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P_4 Activation

A Reactive Niobium Phosphinidene P_8 Cluster Obtained by Reductive Coupling of White Phosphorus**

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Thirty-six years ago, Ginsberg and Lindsell found that Wilkinson's catalyst reacts with white phosphorus (P_4) to form [$RhCl(PPh_3)_2(\eta^2\text{-}P_4)$], the first coordination complex of the P_4 molecule.[1] Since then, interest in P_4 activation chemistry has blossomed and a wealth of information about the reactivity of P_4 towards various transition-metal complexes and main-group fragments has been documented.[2–6] Whereas degradation of P_4 into P_1, P_2, and P_3 ligands are common products of white phosphorus activation, aggregation into P_x units, where x is greater than four, has been seen far less frequently.[5] An interesting case arises with the direct coupling of P_4 units to generate P_8 and P_{12} ligands on mononuclear and polynuclear metal complexes.[7] Presented herein is a remarkable P_8 cluster ligand, which can be formed reproducibly in high yields under mild conditions, along with some initial exploration of its reaction chemistry and discussion of potential applications in generating organophosphorus derivatives.

Previous work in our group has demonstrated the utility of three-coordinate, early-transition-metal fragments for the activation of white phosphorus.[8–13] The work described herein develops a new three-coordinate niobium platform using a previously synthesized 2-adamantylidene-(mesityl)enolate ligand, Mes[^{2}Ad]CO$^-$ (^{2}Ad = 2-adamantylidene, Mes = 2,4,6-trimethylphenyl).[14,15] A three-step synthetic strategy provided the niobium(V) diiodide complex [$NbI_2(OC[^2Ad]Mes)_3$] (**1**) as a bright-red powder after diphenylacetylene deprotection of the corresponding η^2-alkyne complex with elemental iodine (73% yield starting from [$\{NbCl_3(dme)\}_x$] over three steps). Treatment of a THF solution of diiodide **1** at 22 °C with one equivalent of [$Ti\{N(tBu)Ar\}_3$] ($Ar = 3,5\text{-}C_6H_3Me_2$)[16,17] affords [$NbI\{OC[^2Ad]Mes\}_3(thf)$] (**2**) quantitatively along with [$TiI\{N(tBu)Ar\}_3$] as the reduction coproduct. It should be noted that [$Ti\{N(tBu)Ar\}_3$] is a potent halogen atom abstractor and has been used with great success previously as a one-electron reductant.[18] Separation of [$TiI\{N(tBu)Ar\}_3$] is accomplished by repeated crystallization from Et_2O at −35 °C. Purification in this manner, however, greatly diminishes the yield of the desired material, **2**. To avoid this complication, **1** may be treated with one equivalent of samarium diiodide[19,20] in THF. After stirring for one hour, the reduction coproduct SmI_3 may be filtered off as a yellow-gold powder and **2** may be isolated by recrystallization from THF in more than 70% yield. It should be noted that **2** may also be prepared and utilized in situ by this method. Early investigations with this niobium(IV) species suggested that a reactive niobium(III) synthon can form by redox disproportionation upon treatment with an appropriate substrate.

Introduction of two equivalents of P_4 to four equivalents of **2** in toluene leads to the slow formation of two equivalents of **1** and one equivalent of [$\{Nb(OC[^2Ad]Mes)_3\}_2(P_8)$] (**3**) over the course of 24–36 hours (Scheme 1). This reaction proceeds by disproportionation of two equivalents of niobium (IV) into one equivalent of niobium(V) and one of"niobium(III)", which effects the P_4 reductive coupling. It is essential to perform the synthesis of **3** in a nondonor solvent, as solvents such as THF and DME inhibit the disproportionation. A precedent for this disproportionation comes from Wolczanski and co-workers' tris(siloxy)tantalum system.[21] Diiodide **1** can be recovered quantitatively as it precipitates out of solution; three cycles of drying the filtrate, stirring the resulting residue in pentane, and filtering through Celite results in pure compound **3** in 75% yield as an orange powder.

