, Ar), 104.6 (CH, HC(C(Me)Nar2)), 33.00 (CH, Nb=NNb), 28.43 (CH, $\delta_{\text{p}p} = 27.25$ Hz), 25.78 (CH, $\delta_{\text{p}p} = 25.72$ Hz), 25.35 (CH, $\delta_{\text{p}p} = 25.21$ Hz), 23.84 (CH3, HC(C(Me)Nar2)). 31P MAS NMR (202 MHz, 293 K): $\delta_1 = 251.8$, FT-IR (cm$^{-1}$): 2966 (w), 2864 (w), 1512 (s), 1434 (m), 1382 (s), 1362 (s), 1312 (s), 1257 (m), 1226 (s), 1169 (m), 1108 (m), 1013 (s), 933 (s), 847 (s), 793 (s), 773 (m), 756 (m).

UV-vis (toluene): $\lambda_1 = 325$ nm ($\epsilon = 36,000$ L cm$^{-1}$ mol$^{-1}$), $\lambda_2 = 440$ nm ($\epsilon = 4900$ L cm$^{-1}$ mol$^{-1}$). MS: $m/z = 1286.5905$ [M]+ (calc for C66H100N6P4Ta2: C, 54.98; H, 5.13; N, 4.27). Found: C, 55.0; H, 5.1; N, 4.3.

The reaction mixture was stirred for 1 h at room temperature and then filtered to give a green filtrate that was cooled at $-40$ °C and left standing overnight in the freezer. The dark green crystals were then recovered, washed with 2 × 1 mL of Et2O, and dried in vacuo to give 4 as a pink crystalline material (168 mg, 0.064 mmol, 82%). Single crystals suitable for X-ray diffraction were obtained similarly. 1H NMR (400 MHz, CDCl3, 293 K): $\delta = 7.05$ (t, 4H, CHMe2, $\delta_{\text{HH}} = 7.9$ Hz), 6.90 (d, 4H, CHMe2, $\delta_{\text{HH}} = 8.0$ Hz), 6.79 (d, 4H, CHMe2, $\delta_{\text{HH}} = 7.9$ Hz), 5.44 (d, 2H, H, C(C(Me)Nar2), $\delta_{\text{HH}} = 16.7$ Hz), 4.68 (d, 2H, H, C(C(Me)Nar2), $\delta_{\text{HH}} = 16.7$ Hz), 2.80 (sept, 4H, CHMe2, $\delta_{\text{HH}} = 6.7$ Hz), 2.71 (sept, 4H, CHMe2, $\delta_{\text{HH}} = 6.6$ Hz), 2.29 (s, 12H, HC(C(Me)Nar2)), 1.57 (s, 18H, NBu), 1.00 (dd, 24H, CHMeMe, $\delta_{\text{HH}} = 6.6$ Hz).

The reaction mixture was filtered, washed with 1 mL of toluene, and extracted with 3 × 2 mL of $\alpha,\alpha,\alpha$-trifluorotoluene. The dark green suspension was filtered, layered with 12 mL of n-hexane, and left standing at room temperature for 3 days. This gave dark green crystals of 5 that were recovered, washed with n-hexane, and dried in vacuo (236 mg, 0.120 mmol, 77%). Dark green block-shaped single crystals suitable for X-ray diffraction were obtained similarly. The 1H NMR spectrum (600 MHz, CDC13, 223 to 333 K) recorded for this paramagnetic radial species features uninformative broad signals in the 0.5 to +8.9 ppm range. FT-IR (cm$^{-1}$): 2970 (w), 2882 (w), 1645 (w), 1455 (s), 1352 (m), 1315 (m), 1258 (m), 1210 (m), 1178 (w), 1125 (w), 1085 (s), 1022 (w), 978 (s), 932 (m), 856 (s), 795 (s), 771 (s), 755 (s), 679 (m), 683 (m), 659 (m). UV-vis (C2H4Cl2): $\lambda_1 = 912$ nm ($\epsilon = 22,750$ L cm$^{-1}$ mol$^{-1}$), $\lambda_2 = 655$ nm ($\epsilon = 7060$ L cm$^{-1}$ mol$^{-1}$), $\lambda_3 = 435$ nm ($\epsilon = 7100$ L cm$^{-1}$ mol$^{-1}$), $\lambda_4 = 372$ nm ($\epsilon = 17,600$ L cm$^{-1}$ mol$^{-1}$), $\lambda_5 = 330$ nm ($\epsilon = 35,300$ L cm$^{-1}$ mol$^{-1}$). ES-MS: $m/z = 1286.5074$ ([BDI(Nb[Nb])[(μ-η-η'-P)3][μ-η-η'-P]) (Cac for C61H106N6P4Nb2: C, 54.98; H, 5.13; N, 4.3). Anal. Calc for C61H106N6P4Nb2: C, 51.56; H, 3.94; N, 3.11. mp: 221–223 °C.
CoCp2 (1.4 mg, 0.008 mmol, 1 equiv) was added to a 4 mL reaction was stirred for 1 h at room temperature, and the color turned to dark green. The reaction mixture was filtered. The resulting pale, bright lime green solution was concentrated and stored at −40 °C overnight. This produced yellow crystals of 7 that were collected and dried in vacuo (33.0 mg, 0.038 mmol, 24%). Single crystals suitable for X-ray diffraction were grown similarly. 2H NMR (500 MHz, CD2Cl2, 293 K): δ = 7.03 (m, 4H, C–HAr), 6.94 (m, 2H, C–HAr), 6.24 (s, 1H, HC(C(Me)NAr)2), 2.59–2.48 (m, 4H, CHMe2), 1.90 (s, 6H, HC(Me)(CMe)NAr), 1.66 (d, 6H, CHMe2, JHH = 6.4 Hz), 1.07 (d, 6H, CHMe2, JHH = 6.7 Hz), 0.83 (d, 6H, CHMe2, JHH = 6.7 Hz), 0.75 (s, 9H, NtBu). 13C{1H} NMR (125.8 MHz, C6D6, 293 K): δ = 173.53 (C, HC(C(Me)NAr)), 144.83 (C, 144.28 (C, Ar), 139.93 (C, Ar), 129.19 (CH, Ar), 125.07 (CH, Ar), 125.04 (CH, Ar), 113.69 (CH, HC(C(Me)NAr)), 69.89 (CH2), 33.89 (CH, Ph), 30.26 (CH2, NHB=C=NBu), 28.32 (CH, Ph), 26.13 (CH2, HC(C(Me)NAr)), 25.67 (CH3, Ph), 24.99 (CH2Ph), 24.85 (CH2Ph), 24.71 (CH2Ph). 19F NMR, IR, and ESI-MS spectra; X-ray crystallography structural analysis. The authors declare no competing financial interest.

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