

Catalytic Synthesis of the P<sub>16</sub> Macrocyclic (C<sub>6</sub>H<sub>4</sub>P<sub>2</sub>)<sub>8</sub>

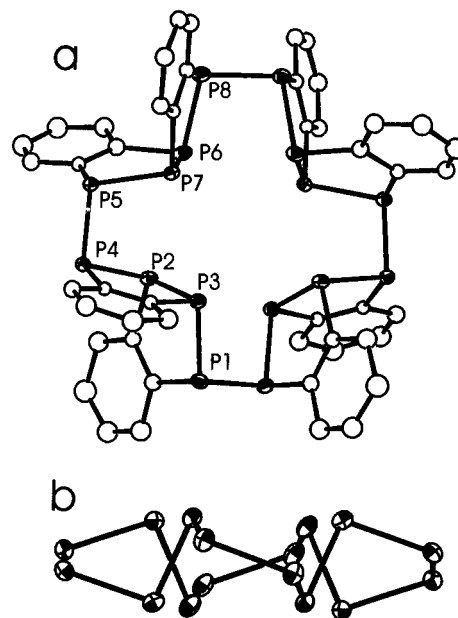
Nola Etkin, Maria C. Fermin, and Douglas W. Stephan\*

Department of Chemistry and Biochemistry  
University of Windsor  
Windsor, Ontario, Canada N9B 3P4

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Extension of the principles of organometallic chemistry to compounds containing transition metal–main group bonds offers a variety of new approaches to metal-mediated syntheses of main group derivatives.<sup>1</sup> We have demonstrated the utility of Zr–P complexes in stoichiometric syntheses of a variety of organophosphorus derivatives.<sup>2</sup> In addition, we have recently described the use of a Zr catalyst in the oligomerization of primary phosphines to organophosphanes (PR)<sub>5</sub> via dehydrocoupling reactions.<sup>3</sup> The development of this catalysis offers a new and facile synthetic route to novel organophosphanes. In targeting these systems, it is noteworthy that the structures of all known organophosphanes and related polyphosphorus anions are based on the propensity of phosphorus to form 3-, 4-, 5-, or 6-membered rings. In this paper, we describe the catalytic dehydro-oligomerization of 1,2-C<sub>6</sub>H<sub>4</sub>(PH<sub>2</sub>)<sub>2</sub> which affords the octamer (1,2-C<sub>6</sub>H<sub>4</sub>P<sub>2</sub>)<sub>8</sub> (**1**). This species contains an unprecedented 16-membered ring of contiguous P atoms. Information regarding intermediates in the formation of **1** is also presented.

Reaction of 20 equiv of 1,2-C<sub>6</sub>H<sub>4</sub>(PH<sub>2</sub>)<sub>2</sub> with the anionic Zr trihydride [Cp\*<sub>2</sub>ZrH<sub>3</sub>][K(THF)<sub>2</sub>]<sup>4</sup> in a THF/toluene mixture at 90 °C for 12 h results in the deposition of the colorless crystalline product **1** in 58% overall yield.<sup>5</sup> Although compound **1** is insoluble in THF, it is slightly soluble in chloroform exhibiting two broad resonances at 38.4 and –4.7 ppm in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum. The absence of one-bond P–H coupling in the <sup>31</sup>P NMR spectrum indicates the cleavage of all P–H bonds. X-ray crystallographic data for **1**<sup>6</sup> reveal that the asymmetric unit contains four (C<sub>6</sub>H<sub>4</sub>P<sub>2</sub>) fragments. These combine in an interleaving pairwise fashion to form a “bracket” or “skewed chair” fragment. This moiety contains two P environments, consistent with the NMR data. The central phosphorus atoms of each of the 5-membered rings forms P–P bonds with the two phosphorus atoms of the neighboring (C<sub>6</sub>H<sub>4</sub>P<sub>2</sub>) fragment resulting in adjoining C<sub>6</sub>H<sub>4</sub>P<sub>3</sub> fragments. The angles between these C<sub>6</sub>H<sub>4</sub>P<sub>3</sub> planes in each “bracket” ranges from 107 to 110°. The two outer phosphorus atoms of these dimeric fragments form P–P bonds to adjacent units. This



**Figure 1.** (a) ORTEP drawing of the molecule **1** with 30% thermal ellipsoids shown. Hydrogen atoms are omitted for clarity. (b) View of the P<sub>16</sub> core of **1** showing the “double-crown” geometry.

