

# Mild P<sub>4</sub> Activation To Give an Anionic Diphosphorus Complex with a Dual Binding Ability at a Single P Site

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Supporting Information

**ABSTRACT:** The anion  $[\text{Mo}_2\text{Cp}_2(\mu\text{-PCy}_2)(\mu\text{-CO})_2]^-$  (**1**;  $\text{Li}^+$  salt) reacts at 290 K with  $\text{P}_4$  to give the diphosphorus-bridged complex  $[\text{Mo}_2\text{Cp}_2(\mu\text{-PCy}_2)(\text{CO})_2(\mu\text{-}\kappa^2\text{:}\kappa^2\text{-P}_2)]^-$  (**2**). The latter reacts with  $\text{MeI}$  and  $\text{ClSnPh}_3$  through a single P atom to give respectively diphosphenyl  $[\text{Mo}_2\text{Cp}_2(\mu\text{-PCy}_2)(\text{CO})_2(\mu\text{-}\kappa^2\text{:}\kappa^2\text{-P}_2\text{Me})]^-$  (**3**) and stannyl  $[\text{Mo}_2\text{Cp}_2(\mu\text{-PCy}_2)(\text{CO})_2\{\mu\text{-}\kappa^2\text{:}\kappa^2\text{-P}_2(\text{SnPh}_3)\}]^-$  (**4**) derivatives, with the P–P–Sn angle in **4** being unexpectedly acute  $[80.3(1)^\circ]$ . According to density functional theory calculations, this novel nucleophilic behavior of **1** is derived from its anionic nature, thus enabling the  $\text{P}_2$  ligand to act in a  $\pi$ -donor-like fashion.

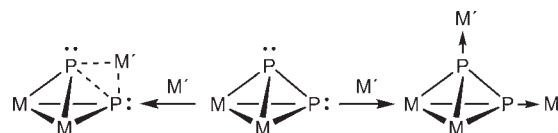
White phosphorus ( $\text{P}_4$ ) activation and functionalization have attracted much attention over the last 40 years,<sup>1,2</sup> in part because of the need to replace the current industrial technology to produce organophosphorus derivatives.<sup>3</sup> In this context, the direct functionalization of  $\text{P}_4$  under mild conditions is a desirable goal to avoid the use of hazardous and toxic chemicals in the above industrial processes.

Many transition-metal complexes have been shown to activate the  $\text{P}_4$  molecule, leading to a great variety of  $\text{P}_n$  complexes ( $n = 1\text{--}24$ ),<sup>4</sup> and some functionalization studies have been carried out as well.<sup>1</sup> Among the different ways to degrade this molecule, symmetrical cleavage to give a  $\mu\text{-}\kappa^2\text{:}\kappa^2\text{-P}_2$  ligand is a relatively well-precedented process.<sup>5</sup> Reactivity studies of the resulting complexes (all of them neutral species so far) have shown that the P atoms can further bind to different metal carbonyl fragments ( $\text{M}'$  in Scheme 1) by using their remaining lone electron pairs.<sup>6</sup>

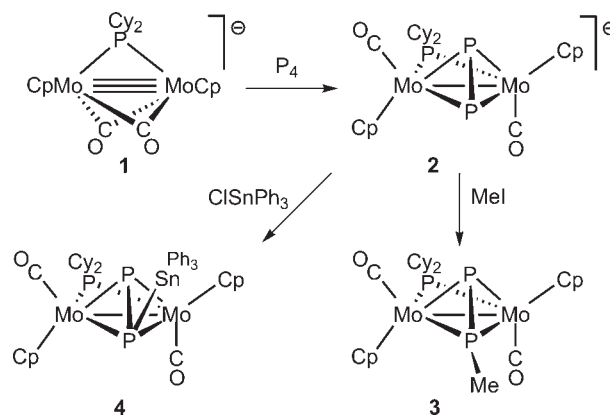
More recently, some reactions with group 11 metal(I) halides and cations have revealed the ability of the  $\mu\text{-}\kappa^2\text{:}\kappa^2\text{-P}_2$  ligands to incorporate metal-based electrophiles also between the P atoms (Scheme 1), therefore allowing for the synthesis of novel polymeric structures and molecular assemblies.<sup>7</sup> This alternative binding mode is actually reminiscent of the addition of the bare  $\text{H}^+$  and  $\text{Li}^+$  cations to the  $\text{P}_4$  molecule, a reaction computed to take place preferentially at a P–P edge rather than at a P vertex.<sup>8</sup>

