

## Main-Group Chemistry

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# Synthesis and Reactivity of a Cyclooctatetraene-Like Polyphosphorus Ligand Complex [Cyclo-P<sub>8</sub>]

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Dedicated to Professor Klaus Jurkschat on the occasion of his 70<sup>th</sup> birthday

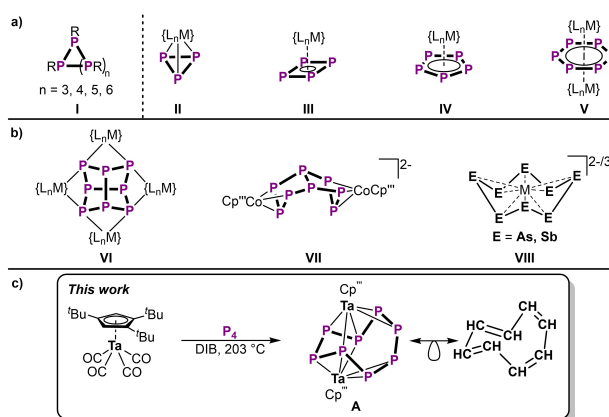
**Abstract:** The thermolysis of Cp<sup>'''</sup>Ta(CO)<sub>4</sub> with white phosphorus (P<sub>4</sub>) gives access to [(Cp<sup>'''</sup>Ta)<sub>2</sub>(μ<sub>4</sub>η<sup>2:2:2:2:2:2:1:1:1</sup>-P<sub>8</sub>)] (**A**), representing the first complex containing a cyclooctatetraene-like (COT) *cyclo*-P<sub>8</sub> ligand. While ring sizes of *n* > 6 have remained elusive for *cyclo*-P<sub>*n*</sub> structural motifs, the choice of the transition metal, co-ligand and reaction conditions allowed the isolation of **A**. Reactivity investigations reveal its versatile coordination behaviour as well as its redox properties. Oxidation leads to dimerization to afford [(Cp<sup>'''</sup>Ta)<sub>4</sub>(μ<sub>4</sub>η<sup>2:2:2:2:2:2:2:2:1:1:1:1:1:1</sup>-P<sub>16</sub>)](TEF)<sub>2</sub> (**4**, TEF = [Al(OC(CF<sub>3</sub>)<sub>3</sub>)<sub>4</sub>]<sup>-</sup>). Reduction, however, leads to the fission of one P–P bond in **A** followed by rapid dimerization to form [K@[2.2.2]cryptand]<sub>2</sub>[(Cp<sup>'''</sup>Ta)<sub>4</sub>(μ<sub>4</sub>η<sup>2:2:2:2:2:2:2:2:1:1:1:1:1</sup>-P<sub>16</sub>)] (**5**), which features an unprecedented chain-type P<sub>16</sub> ligand. Lastly, **A** serves as a P<sub>2</sub> synthon, via ring contraction to the triple-decker complex [(Cp<sup>'''</sup>Ta)<sub>2</sub>(μ<sub>4</sub>η<sup>6:6</sup>-P<sub>6</sub>)] (**B**).

Carbocyclic compounds are of tremendous importance as e.g. in organic drug-like molecules or ligands in transition metal catalysts. Closely related cyclic oligo-phosphorus compounds, although synthetically more challenging, have also gained considerable attention over the past decades.<sup>[1]</sup> This development was initiated by the fundamental interest in the close relationship (diagonal relationship, isolobality

between P and CH)<sup>[2]</sup> of oligo-phosphorus compounds with carbon-based species. In addition, the field of white phosphorus (P<sub>4</sub>) activation has been growing significantly in recent years and has thus raised additional interest in these compounds from an application-oriented perspective.<sup>[3]</sup>

Simple organically substituted cyclic oligo-phosphines (RP)<sub>*n*</sub> (**I**, Scheme 1a) were already prepared as early as 1877.<sup>[4]</sup> Since then, development of various synthetic protocols has yielded (RP)<sub>*n*</sub> compounds (*n* = 3–6), in which the sterics of R govern the overall ring size.<sup>[1a–c,5]</sup> Notably, however, the ring size of *n* = 6 could not be exceeded and larger organo-polyphosphines, such as 'Bu<sub>6</sub>P<sub>8</sub>, form bicyclic systems.<sup>[6]</sup>

Besides organic substitution, oligo-phosphorus species can also be stabilized via coordination to transition metals. Very prominently, the Figueroa group recently was able to stabilize the elusive P<sub>2</sub> at a mononuclear iron center.<sup>[7]</sup> Besides, several completely unsubstituted cyclic P<sub>*n*</sub> ligands (*n* = 3–6), could be stabilized within the coordination sphere of transition metals (Scheme 1a). While *cyclo*-P<sub>*n*</sub> (*n* = 3–5) ligands can be obtained within sandwich type complexes (**II**,<sup>[8]</sup> **III**,<sup>[9]</sup> **IV**<sup>[10]</sup>), *cyclo*-P<sub>6</sub> (**V**)<sup>[11]</sup> could this far only be obtained within triple-decker complexes. Even though complexes with far larger oligo-phosphorus moieties (up to



**Scheme 1.** a) Known *cyclo*-(PR)<sub>*n*</sub> (**I**, R = alkyl or aryl) and *cyclo*-P<sub>*n*</sub> structural motifs for *n* = 3–6 (**II–V**), b) selected P<sub>8</sub> species (**VI–VIII**, {L<sub>*n*</sub>M} = {Cp<sup>\*</sup>Sm}, {(<sup>dmp</sup>nacnac)Fe} (<sup>dmp</sup>nacnac = [{N(C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-2,6)C(Me)<sub>2</sub>CH}]<sup>-</sup>), {(1,1'-Fc(NSi<sup>t</sup>BuMe<sub>2</sub>)<sub>2</sub>Sc)} and crown-shaped *cyclo*-E<sub>8</sub><sup>3-</sup>-containing compounds (**VIII**, E = As, Sb, M = Cr, Mo, Nb, Ta), c) synthesis of [(Cp<sup>'''</sup>Ta)<sub>2</sub>(μ<sub>4</sub>η<sup>6:6</sup>-P<sub>6</sub>)] (**A**).

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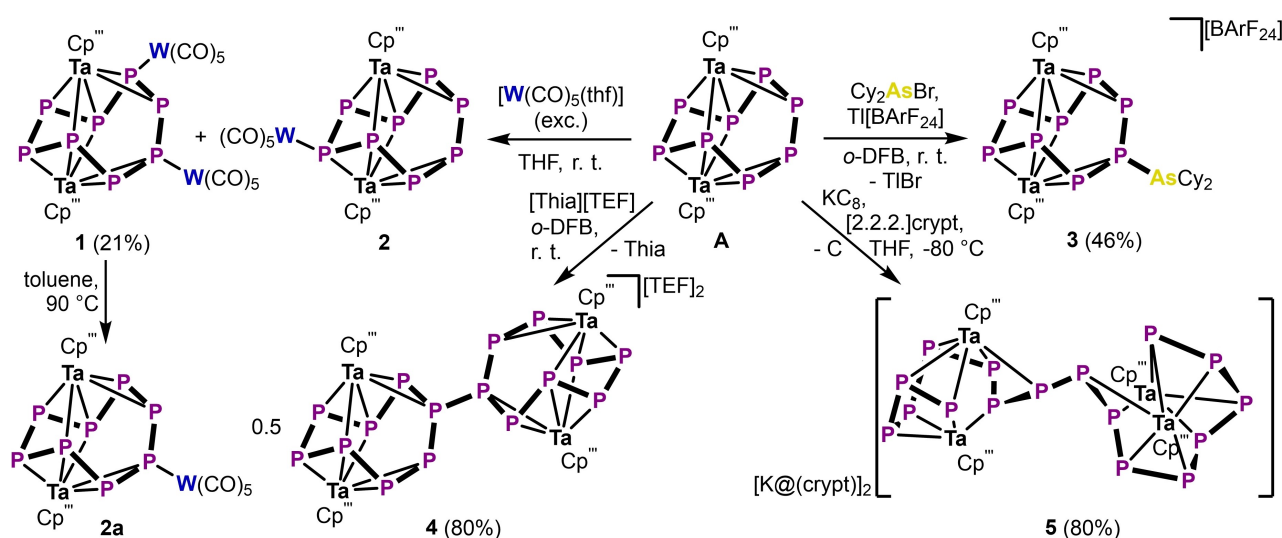
24 P-atoms) are known, such species unexceptionally feature aggregated polycyclic structural motifs.<sup>[12]</sup> Thus, monocyclic all-phosphorus species with more than six ring atoms are unknown to date. These facts raised the question whether compounds featuring larger all-phosphorus rings are accessible and how such species can be stabilized. Such compounds would be optimal starting materials on the way towards extended oligo-phosphorus frameworks. Additionally, their large ring size could allow for their use as transfer reagents of smaller  $P_n$  units under ring contraction. While the isolobal relationship of *cyclo*- $P_8$  to cyclooctatetraene (COT) renders its coordinative stabilization viable, known  $P_8$  ligand complexes feature polycyclic arrangements,<sup>[13]</sup> as e.g. the cunean type (**VI**)<sup>[14]</sup> or related (**VII**)<sup>[15]</sup> structures (Scheme 1b). While highly ionic crown-shaped *cyclo*- $E_8^{8-}$  structural motifs (**VIII**)<sup>[16]</sup> could be obtained for the heavier congeners arsenic and antimony, their transfer to phosphorus has not yet been possible. However, a neutral *cyclo*- $As_8$  ligand could be stabilized within a niobium complex,<sup>[17]</sup> which provides a good starting point for investigations to realize a group 5 *cyclo*- $P_8$  ligand complex.

Herein the synthesis and isolation of a tantalum complex are presented featuring an unprecedented COT-like *cyclo*- $P_8$  ligand, which notably is the largest cyclic all-phosphorus species known to date. Moreover, the reactivity of this exotic compound demonstrates its versatility as building block for large entities in phosphorus chemistry and as a  $P_2$  source by ring contraction reactions.

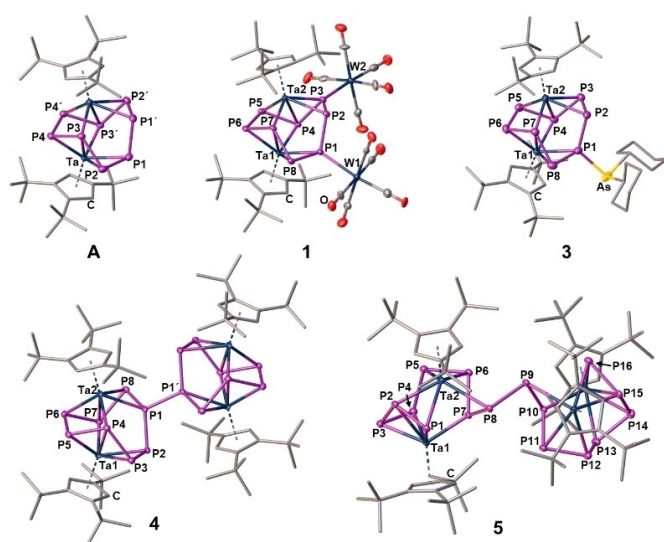
Careful choice of the metal, the  $Cp^R$  ligand and the reaction conditions enabled the synthesis of  $[(Cp^R Ta)_2(\mu_4, \eta^{2:2:2:2:1:1:1:1}-P_8)]$  (**A**,  $Cp^R = 1,2,4-tBu_3C_5H_2$ ) via co-thermolysis of  $P_4$  with  $Cp^R Ta(CO)_4$  in boiling 1,3-diisopropylbenzene (Scheme 1c). After chromatographic separation (see Supporting Information) from the byproducts,  $[(Cp^R Ta)_2(\mu_4, \eta^{6:6:6:6}-P_8)]$  (**B**, 20%) and  $[(Cp^R Ta)_3(\mu_3, \eta^{1:1:1:1:1:1}-P_4)(\mu_3, \eta^{1:1:1}-P_2)]$  (**C**, 7%), **A** was isolated as a dark red solid in 41% yield. Assessing the *cyclo*- $P_8$  ligand's potential for coordination chemistry, it was reacted with excess  $[W(CO)_5-$

(thf)] (Scheme 2). The major product of this reaction is the tetranuclear  $[(Cp^R Ta)_2(\mu_4, \eta^{2:2:2:2:1:1:1:1}-P_8)\{W(CO)_5\}_2]$  (**1**). However, the chromatographic separation of **1** from the trinuclear side product  $[(Cp^R Ta)_2(\mu_3, \eta^{2:2:2:2:1:1:1:1}-P_8)\{4-W(CO)_5\}]$  (**2**), which decomposes during workup, is difficult and results in rather low isolated yields of 21%. Interestingly, thermolysis of **1** affords cleavage of only one  $\{W(CO)_5\}$  fragment, and formation of  $[(Cp^R Ta)_2(\mu_3, \eta^{2:2:2:2:1:1:1:1}-P_8)\{1-W(CO)_5\}]$  (**2a**), which can be followed spectroscopically. These results suggested that the selective functionalization of **A** could also be achieved with Lewis-acidic cationic main group electrophiles. