Phosphorus-Rich Organic Molecules

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A Niobium-Mediated Cycle Producing Phosphorus-Rich Organic Molecules from White Phosphorus (P_4) through Activation, Functionalization, and Transfer Reactions**

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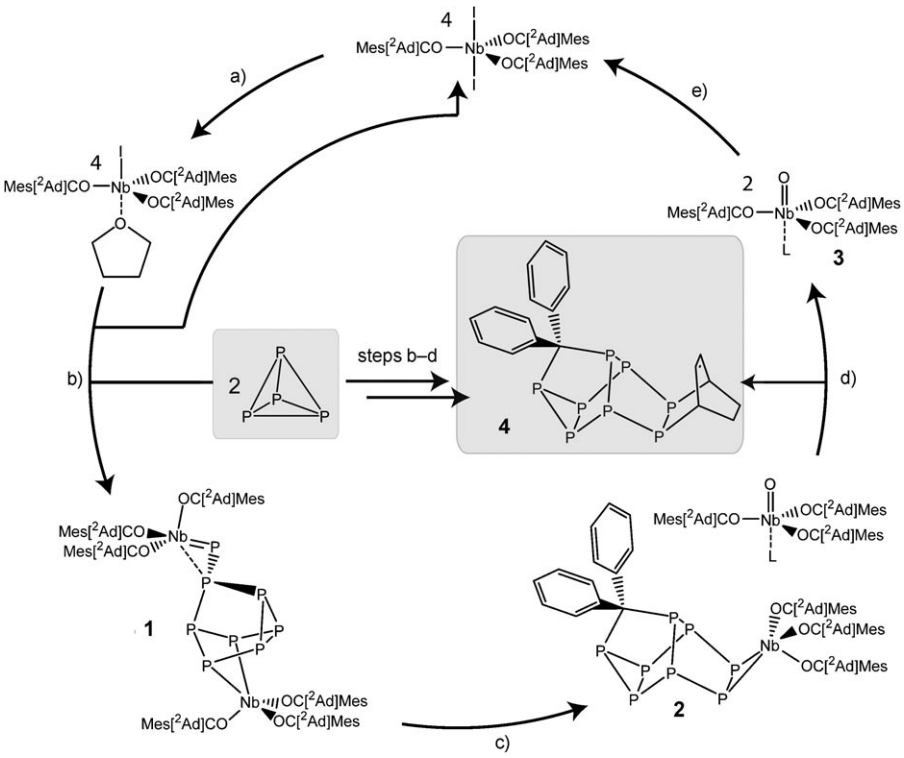
Recently there has been a resurgence in chemistry of the p-block elements that has been driven by its natural intersection with transition-metal chemistry. Using the inherent reactivity of transition-metal–heteroatom multiple bonds, researchers have begun to explore the potential of building up main-group molecules atop transition-metal scaffolds. Examples of such a strategy are found in Group 15, particularly with regard to the chemistry of the terminal nitride and phosphide functional groups.[2,3] While much of this chemistry has remained confined to the protective coordination sphere of the metal complex, it is becoming increasingly evident that the transfer of such ligands is chemically feasible.[4–11]

One interesting target along these lines is the incorporation of P_4-derived phosphorus atoms into organic frameworks by P-atom transfer reactions mediated by transition-metal complexes. This would circumvent the need for PCl_3 as an intermediate in the synthesis of organophosphorus molecules.[12] There are limited examples of such methods reported to date and we are endeavoring to expand this reaction base.[6,9,13] Recently we reported on the synthesis of $[(P_8)\{Nb(OC[^2Ad]Mes)_3\}_2]$ (**1**; ^2Ad = 2-adamantylidene, Mes = 2,4,6-trimethylphenyl) (Scheme 1, steps a and b), a unique dinuclear species bearing metal–phosphorus multiple bonding character that arises from white-phosphorus activation. Subsequently we expanded on the use of **1** in the preparation of $[Ph_2CP_8Nb(OC[^2Ad]Mes)_3]$ (**2**) as described in Scheme 1 (step c).[14,15] Complex **2** is a remarkable carbophosphorus cluster that arises through a rearrangement of the nortricyclic core of **1** following reaction with benzophenone. Herein we complete our synthetic cycle by effecting the liberation of the organophosphorus cluster from **2**. This process generates unusual phosphorus-rich organic molecules by taking advantage of the propensity of niobium to form the strong niobium–oxo bond in the $[ONb(OC[^2Ad]Mes)_3]$ complex (Scheme 1, step d), which we can then recycle to our starting material, $[I_2Nb(OC[^2Ad]Mes)_3]$ (Scheme 1, step e).