Here we report that the triply bonded anion  $[\text{Mo}_2\text{Cp}_2(\mu\text{-PCy}_2)(\mu\text{-CO})_2]^-$  (**1**;  $\text{Li}^+$  salt,  $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ),<sup>9</sup> an unsaturated complex quite reactive toward many different electrophiles based on either p- or d-block elements,<sup>9,10</sup> is able to activate the  $\text{P}_4$  molecule under mild conditions to give  $[\text{Mo}_2\text{Cp}_2(\mu\text{-PCy}_2)(\text{CO})_2(\mu\text{-}\kappa^2\text{:}\kappa^2\text{-P}_2)]^-$  (**2**), the first anionic diphosphorus complex to be reported.<sup>11</sup> The reaction of **2** toward simple electrophiles such as  $\text{MeI}$  and  $\text{ClSnPh}_3$  (Scheme 2) not only allows for the synthesis of complexes having novel coordina-

Scheme 1



Scheme 2

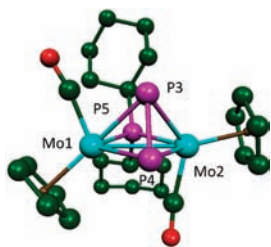


tion modes of diphosphorus ligands but also unveils that the  $\text{P}_2$  ligand in **2** displays a unique donor behavior: in addition to the traditional lone-pair-derived basicity of the P atoms, there is another donor ability originating from the presence in the anion of high-energy bonding orbitals with both  $\sigma(\text{Mo-P})$  and  $\pi(\text{P-P})$  character [according to density functional theory (DFT) calculations], leading to binding of the electrophile also in a terminal way but now at nearly right angles with respect to the P–P edge. To our knowledge, this is an unprecedented behavior for either  $\text{P}_4$  itself or any metal complex having a  $\text{M}_2\text{P}_2$  tetrahedral core.

Tetrahydrofuran solutions of **2** ( $\text{Li}^+$  salt) were readily prepared by stirring a solution of the anion **1** with 1 equiv of  $\text{P}_4$  at 290 K. According to DFT calculations (Figure 1 and the Supporting Information), the anion displays a  $\text{Mo}_2\text{P}_2$  tetrahedral core, with the  $\text{P}_2$  ligand symmetrically bridging the metal atoms. The  $\text{PCy}_2$  ligand is placed almost in the plane defined by one of the  $\text{Mo}_2\text{P}$  triangles, and the coordination sphere of the metals is completed by

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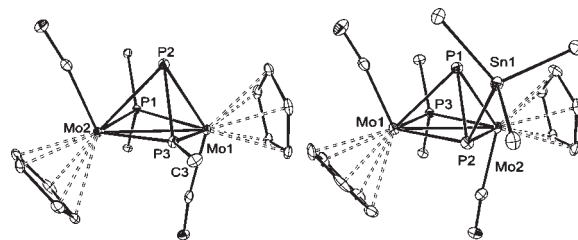


**Figure 1.** DFT-optimized structure of **2**. Select bond lengths Mo1–Mo2 = 3.025 Å, P3–P4 = 2.095 Å, Mo1–P3 = 2.565 Å, Mo2–P3 = 2.528 Å, Mo1–P4 = 2.572 Å, Mo2–P4 = 2.573 Å.

Cp and CO ligands arranged in a slightly distorted transoid arrangement because of the proximity of the “axial” P3 atom. The computed P–P length of 2.095 Å is comparable to the value of 2.079(2) Å measured in the neutral complex  $[\text{Mo}_2\text{Cp}_2(\text{CO})_4(\mu\text{-}\kappa^2\text{:}\kappa^2\text{-P}_2)]^5$  and is significantly shorter than the experimental value of 2.21 Å and is significantly shorter than the experimental value of 2.21 Å for the P<sub>4</sub> molecule. This might suggest the presence of some  $\pi(\text{P}-\text{P})$  bonding character in that bond (see below). The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **2** at 298 K displays only a very broad resonance at –166.4 ppm for the P<sub>2</sub> ligand. Upon cooling to 163 K, this resonance splits into two broad resonances at –80.0 and –273.0 ppm, in agreement with the chemical inequivalence of the P atoms. The above observations are also indicative of the occurrence of a fluxional process for **2** in solution, probably consisting of libration of the P<sub>2</sub> unit around the Mo–Mo axis, so as to exchange their chemical environments. Yet, the IR spectrum of **2** indicates that the situation in solution is even more complex because it exhibits four C–O stretching bands, thus revealing the presence of more than a single species in solution, rapidly exchanging on the NMR time scale. This is likely due to the presence of strong ion pairs in fast equilibrium with the solvent-separated ions,<sup>9b</sup> a matter under current study.