results in angles between adjacent phenyl ring planes within the linked “brackets” of 21.91°. Two linked dimeric units constitute the asymmetric unit while the combination of four such dimers affords the 2-fold symmetric, macrocyclic molecule **1**. While metric parameters of **1** are typical of organophosphorus species, the central 16-membered ring of contiguous P–P bonds is unprecedented.<sup>7</sup> The geometry of the central phosphorus atom core of **1** (Figure 1b) is reminiscent of a crown ether. Each of the phosphorus atoms of **1** is a chiral center. Although the centrosymmetric nature of the space group requires a racemic compound, the arbitrary assignment of higher priority to P atoms with exocyclic P–P bond, reveals that the handedness of each of the 16 phosphorus atoms in individual molecules of **1** is the same. The lone pairs of electrons on the two sets of alternating central phosphorus atoms (P2, P3, P6', P7' and P2', P3', P6, P7) are oriented on either side of the macrocycle. The central cavity is roughly 5.10 Å in diameter as the transannular P–P distances range from 4.92 (P6–P3') to 5.29 Å (P7–P3'). This conformation of **1** can thus be described as a “double crown” offering the potential of two sites for metal complexation. Furthermore, examination of the packing of **1** in the solid state reveals that the central cavities of the P<sub>16</sub> macrocyclic rings are aligned so as to generate channels through the crystal. These structural features suggest the potential for metal atom complexation and/or intercalation, aspects that are under current investigation.

In efforts to understand the process of formation of **1**, a catalyst/phosphine mixture was heated only for a short time (30 min). Extraction of the organophosphorus product into hexane resulted in the isolation of the dimeric organophosphane species (C<sub>6</sub>H<sub>4</sub>(PPH))<sub>2</sub> (**2**).<sup>5</sup> The <sup>31</sup>P NMR of **2** shows doublets of doublets at –0.98 and –44.0 ppm. The presence of hydrogen atoms on *exo* phosphorus atoms is consistent with the *J*<sub>PH</sub> coupling of 201 Hz to the upfield resonance, in agreement with the formulation. The isolation of **2** suggests that it is formed initially in the catalytic cycle, and it subsequently undergoes dehydrocoupling to afford the macrocyclic product **1**.

(7) (a) Baudler, M. *Angew. Chem.* **1982**, *94*, 520. (b) Baudler, M. *Angew. Chem.* **1987**, *99*, 429.

(1) *Inorganometallics*; Fehlner, T. P., Ed.; Plenum Press: New York, 1992.

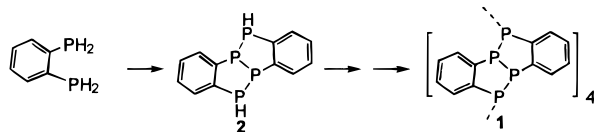
(2) (a) Breen, T. L.; Stephan, D. W. *J. Am. Chem. Soc.* **1995**, *117*, 12645. (b) Breen, T. L.; Stephan, D. W. *J. Am. Chem. Soc.* **1996**, *118*, 4204. (c) Breen, T. L.; Stephan, D. W. *Organometallics* **1996**, *15*, 4509. (d) Breen, T. L.; Stephan, D. W. *Organometallics* **1997**, *16*, 365.

(3) Fermin M. C.; Stephan, D. W. *J. Am. Chem. Soc.* **1995**, *117*, 12645.

(4) Stephan, D. W. U.S. Patent 08/571,294.

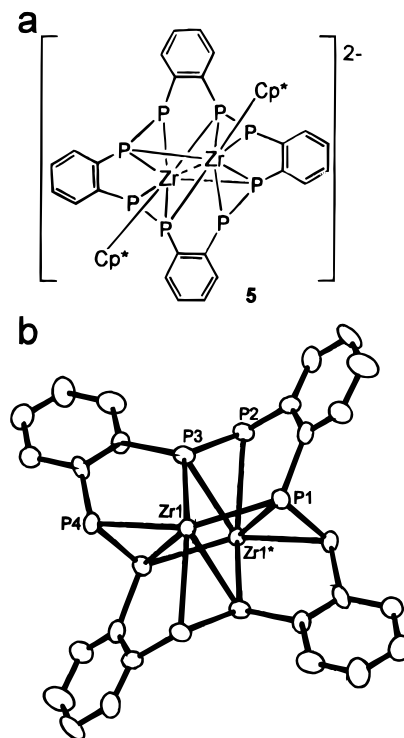
(5) Spectroscopic data For **1**: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C) 7.69 (8H), 7.43 (8H), 7.27 (8H), 7.21 (8H); <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 25 °C) 128.6 (*J*<sub>PC</sub> = 41, 38 Hz), 127.0, 125.3, 123.7 (*J*<sub>PC</sub> = 28 Hz); <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 25 °C) 38.4 (br, m), –4.7 (br, m). For **2**: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C) 7.57 (2H), 7.19 (2H), 6.76 (2H), 6.58 (2H), 4.67 (2H), (*J*<sub>PH</sub>) = 201 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C) 136.9 (*J*<sub>PC</sub> = 12 Hz), 136.4 (*J*<sub>PC</sub> = 38 Hz), 132.7, 130.3; <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C) –0.98 (d of d, *J*<sub>PP</sub> = 156 Hz, *J*<sub>PH</sub> = 70 Hz), –44.0 (d of d, *J*<sub>PP</sub> = 156, *J*<sub>PH</sub> = 70 Hz). For **3**: <sup>31</sup>P{<sup>1</sup>H} NMR (THF-*d*<sub>8</sub>, 25 °C) 39.6 (*J*<sub>PP</sub> = 127 Hz), 40.1 (*J*<sub>PP</sub> = 127 Hz). For **4**: <sup>31</sup>P{<sup>1</sup>H} NMR THF-*d*<sub>8</sub>, 25 °C) –4.1 (*J*<sub>PH</sub> = 181 Hz). For **5**: <sup>31</sup>P{<sup>1</sup>H} NMR (THF-*d*<sub>8</sub>, 25 °C) 327.4 (*J*<sub>PP</sub> = 510, 467 Hz), 257.4 (*J*<sub>PP</sub> = 510, 467 Hz). Elemental analyses data for **1** and **2** are deposited as Supporting Information.