Scheme 1. a) 4 equiv SmI_2, loss of 4 equiv SmI_3, >95% yield; b) 2 equiv P_4 (as shown) with quantitative loss of 2 equiv of $[I_2Nb(OC[^2Ad]Mes)_3]$ which is cycled back, 82% yield of **1**; c) 1 equiv $OCPh_2$, 76% yield of **2**, L = OEt_2; d) 2 equiv ONC_5H_5, 20 equiv 1,3-cyclohexadiene, 72% yield of **4** (by NMR), 48% yield of isolated **4**, L = ONC_5H_5; e) 2 equiv $O(OCCF_3)_2$ followed by 4 equiv $ISiMe_3$ to recycle both equiv of $[ONb(OC[^2Ad]Mes)_3]$ formed in the cycle, 72% yield of $[I_2Nb(OC[^2Ad]Mes)_3]$.

We have previously described **2** as having a niobium–phosphorus interaction that may be regarded as side-on coordination of a diphosphene (RP=PR) to a strongly π-donating d^2 niobium center.[15] This leads to the notion that

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when the [Nb(OC[^{2}Ad]Mes)$_3$] fragment is removed what remains is a diphosphene, a PP unsaturated species that would react with an appropriate substrate. This viewpoint has proven useful when considering substrates for reactivity studies involving this complex. It was found that treatment of **2** with two equivalents of pyridine-*N*-oxide as a suspension in Et_2O containing 20 equivalents of 1,3-cyclohexadiene leads rapidly to a yellowing of the solution as bright yellow [ONb(OC[^{2}Ad]Mes)$_3$(ONC$_5$H$_5$)] (**3**) is formed. This is easily confirmed by the characteristic peaks in the ^{1}H NMR spectrum (see the Supporting Information). The fate of the phosphorus cluster is easily determined by a combination of ^{1}H and ^{31}P NMR analysis of the crude reaction mixture. The ^{1}H NMR spectrum reveals a single olefinic resonance at $\delta =$ 5.80 ppm as well as three aliphatic and three aromatic resonances. The ^{31}P NMR spectrum clearly indicates retention of the core structure of the starting material as shown in Figure 1. This led us to postulate the formation of the Diels–Alder cycloaddition product that would form upon reaction of the liberated (*Z*)-diphosphene with 1,3-cyclohexadiene, [(C$_6$H$_8$)P$_8$CPh$_2$] (**4**) (Scheme 1, step d). This reaction is a rare instance of reactive diphosphene liberation from a transition-metal complex and the first instance of the use of pyridine-*N*-oxide to effect such a transformation.[16–18]

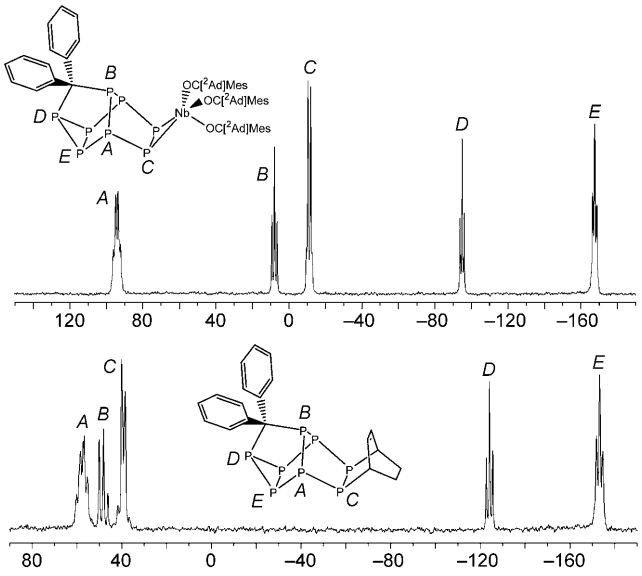


Figure 1. ^{31}P NMR spectra of molecules **2** (top) and **4** (bottom) taken in C_6D_6 at 20 °C and 202 MHz.