The anion **2** reacts rapidly with MeI at 290 K to give the diphosphenyl complex  $[\text{Mo}_2\text{Cp}_2(\mu\text{-PCy}_2)(\text{CO})_2(\mu\text{-}\kappa^2\text{:}\kappa^2\text{-P}_2\text{-Me})]$  (**3**). The structure of **3** (Figure 2) is related to that of **2** after the addition of a Me<sup>+</sup> group to the lone electron pair of the “basal” P4 atom. The resulting position is closer to the Mo<sub>2</sub>P plane than anticipated (the Mo<sub>2</sub>PC torsion angle is 173.3°), yet the P2–P3–C3 angle of 122.8(1)° is only somewhat smaller than those for the diphosphene complex  $[\text{Fe}_2(\text{CO})_6(\mu\text{-}\kappa^2\text{:}\kappa^2\text{-P}_2^t\text{Bu}_2)]$  (average P<sub>2</sub>C angle of ca. 131°),<sup>12</sup> and the P–P length remains short [2.085(1) Å]. We note, however, the significant contraction of the corresponding P–Mo lengths (ca. 2.41 Å), while the “axial” P atom remains essentially unperturbed (Mo–P of ca. 2.53 Å).

The spectroscopic data in solution for **3** suggest the retention of the structure found in the solid state. Thus, the P<sub>2</sub>Me ligand gives rise to separated  $^{31}\text{P}$  NMR resonances at –84.3 (PMe) and –293.2 (P) ppm with a large mutual coupling of 503 Hz, a value very close to the figures usually found for either free or  $\kappa^1$ -bound diphosphene complexes,<sup>13</sup> therefore suggestive of the presence of significant  $\pi(\text{P}-\text{P})$  bonding character in the P–P bond, as was also suggested for **2**. We should remark that compound **3** seems to be the first example of a  $\mu\text{-}\kappa^2\text{:}\kappa^2$ -diphosphenyl complex. The closest precedent in the literature is the triiron complex  $[\text{Fe}_3\text{Cp}^*(\mu\text{-}\kappa^2\text{:}\kappa^3\text{-P}_2^t\text{Bu})(\text{CO})_8]$ ,<sup>14</sup> a molecule presumed to display also a tetrahedral M<sub>2</sub>P<sub>2</sub> core. Instead, the most common coordination modes of diphosphenyl ligands are those involving terminal coordination of phosphorus ( $\kappa^1$  or  $\mu\text{-}\kappa^1\text{:}\kappa^1$  modes).<sup>13</sup> Further work on the reactions of **2** with



**Figure 2.** ORTEP diagram (30% probability) of compounds **3** (left) and **4** (right), with H atoms and Cy and Ph rings (except C1 atoms) omitted for clarity. Select bond lengths (Å) and angles (deg): compound **3**, Mo1–Mo2 = 3.0172(4), Mo1–P2 = 2.521(1), Mo1–P3 = 2.399(1), P2–P3 = 2.085(1), P2–P3–C3 = 122.8(1); compound **4**, Mo1–Mo2 = 2.9860(7), Mo2–P1 = 2.420(2), Mo2–P2 = 2.498(2), P1–P2 = 2.201(2), P2–Sn1 = 2.533(2), P1–P2–Sn1 = 80.3(1).

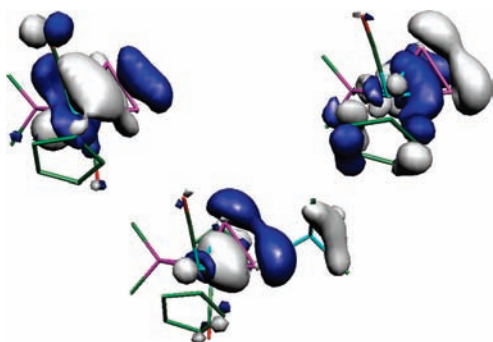
other C-based and related electrophiles is underway to establish the potential of these reactions to obtain novel organophosphorus ligands.

The reaction of **2** with  $\text{ClSnPh}_3$  also proceeds rapidly at 290 K, now to give the stannyl compound  $[\text{Mo}_2\text{Cp}_2(\mu\text{-PCy}_2)(\text{CO})_2(\mu\text{-}\kappa^2\text{:}\kappa^2\text{-P}_2(\text{SnPh}_3))]^6$  (**4**). Its solid-state structure (Figure 2) is analogous to that of **3**, except for the unexpected and unprecedented positioning of the SnPh<sub>3</sub> electrophile, now defining a P–P–Sn angle of only 80.3(1)°. Other significant differences are as follows: (a) the basal Mo–P lengths of ca. 2.49 Å are now longer than the axial Mo–P lengths of ca. 2.43 Å and (b) the P–P distance [2.201(2) Å] is significantly elongated, compared to those in **2** and **3**, and now approaches a single-bond value.