(6) X-ray data For **1**: C<sub>2</sub>/c, *a* = 13.81(3) Å, *b* = 26.61(2) Å, *c* = 15.711–(8) Å, β = 105.16(6)°, *V* = 5571(9) Å<sup>3</sup>, *R* = 8.40%, *R*<sub>w</sub> = 8.00%. For **5**: P2<sub>1</sub>/n, *a* = 13.4790(6) Å, *b* = 12.6133(5) Å, *c* = 22.1297(10) Å, β = 93.319(1)°, *V* = 3756.1(2) Å<sup>3</sup>, *R* = 9.41%, *R*<sub>w</sub> = 11.10%.



The nature of the Zr intermediates proved to be more elusive. Stoichiometric reactions of 1,2-C<sub>6</sub>H<sub>4</sub>(PH<sub>2</sub>)<sub>2</sub> with [Cp\*<sub>2</sub>ZrH<sub>3</sub>]<sup>-</sup> were monitored via <sup>31</sup>P NMR spectroscopy. The initial species formed in the reaction of 1 equiv of 1,2-C<sub>6</sub>H<sub>4</sub>(PH<sub>2</sub>)<sub>2</sub> exhibits a doublet of doublets in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum at 39.6 and 40.1 ppm. In the presence of a second equivalent, a single doublet in the <sup>31</sup>P NMR spectrum is observed. While these signals were tentatively attributed to the chelate complex anions<sup>5</sup> (Cp\*<sub>2</sub>ZrH[(PH)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>])<sup>-</sup> (**3**) and (Cp\*<sub>2</sub>Zr[(PH)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>)<sup>-</sup> (**4**), respectively, neither of these two compounds could be isolated, despite repeated attempts. In the presence of excess phosphine a new species **5** is formed as evidenced by the two sets of doublet of doublets at 327 and 257 ppm in the <sup>31</sup>P NMR spectrum.<sup>5</sup> P–P couplings of 510 and 467 Hz are seen, while no P–H coupling is evident. While **5** appeared to be the only P-containing species in solution, <sup>1</sup>H NMR indicated a complex mixture of Cp\*<sub>2</sub>Zr species. Consequently, attempts to isolate **5** in bulk were also unsuccessful. Nonetheless, on standing for several days, two or three extremely small crystals of **5** were obtained. The structure of **5** was elucidated by X-ray crystallographic methods.<sup>6</sup> Compound **5** is comprised of a dimeric Zr dianion (Figure 2) and two K counterions. The Zr···Zr distance in the dianion is 3.300(3) Å, and each Zr atom is coordinated to a pentamethylcyclopentadienyl ligand as well as six P atoms. Four 1,2-C<sub>6</sub>H<sub>4</sub>P<sub>2</sub> are linked in a macrocyclic array about the two Zr atoms. Alternating P atoms bridge the two Zr atoms with the Zr–P bridging distance ranging from 2.681(5) to 2.827(5) Å. The remaining four P atoms form terminal Zr–P bonds, two on each Zr. The average terminal Zr–P distance is 2.712(5) Å. The K counterion is coordinated to three THF molecules while the closest approach to the cation to the Zr<sub>2</sub> anion is K1–P4 at distance of 3.335(6) Å. The characterization of **5** suggest the possibility that a monocyclopentadienyl-zirconium species, perhaps structurally related to **5**, mediates the formation of **1**. This is further supported by the observation that heating of solutions containing excess diphosphine and **5** results in formation of **1** and consumption of **5**. Nonetheless, precise mechanistic details remain the subject of continuing study.

In conclusion, the present results establish a Zr-catalyzed synthesis of the unique organophosphorus oligomer **1**. While



**Figure 2.** (a) Line drawing of the dianion of **5**. (b) ORTEP drawing of the dianion **5** with 30% thermal ellipsoids shown. Cp\* ligands and hydrogen atoms are omitted for clarity.

**1** contains the unprecedented structural feature of a contiguous P<sub>16</sub> ring, the synthesis of **1** suggests catalytic dehydrocoupling offers considerable potential for new materials. Studies designed to exploit this potential and illuminate mechanistic details are in progress.

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**Supporting Information Available:** Spectroscopic data and tables of crystallographic parameters, hydrogen atom parameters, and thermal parameters for **1** and **5** (13 pages). See any current masthead page for ordering and Internet access instructions.

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