The P_8 core of **3** is of great interest as it evidently originates from the coupling of two molecules of P_4. ^{31}P NMR spectroscopy assists in understanding the covalent structure of the P_8 cage in **3** (Figure 1). There are five distinct phosphorus environments spanning the −122 to 380 ppm range. From the NMR data, the structure shown in Figure 1 was proposed. Assuming a rigid bonding model, one may expect eight inequivalent phosphorus atoms. However, the resonances arising from phosphorus C1/C2, D1/D2, and E1/E2 are time averaged in solution owing to rapid reductive elimination of the C1/E1 bond and concomitant oxidative addition of the C2/E2 bond at the niobium. This process generates a virtual mirror plane that bisects the phosphorus C1/2 and E1/2 bonds making phosphorus C1 and E1 chemically equivalent to C2 and E2, respectively, in turn equating D1 and D2 on the NMR time scale at 20 °C.

To understand better the bonding in the phosphorus cluster **3**, a variable temperature (VT) NMR experiment was carried out (see Supporting Information, Figure 1S). There are two points of interest in the VT study: as the temperature is increased from 10 to 70 °C, the peaks corresponding to phosphorus C1/2 and E1/2 broaden and eventually coalesce, and the peak corresponding to phosphorus B broadens significantly and is barely visible above the baseline by

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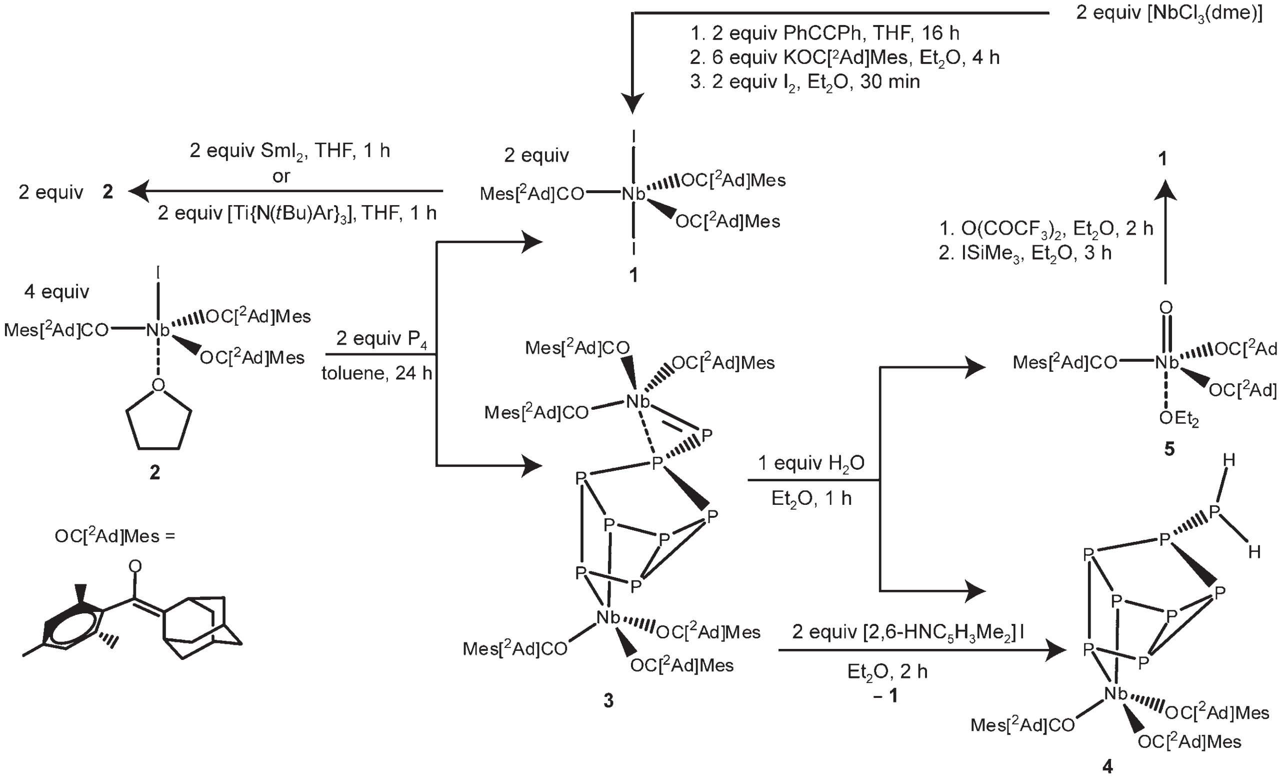

Scheme 1. Reaction cycle for compounds **1** to **5**. ^{2}Ad = 2-adamantylidene, Mes = 2,4,6-trimethylphenyl, Ar = 3,5-$C_6H_3Me_2$.