The NMR spectra for **4**, however, reveal the presence of two isomers and dynamic effects in solution. Thus, the  $^{31}\text{P}$  NMR spectrum at 293 K exhibits just a broad resonance at –148.0 ppm for the P<sub>2</sub> group. Upon lowering of the temperature, this resonance further broadens and eventually splits into two broad doublets, with these appearing at +38.8 and –341.4 ppm with a low  $^1\text{J}(\text{P}-\text{P})$  coupling of 185 Hz at 178 K, corresponding to the major isomer, presumably the one present in the crystal. A minor isomer (ca. 10% abundance) is also detected at that temperature, with this one displaying P<sub>2</sub> resonances at –92.5 and –239.6 ppm, now with a high mutual P–P coupling of 475 Hz, comparable to that observed for **3**, and therefore suggesting that this minor isomer might be structurally related to **3**, a matter to be addressed through further research.

DFT calculations on **3** and **4** gave optimized geometries in good agreement with the experimental structures (see the Supporting Information), although the P–P–Sn angle in **4** was computed to be 95.0°, somewhat above the experimental value, but still far from the ca. 121° computed for the P–P–C angle in **3**. We also optimized the structure of the SnH<sub>3</sub> analogue of **4**, and this yielded an even shorter P–P–Sn angle of 89.2°, thus ruling out steric or crystal lattice effects behind the anomalous structure of the tin compounds. Instead, these structural differences can be attributed to the distinct electronic interactions taking place between **2** and the respective electrophiles (Figure 3).

Although there is a large orbital mixing in all cases, the formation of **3** can be understood as derived from interaction of the incoming electrophile with the HOMO–2 orbital in **2** (–1.60 eV), with this having a large lone-pair character of the basal P atom (see the Supporting Information), and therefore having little effect on the P–P bonding, in agreement with the



**Figure 3.** Select molecular orbital for compounds **2** (upper, from left to right, the HOMO-1 and HOMO-7 orbitals) and **4** (lower, HOMO-25), viewed along the Mo-Mo bond, with Cy and Ph rings omitted.

structural data. In contrast, the formation of **4** follows from interaction with the HOMO-1 (-1.17 eV) and HOMO-7 (-3.40 eV) orbitals in the anion (Figure 3), with these having significant  $\sigma(\text{Mo}-\text{P})$  and  $\pi(\text{P}-\text{P})$  bonding character. These orbitals give a good overlap with the acceptor orbital of the electrophile at P-P-Sn angles of ca.  $90^\circ$ , as is clearly appreciated from the shape of the orbital accounting for the P-Sn bond in **4** [HOMO-25, -8.60 eV; main atomic contributions, Mo1 (10%), Mo2 (8%), Sn (8%), P4 (13%), and P5 (20%)]. Thus, not only is the unusual positioning of the SnPh<sub>3</sub> group in **4** explained but also the substantial increase in the P-P length and the dramatic decrease in the P-P coupling operated at the P<sub>2</sub> ligand. These effects are reminiscent of those observed upon coordination of the double P=P bond of diphosphenes to metal fragments, except for the fact that in the case of **4** only one of the P atoms is involved. This enables us to speak of a novel and peculiar  $\pi$ -donor-like ability of the P<sub>2</sub> ligand in complexes with M<sub>2</sub>P<sub>2</sub> cores. For this interaction to be effective, it is necessary that some of the frontier orbitals have significant  $\pi(\text{P}-\text{P})$  bonding character, which in the case of **2** we attribute to its anionic nature. Indeed, a large electron density at the dimetal center should restrain the electron flow from the P<sub>2</sub> ligand to the dimetal fragment, thus contributing to the development of some multiplicity in the P-P bond. The presence of P-P bonding character (rather than lone-electron-pair character) in the frontier orbitals is not new in the chemistry of phosphorus: actually, the HOMO in P<sub>4</sub> is a  $\sigma(\text{P}-\text{P})$  bonding orbital,<sup>15</sup> and the HOMO in the diphosphene complex [AuCl( $\kappa^1$ -P<sub>2</sub>Me<sub>2</sub>)] is the  $\pi(\text{P}-\text{P})$  bonding orbital.<sup>16</sup> Initial experiments indicate that compounds analogous to **4** can be made upon the reaction of **2** with other metal compounds, and further work in that direction is now underway to establish the generality and chemical implications of the new binding ability of the P<sub>2</sub> ligand here uncovered.

In summary, we have reported the first example of an anionic complex having a  $\mu$ - $\kappa^2$ -P<sub>2</sub> ligand via mild activation of P<sub>4</sub>. The anion **2** displays a unique dual basicity involving the basal atom of the P<sub>2</sub> ligand because binding to the incoming electrophile can be accomplished using the nonbonding electron pair at phosphorus or using molecular orbitals having  $\sigma(\text{Mo}-\text{P})$  and  $\pi(\text{P}-\text{P})$  bonding character.

## ■ ASSOCIATED CONTENT

**S** **Supporting Information.** Experimental procedures and spectroscopic data for new compounds, details of DFT

calculations on compounds **2-4**, and CIF files for compounds **3** and **4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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