Separation of **3** from the phosphorus-containing product is achieved by precipitation from an Et_2O solution, affording **4** as a white powder in 40 to 50 % yield. Complex **3** is isolated in subsequent crystallizations as a fine yellow powder, which is recycled back to [I$_2$Nb(OC[^{2}Ad]Mes)$_3$] as previously reported to close our synthetic cycle.[15] X-ray diffraction quality crystals of **4** were grown from toluene/hexane (3:1) at −35 °C for two days. The crystal structure (Figure 2) shows that the C$_6$H$_8$ unit binds *exo* to the phosphorus cluster with the double bond between C104 and C105 (with a C−C distance of 1.330(3) Å), which is likely the result of secondary orbital

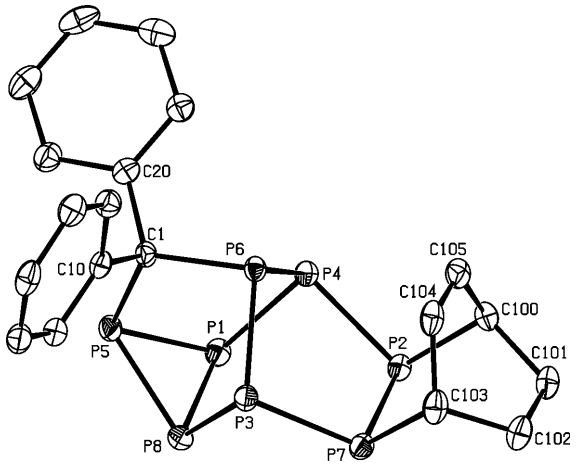
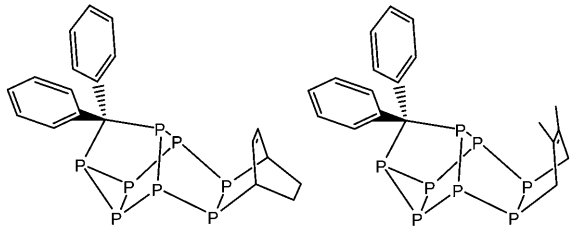


Figure 2. Molecular structure of compound **4** with thermal ellipsoids depicted at 50 % probability. Hydrogen atoms are omitted for clarity.[1]

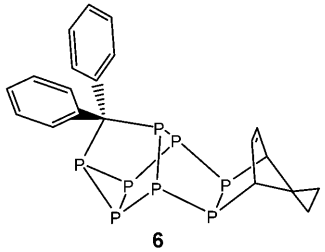
interactions (directed by P6), a common feature of Diels–Alder chemistry.[19] The remainder of the CP$_8$ core deviates little from that described previously for **2**.[15]

The yield of isolated **4** is limited due to the inefficient trapping of the transient diphosphene by cyclohexadiene. By NMR analysis, the best trapping yield we have seen is 72 % by the procedure described above. Increasing the diene concentration did not improve yields, and a solvent screening showed Et_2O to be the best choice for this experiment. The fate of the untrapped cluster could not be determined.

In addition to 1,3-cyclohexadiene, 2,3-dimethylbutadiene was also found to be capable of trapping the liberated carbophosphorus cluster with approximately equal efficiency to yield (C$_6$H$_{10}$)P$_8$CPh$_2$ (**5**). The yield of the diene-trapped phosphorus cluster is, however, significantly improved by moving to spiro[2.4]hepta-1,6-diene, a more reactive Diels–Alder diene.[20] By referencing to an internal standard of PPh_3 at a known concentration we confirm formation in excess of 95 % yield of the diene-trapping product, (C$_7$H$_8$)P$_8$CPh$_2$ (**6**). This phosphorus-rich organic molecule has very similar ^{31}P NMR features to compound **4** and the ^{1}H NMR spectrum clearly indicates the presence of the intact cyclopropane



4 **5**

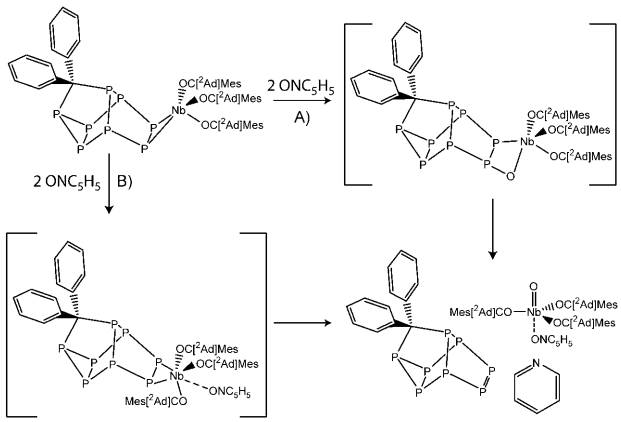


6

group with the methylene protons resonating at $\delta = -0.08$ ppm (see the Supporting Information Figure 2s and 3s). Unfortunately, the increased solubility of **6** in hydrocarbon solvents hinders its clean separation from **3**.

Polyphosphorus clusters bearing organic substituents are not uncommon in the literature. The work of Baudler and co-workers defined the field of monocyclic and polycyclic organophosphanes. These previously known organophosphanes are typically synthesized by treatment of a preformed polyphosphorus Zintl ion with an appropriate alkyl halide or by dehalogenation of mixtures of PX_3 and $RPCl_2$ by magnesium metal.[21] Some reports have also shown the use of P_4 as a direct precursor to such species.[21,22] Recently, Bertrand and co-workers discovered that certain cyclic alkyl aminocarbenes (CAACs) are capable of P_4 activation chemistry leading to carbene-substituted P_4 and P_{12} complexes depending on the conditions chosen.[23,24] The unique feature of **4** is that it is not merely a phosphorus cluster with surface functional groups, but rather a carbophosphorus cluster with additional organic functionality on its surface. Further, the modular synthesis of compound **4** and its derivatives allows for easy variation of the substitution on the polyphosphorus cage. For instance, the embedded CPh_2 unit in **4** may be changed by using a different ketone as a reaction partner for $[(P_8)\{Nb(OC[^2Ad]Mes)_3\}_2]$ as has been previously shown.[15] The diene-derived fragment is likewise limited only by diene selection.

Two possible pathways for the formation of the (*Z*)-diphosphene precursor to phosphorus cluster **4** (Scheme 2) have been investigated by DFT methods. Pathway A (Scheme 2) involves formation of an NbPPO metallacyclic intermediate[9] following deoxygenation of an equivalent of pyridine-*N*-oxide, whereas pathway B assumes loss of niobium–oxo without going through a metallacyclic species. The total bonding energies of the reactants, the proposed intermediates, and the final products (all relative to restricted spherical-atom fragments) were calculated and have shown both pathways to be viable. Formation of the NbPPO metallacycle was calculated to be 50 kcal mol^{-1} downhill of the starting materials and only a very small (6 kcal mol^{-1}) uphill progression for the breakup of the metallacycle to give niobium–oxo was found. The final products (**3**, **4**, and pyridine) were overall 83 kcal mol^{-1} downhill from the starting materials supporting the notion that this is a very thermodynamically favorable process (Figure 3 and the Supporting Information).



Scheme 2.

The physical and electronic properties of **4** have been investigated (for details see the Supporting Information, Figure 9s and 10s). Preliminary reactivity studies of **4** suggest that its reactivity is similar to that of P_4. For example, treatment of **4** with ten equivalents of I_2 at −116 °C gives, upon warming, clean formation of four equivalents of PI_3 ($\delta(^{31}P) = 174.2$ ppm in C_6D_6) and what we have assigned (by ^1H and ^{31}P NMR spectroscopy as well as MALDI-MS) as one

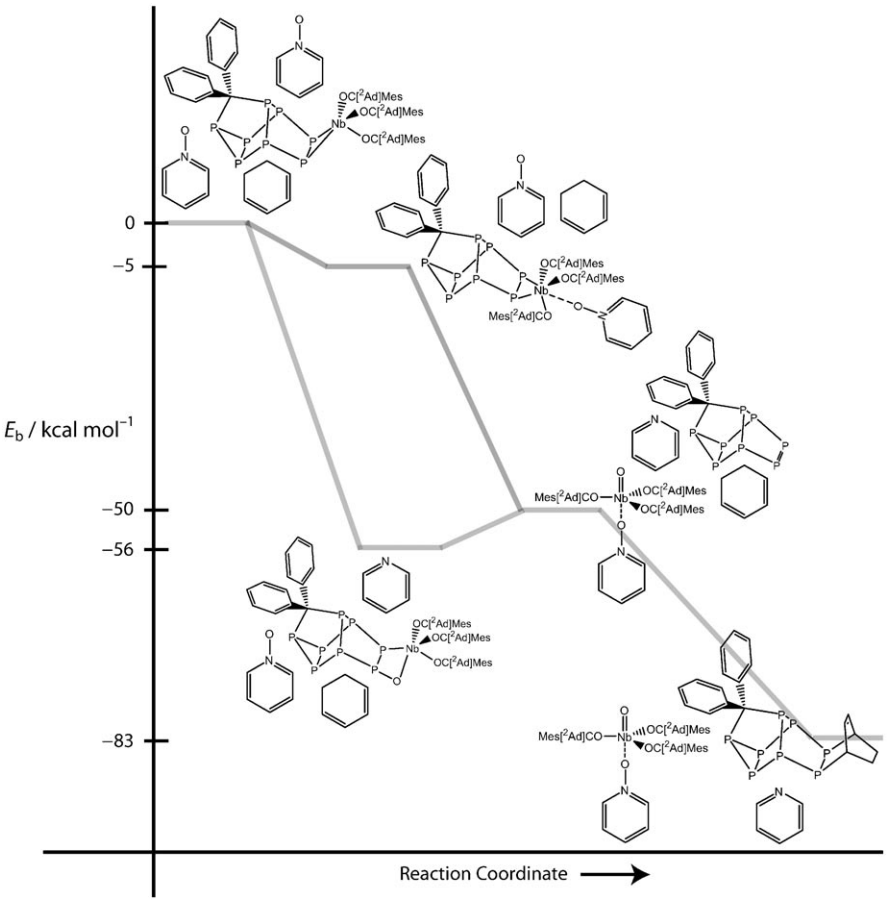


Figure 3. Total bonding energy E_b of all the reactants, proposed intermediates, and products involved in the formation of compound **4** versus reaction coordinate.

equivalent of $(I_2P)_2(C_6H_8)$ and one equivalent of $(I_2P)_2CPh_2$ ($\delta(^{31}P) = 138.34$ and 133.95 ppm in C_6D_6, see the Supporting Information, Figure 11s and 12s).[25–27] This reactivity mimics that which might be expected for a functionalized P_4 molecule.[28] Consistent with the electrochemistry data, we were unable to effect cluster reduction of **4** using a variety of reducing agents, and all of the observed oxidation chemistry resulted in fragmentation as described for I_2.

This work has demonstrated the use of a metal-complexed phosphorus cluster as a starting point for the synthesis of phosphorus-rich organic molecules. These organophosphanes represent a new and unique class of phosphorus clusters bearing cyclic olefins as substituents as well as a cluster-incorporated carbene unit. The robust nature of these clusters, both thermally and chemically, makes them potentially attractive as main-group precursors to phosphorus-rich materials. Additionally, this work exemplifies the natural nexus of main-group and transition-metal chemistry by demonstrating the synthesis of unique main-group species using concepts and methods provided by transition-metal chemistry.

Experimental Section

4: $[Ph_2CP_8Nb(OC[Ad]Mes)_3]$ (1.448 g, 1 equiv) was suspended in Et_2O (60 mL). Cyclohexadiene (1.72 g, 20 equiv) was added to the stirred suspension. To this mixture was added pyridine-*N*-oxide (305 mg, 3 equiv) as a solid. The mixture was allowed to stir for 10 h. After this time there was a gray-white precipitate that had formed. The precipitate, a gray solid (presumably the untrapped material) was removed by filtering the reaction mixture through a pad of Celite. An aliquot from the reaction filtrate was taken for ^1H NMR analysis and revealed only two species, the oxoniobium complex **3** and compound **4**. The filtrate was dried and then slurried in Et_2O (20 mL), resulting in formation of an off-white precipitate. This precipitate was isolated on a frit, washed with Et_2O (50 mL) and pentane (20 mL) and dried under reduced pressure resulting in 203 mg (38% yield). The filtrate was concentrated and placed in the glovebox freezer for additional crops resulting in an additional 51 mg of white powder. Yield: 254 mg (48% yield); ^1H NMR (20 °C, 500 MHz, C_6D_6): $\delta = 0.78$ (br, 2H), 1.06 (br, 2H), 2.54 (br, 2H), 5.80 (≈ q, 2.74 Hz, 2H), 6.89 (m, 6H), 7.55 (d, 7.53 Hz, 4H); ^{13}C NMR (20 °C, 126 MHz C_6D_6): $\delta = 24.6$ (m, CH_2), 30.8 (m, CH), 39.4 (m, PCP), 128.7 (s, Ar), 128.9 (s, Ar), 128.9 (s, Ar), 132.1 (br, C=C), 145.0 (s, Ar); ^{31}P NMR (20 °C, 202 MHz, C_6D_6): $\delta =$ −173.2 (t, 230 Hz, 2P), −124.0 (t, 245 Hz, 1P), 39.3 (pseudo d, 220 Hz, 2P), 48.3 (t, 327 Hz, 1P), 57.2 ppm (m, 2P). Elemental analysis calcd. for $C_{19}H_{18}P_8$: C 46.16, H 3.67; found: C 46.88, H 4.05. m.p.: 165–168 °C (dec).

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[1] CCDC-696072 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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