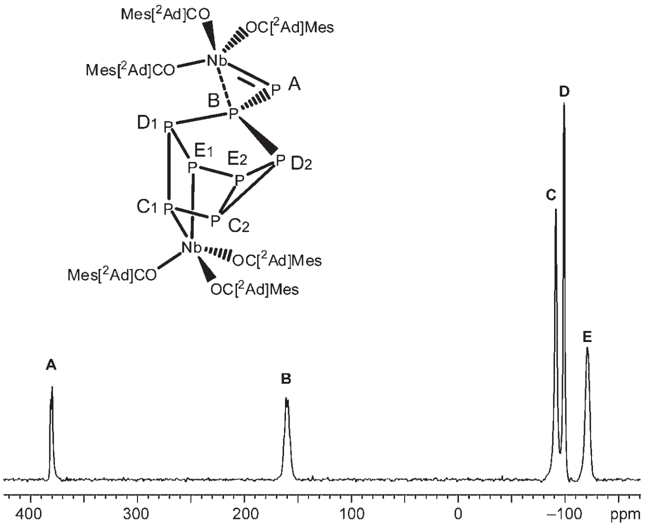

Figure 1. ^{31}P NMR spectrum of [{Nb(OC[^{2}Ad]Mes)$_3$}$_2$(P_8)] (**3**) in C_6D_6 at 22 °C.

70 °C. This is interpreted to be the result of the fluxional process described above at room temperature, along with an inversion at phosphorus B. If this inversion is rapid an additional virtual mirror plane is generated making phosphorus C1/2 chemically equivalent to phosphorus E1/2. The two processes operating in unison make all the phosphorus atoms C and E equivalent, and is responsible for the coalescence observed at 70 °C in the ^{31}P NMR spectrum.

The resonances at $\delta = 380$ and 160 ppm are characteristic of a niobium-bound phosphinophosphinidene.[9] The NMR data, then, are consistent with a model based on a P_7 nortricyclic core with a phosphinophosphinidene moiety connected to one of the three bridges. This structure and the NMR data described above are quite reminiscent of those reported for related P_7 complexes synthesized by Eichhorn and co-workers.[22–24] To add further support to our structural assignment, the results of NMR shielding calculations performed using DFT methods on a model system are in agreement with the observed data and chemical-shift assignments (Supporting Information, Figure 2S, Table 1S).

Recently, the first example of such a P_8 core was established by Wright and co-workers.[25] They discovered that two equivalents of [($Me_3Si)_3$SiK([18]crown-6)] treated with two equivalents of P_4 gives rise to a $[P_8R_2]^{2-}$ species with a P_8 core that is structurally similar to **3**. The distinguishing feature of **3**, however, is that the P_8 architecture is bare apart from niobium coordination, providing a potentially useful unit for functionalization and elaboration. Toward this end, some initial studies of the reactivity of **3** have been carried out. Treatment of **3** with one equivalent of H_2O in Et_2O at 22 °C results in formation of [(P_7PH_2)Nb(OC[^{2}Ad]Mes)$_3$] (**4**). This species can be isolated in 30 % yield as a yellow-orange solid from the reaction mixture; however, it should be noted that the reaction is not quantitative. It can be shown by ^{1}H NMR spectroscopy that [ONb(OC[^{2}Ad]Mes)$_3$(Et_2O)] (**5**) forms as the reaction coproduct; however, it gets scavenged by the water that was added, and the final mixture contains **4**, a small amount of oxo **5**, and significant amounts of

MesC(O)[^{2}Ad]. Despite these complications, **4** crystallizes from a benzene solution (slow evaporation) over the course of several days.

A low-temperature X-ray crystallography study shows that **4** contains a P_8 core much like that described above for complex **3** (Figure 2).[26] It should be noted that, as expected for such a structure, there are two short and two long P···Nb contacts at 2.624(14) Å, 2.706(12) Å and 2.849(4) Å, 2.921(5) Å respectively (see Supporting Information for refinement details and Table 2S for crystallographic data).

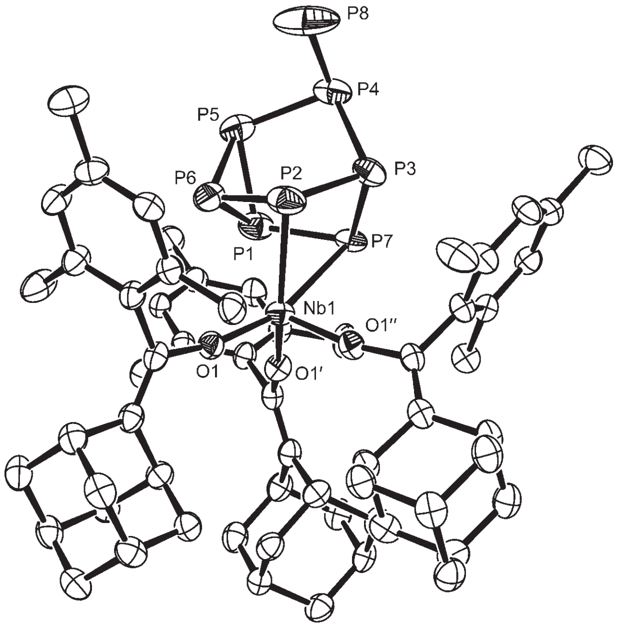

Figure 2. ORTEP of [Nb(OC[^{2}Ad]Mes)$_3$(P$_7$PH$_2$)] (**4**) with ellipsoids set at 50% probability and hydrogen atoms omitted for clarity.

Despite this asymmetry in the solid state, the ^{31}P NMR spectrum for this molecule shows a 2:2:2:1:1 pattern as described for **3**, further corroborating our hypothesis for the molecular structure of **3** (see Supporting Information, Figure 3S, for an NMR spectrum of **4**). In searching for a quantitative synthesis of **4**, other proton sources were investigated. Our most successful alternate synthesis involves treatment of **3** with two equivalents of 2,6-lutidinium iodide, which results in cleaner conversion into one equivalent of **4** and one equivalent of diiodide **1**. Diiodide **1** precipitates cleanly out of solution in 90% yield and **4** may be recrystallized from toluene/Et$_2$O in 30% yield. It is useful, then, that diiodide **1** may be reintroduced into our reaction cycle without further workup.

In summary, a P_8Nb_2 cluster has been synthesized through direct activation and reductive coupling of white phosphorus. Octaphosphorus cluster **3** can be synthesized cleanly in high yields and under mild conditions. Complex **3** contains a reactive phosphinophosphinidene moiety, and we hope that its formation can be exploited in a number of chemical transformations. One such transformation has been shown herein, and involves hydrolysis resulting in isolation of **4**. The potential for this chemistry to lead to a wide range of substituted P_8 clusters is inferred. Preliminary reactivity studies of the diniobium octaphosphorus cluster complex with carbonyl compounds and with organic nitriles suggest fruitful pathways for P_8 cluster functionalization and complete liberation from the niobium centers. It will be of interest to harness such reactivity for P_8 cluster delivery and incorporation as a structural subunit.

Experimental Section

All manipulations were performed in an inert atmosphere of dinitrogen using standard techniques in a Vacuum Atmospheres MO-40M glove box. Dry, oxygen free solvents were employed. NMR spectra were recorded on Bruker Avance 400 or Varian Inova 500 spectrometers. ^{31}P NMR shifts are reported relative to neat H_3PO_4. Full experimental details for diiodide **1**, monoiodide **2**, and oxo compound **5** can be found in the Supporting Information.

3: A THF solution of **2** (5.72 g, 5.04 mmol), prepared in situ, was added to a solution of P_4 (335 mg, 2.52 mmol) in toluene (50 mL). THF was removed from the solution under reduced pressure. As solvent evaporated it was replaced by additional toluene. This process of evaporation and solvent replacement was continued for 8 h. After this time significant red precipitate (**1**) had begun to form, indicating that the disproportionation was proceeding. The flask was sealed with a rubber stopper and allowed to stir for 36 h. After this time, the solution was taken to dryness under reduced pressure. Diethyl ether (50 mL) was added and the bright red solid **1** was collected on a frit in quantitative yield (3.0 g). The filtrate was taken to dryness, and the resulting residue redissolved in 50 mL of pentane. The solution was then filtered through a pad of celite. This process was repeated twice to remove any insoluble material. The final pentane solution was concentrated to 15 mL and placed in a glove-box freezer to induce precipitation. Yield: 2.2 g (82%); ^{1}H NMR (20°C, 500 MHz, C_6D_6): $\delta = 1.6$–2.2 (78H, multiple overlapping peaks, ^{2}Ad-H), 2.22, 2.27 (18H, s, *p*-Me), 2.37, 2.47 (36H, s, *o*-Me), 3.34, 3.43 ppm (6H, s, allylic H): $\delta = 6.82$, 6.88 ppm (12H, s, Ar-H); ^{13}C NMR (20°C, 126 MHz, C_6D_6): $\delta = 147.61$, 137.44, 137.27, 136.94, 136.85, 134.61, 133.84, 131.66, 129.29, 128.87, 128.63, 128.37, 127.45, 39.77, 39.49, 39.32, 39.22, 39.04, 37.70, 37.38, 34.48, 30.87, 30.58, 29.14, 28.87, 21.39, 20.58 ppm; ^{31}P NMR (20°C, 202 MHz, C_6D_6): $\delta = 379$ (1P, d, $^1J_{PP} = 356$ Hz, P_A), 161 (1P, m, P_B), -92 (2P, br, $P_{C1/2}$), -100 (2P, br, $P_{D1/2}$), -122 ppm (2P, br, $P_{E1/2}$). Elemental analysis (%) calcd for $C_{120}H_{175}Nb_2P_8$: C 67.92, H 7.12, P 11.67; found: C 67.04, H 7.09, P 11.61.

4: Method 1 (with H_2O): **3** (500 mg, 0.235 mmol) was dissolved in 150 mL of Et_2O in a 300 mL Schlenk flask. The flask was removed from the glove box and placed under a positive pressure of argon on a Schlenk line. The flask was chilled in an ice water bath. H_2O (4.14 mg, 0.236 mmol) was syringed into the flask as a stock solution in THF. The solution was allowed to stir for 2 h during which time the solution progresses from a bright orange homogeneous state to a yellow-orange inhomogeneous mixture. After 2 h, the volatiles were removed under reduced pressure and the flask was brought back into the glovebox. The residue was slurried with Et_2O and the solids were collected on a frit. The solids were washed three times with pentane (20 mL) and were then dried. Dissolving in benzene and allowing a slow evaporation over several days afforded X-ray quality crystals. Yield: 83 mg (30%); ^{1}H NMR (20°C, 500 MHz, C_6D_6): $\delta =$ 1.55–2.15 (38H, multiple overlapping peaks, ^{2}Ad-H, P-H), 2.19 (9H, s, *p*-Me), 2.49 (18H, s, *o*-Me), 3.45 (3H, s, allylic H), 6.89 ppm (6H, s, Ar-H); ^{31}P NMR (20°C, 126 MHz, C_6D_6): $\delta = 89$ (1P, q, P_B), -65 (2P, br, P_E), -84 (2P, br, P_D), -87.5 (2P, br, P_C), -203 ppm (1P, d, P_A, $^1J_{PH} = 196$ Hz). Method 2 (with 2,6-lutidinium iodide): **3** (500 mg, 0.235 mmol) was dissolved in Et_2O (10 mL) and was added to solid 2,6-lutidinium iodide (111 mg, 0.471 mmol). The mixture was allowed to stir for 4 h during which time there was copious precipitation of **1** and **4**. The mixture was filtered through a medium-porosity frit and the solids were collected and washed with Et_2O (20 mL). The solids were then washed with toluene (40 mL) and Et_2O (10 mL) into a fresh filtration flask, leaving **1** (249 mg, 89% yield) on the frit as a bright red solid. The filtrate was then concentrated to a volume of 5 mL and was stored at -35 °C, allowing **4** to crystallize as a pumpkin-orange solid. X-ray quality crystals were grown from a benzene solution (slow evaporation) and a unit-cell determination confirmed the identity of this material. Yield 85 mg (30%).

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[26] CCDC-661696 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.