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Activation of White Phosphorus by Reduction in the Presence of a Zirconium Diamidodiphosphine Macrocycle: Formation of a Bridging Square-Planar *cyclo*-P_4 Unit**

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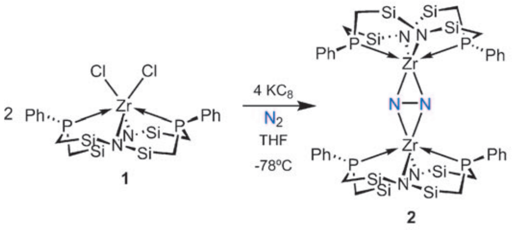
The direct incorporation of the Group 15 elements into transition-metal complexes may be a useful way to utilize these materials for further elaboration.[1] The two lightest elements of this group are nitrogen and phosphorus, both of which are essential to all life on this planet, but in their elemental forms can be deadly. For example, elemental nitrogen occurs as N_2, which, in its gaseous form, cannot support aerobic life, and one of the allotropes of phosphorus, P_4, is a severe bone toxin.[2] While activation of dinitrogen is difficult because of its intrinsic inertness,[3] elemental phosphorus, especially white phosphorus, is quite reactive. In fact, P_4 is so reactive to O_2 that it must be protected by storage under water.[4]

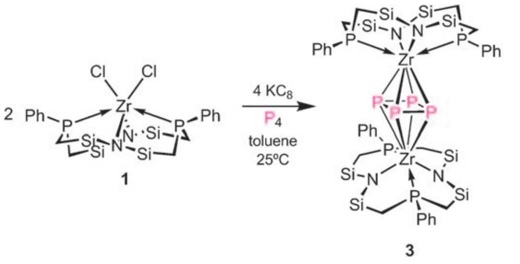
A standard method for the activation of N_2 is to reduce a metal complex in the presence of dinitrogen.[3,5,6] For example, we and others have used this procedure to produce Group 4 complexes containing side-on bound N_2 moieties bridging between two metal centers; a particularly relevant example is shown in Equation (1) (the methyl groups on Si are omitted for clarity), wherein the bridging dinitrogen moiety is formally a $[N_2]^{4-}$ fragment.[7,8]



(1)

In an effort to extend this method to other members of Group 15, we performed the reduction sequence using white phosphorus, and obtained a new dinuclear zirconium complex that has an intact P_4 unit. Herein we describe the full details of this study along with initial reactivity studies.

The addition of a toluene solution of P_4 to a mixture of $[ZrCl_2(P_2N_2)]$ (where $P_2N_2 = PhP(CH_2SiMe_2NSiMe_2CH_2)_2PPh$)[9] and potassium graphite (KC_8) resulted in the formation of a deep purple solution from which purple crystals of $[\{(P_2N_2)Zr\}_2(P_4)]$ (**3**) could be obtained [Eq. (2); the methyl groups on Si are omitted for clarity].



(2)

The ^1H NMR spectrum of **3** in solution shows signals that are consistent with high symmetry (the P_2N_2 silylmethyl groups give rise to two singlets, and the methylene PCH_2Si protons give rise to an ABX_2 pattern); the ^{31}P NMR spectrum is especially diagnostic as it consists of two binomial quintets with a $^2J_{PP} = 20$ Hz, which indicates that all four phosphines of the P_2N_2 ligand are equivalent as are all four phosphorus atoms of the P_4 moiety. Since the $\{(P_2N_2)Zr\}$ fragment is at best C_{2v} symmetric, to render all four phosphorus atoms of the coordinated P_4 unit equivalent requires a symmetric static structure or a fluxional process.

X-ray quality crystals were obtained from a toluene solution of **3** and subjected to single-crystal X-ray analysis (Figure 1). What is clearly evident is that the two $Zr(P_2N_2)$ units are bridged by a planar square of phosphorus atoms; this P_4 unit symmetrically bridges the two Zr centers with Zr–P bond lengths that range from 2.7181(10) to 2.7371(10) Å and are just slightly longer than the zirconium to phosphine distances in the $Zr[P_2N_2]$ units (avg. 2.727 Å). The two $Zr(P_2N_2)$ units are twisted about 90° to each other. Overall, the geometry of the molecule is almost D_{2d} symmetric, which is consistent with the solution data mentioned above. In other words, this symmetric static structure accounts for the equivalency of all of the phosphorus atoms of the bridging P_4 unit and the phosphine donors.

The P_4 unit is essentially flat (deviation from the plane defined by P5-P6-P7-P8 is 0.01 Å) with virtually identical P–P separations (range from 2.2398(13) to 2.2407(13) Å) that

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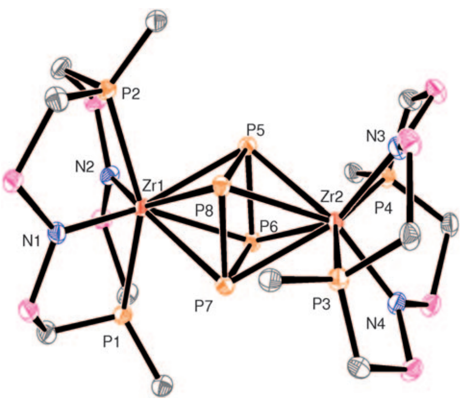
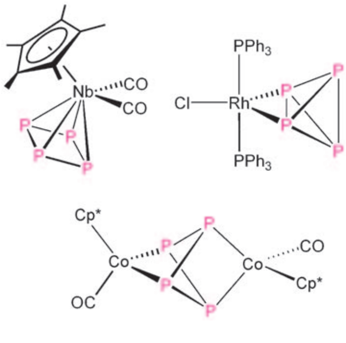


Figure 1. ORTEP of **3** (thermal ellipsoids set at 50% probability). The methyl groups on the Si centers have been omitted for clarity; only the ipso carbon atoms on the P–Ph groups are shown (C gray, Si purple). Selected bond lengths [Å] and bond angles [°]: Zr1–P1 2.7268(10), Zr1–P2 2.7275(10), Zr1–P5 2.7181(10), Zr1–P6 2.7354(10), Zr1–P7 2.7202(10), Zr1–P8 2.7355(10), Zr2–P3 2.7263(10), Zr2–P4 2.7271(10), Zr2–P5 2.7371(10), Zr2–P6 2.7201(10), Zr2–P7 2.7358(10), Zr2–P8 2.7195(10), P5–P6 2.2407(13), P6–P7 2.2407(13), P7–P8 2.2407(13), P8–P5 2.2398(13), Zr1–N1 2.207(3), Zr1–N2 2.206(3), Zr2–N3 2.206(3), Zr2–N4 2.205(3); P5-P6-P7 89.99(5), P6-P7-P8 89.98(5), P7-P8-P5 90.02(5), P8-P5-P6 90.00(5), P1-Zr1-P2 153.07(3), P3-Zr2-P4 153.10(3), Zr1-P5-Zr2 109.00(3).

correspond to P–P single bonds,[10] as found in elemental P_4,[11] for example. Moreover, the bridging P_4 unit in **3** is a perfect square with bond angles ranging from 89.98(5) to 90.02(5)°.

In terms of a simple formalism, the bridging tetraphosphorus unit in **3** can assigned as a $[P_4]^{4-}$ fragment, which corresponds to the D_{2d} P_4H_4 molecule[10] fully deprotonated. Planar P_4 units that are formally dianionic are known; for example, the compound $Cs_2P_4{\cdot}2NH_3$ for which the X-ray crystal structure shows[12] a planar square of phosphorus atoms with P–P bond lengths that are 2.146(1) Å, significantly shorter than those observed in **3**. Other P_4 units exist bound to transition-metal complexes in a variety of ways,[13–20] but none match what is reported in this investigation. Mononuclear Group 5 complexes of P_4 are known, for example, $[Cp^*Nb(CO)_2(\eta^4\text{-}P_4)]$ ($Cp^* = C_5Me_5$; Scheme 1) and its tantalum congener[21,22] have been isolated; in addition, the Group 9 complex $[RhCl(PPh_3)_2(\eta^2\text{-}P_4)]$ is known wherein the P_4 unit is essentially an intact tetrahedral array of phosphorus atoms (Scheme 1).[13] In these mononuclear examples, the P_4 unit can be considered formally neutral or dianionic. With $[Cp^*Co(CO)_2]$ the P_4 molecule is ring-opened to generate a mixture of complexes, one of which, $[\{Cp^*Co(CO)\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}P_4)]$ (Scheme 1), contains a bridging butterfly-distorted P_4 ring that is formally a tetraanion.[23] A similar bonding mode was recently observed for $[\{(NacNac)Al\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}P_4)]$ (NacNac = *N*,*N*-diisopropylphenyl-2,4-pentanediiminato).[24]



Scheme 1.

Other dinuclear and polynuclear systems have been reported with bridging P_4 units many of which formally involve a neutral or a dianionic P_4 moiety.[1,13,17,18,25]

The reactivity of the dizirconium P_4 complex **3** has not yet been extensively examined. However, addition of two equivalents of KC_8 to a toluene solution of **3** results in the incorporation of two potassium ions; this new complex **4** can be isolated a dark purple solid and analyzes for $[\{(P_2N_2)Zr\}_2P_4K_2]$. The NMR spectroscopic data of **4** are distinct from that of **3**, but show similar features. For example, the ^{31}P NMR spectrum shows two broad resonances at $\delta = 4.92$ and 2.05 ppm, and the ^{1}H NMR spectrum displays a similar symmetric pattern to that of **3** on the basis of only two resonances for the silylmethyl protons; interestingly, the presence of highly deshielded *o*-phenyl protons on the phosphorus–phenyl substituents of the P_2N_2 ancillary ligand could indicate that both K^+ ions interact with both the bridging P_4 unit and the phosphorus–phenyl π-systems. Variable temperature ^{31}P NMR studies indicate that there is a fluxional process in operation as broadening and decoalescing of both phosphorus resonances are observed as the temperature is lowered; at 185 K, four new broad resonances are observed that correspond to two inequivalent environments for the ligand phosphines, and two inequivalent phosphorus nuclei for the bridging P_4 unit. No coupling information was evident owing to the broad signals. Unfortunately, despite several attempts, we were unable to grow crystals of the solvent free complex **4**. However, addition of triglyme ($MeO(CH_2CH_2O)_3Me$) to a toluene solution of $[\{(P_2N_2)Zr\}_2P_4K_2]$ resulted in a color change to deep blue and precipitation of X-ray quality crystals of a new material of the formula $[\{(P_2N_2)Zr\}_2P_4K_2]{\cdot}(\text{triglyme})_3$ (**5**) The solid state structure clearly shows that **5** is a salt with a separated cation of $[K(\text{triglyme})_2]^+$; the molecular structure of the anionic portion of **5** is shown in Figure 2.

The dizirconate unit has a U-shaped P_4 fragment with a single $[K(\text{triglyme})]^+$ cation associated with one side of the bridging tetraphosphido moiety. Two of the three P–P bonds are shorter that found in **3**, (P5–P6, 2.1368(14) and P7–P8, 2.1520(14) Å), with the remaining bond, P6–P7, slightly longer at 2.3808(14) Å; the distance between P5 and P8 is 3.431 Å, consistent with no bond. The shorter P–P bond lengths in **5** are quite similar to those found in Cs_2P_4 (2.147 Å)[12] and in diuranium derivative (2.157 Å).[25] The alternating short–long–short P–P bond lengths in the acyclic P_4 unit **5** are reminiscent of some neutral diiron structures, although in those cases, there are no associated potassium cations.[26,27] In the ^{31}P NMR spectrum recorded in [D$_8$]THF solution at ambient temperature, **5** displays two binomial quintets for the phosphorus nuclei of the P_4 unit and the ancillary $[P_2N_2]$ ligands at $\delta = 19.44$ and 7.26 ppm ($^2J_{PP} = 13.0$ Hz), respectively. Interestingly, this spectrum is distinct

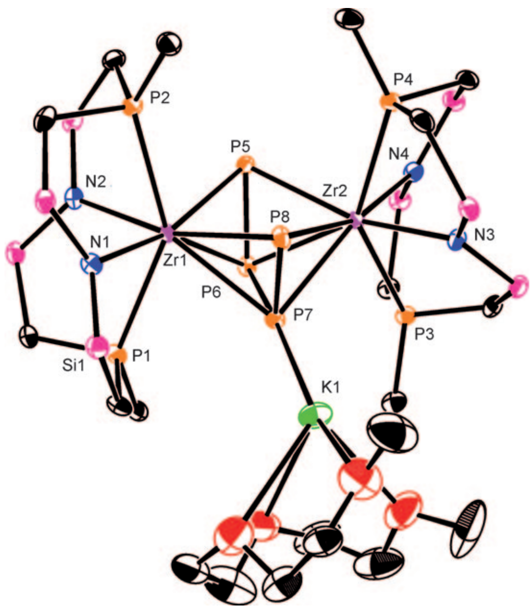


Figure 2. ORTEP of the anion of **5** (thermal ellipsoids set at 50% probability). The [K(triglyme)$_2$]$^+$ ion is not shown; the methyl groups on the Si centers have been omitted for clarity; only the ipso carbon atoms on the P–Ph groups are shown. Selected bond lengths [Å] and bond angles [°]: Zr1–P1 2.6901(10), Zr1–P2 2.7258(10), Zr1–P5 2.6375(10), Zr1–P6 2.6935(10), Zr1–P7 2.7425(11), Zr1–P8 2.6523(10), Zr2–P3 2.7311(11), Zr2–P4 2.7088(10), Zr2–P5 2.6498(10), Zr2–P6 2.7450(10), Zr2–P7 2.6761(10), Zr2–P8 2.6601(10), P5–P6 2.1368(14), P6–P7 2.3808(14), P7–P8 2.1520(14), P8···P5 3.431, Zr1–N1 2.376(3), Zr1–N2 2.351(3), Zr2–N3 2.326(3), Zr2–N4 2.354(3), P7–K1 3.1933(15), P8–K1 3.6107(15); P5-P6-P7 103.66(5), P6-P7-P8 104.65(5), P1-Zr1-P2 142.51(3), P3-Zr2-P4 141.59(3), Zr1-P5-Zr2 93.89(3).

from that of the triglyme-free material **4** also run in $[D_8]$THF, which indicates that **5** does not convert into the THF-solvated form of **4** in the presence of excess THF. As the temperature of a solution of **5** in $[D_8]$THF is lowered, the ^{31}P resonance arising from the bridging tetraphosphido unit broadens substantially and shifts downfield to approximately $\delta =$ 29 ppm with the appearance of a shoulder, but even at 223 K, no clear evidence of distinct resonances for inequivalent phosphorus nuclei is observed. The signal arising from the phosphorus nuclei in the P_2N_2 unit does not broaden as the temperature is lowered. The solid-state structure is clearly different than that found in solution; it is likely that both K$^+$ ions exchange on the NMR time scale but on average are associated with the bridging P_4 unit. The solvent dependence of the solution structures of **4** and **5** in the presence of ether donors is still under investigation.

The over-reduced potassium salts **4** and **5** are exceedingly air-sensitive. Even trace amounts of O_2 result in conversion back into **3** which has the symmetrical square of phosphorus atoms. This transformation can also be achieved by addition of one equivalent of I_2 to **4**, which generates **3** cleanly. Future work will focus on the reactivity patterns of these activated P_4 fragments and their ability to engage in assembly of higher order structures.[28]

Even with the large amount of literature that deals with the activation of white phosphorus by transition-metal complexes, the isolation of a cyclic $[P_4]^{4-}$ fragment and an acyclic $[P_4]^{6-}$ moiety each represents a new motif in phosphorus chemistry.

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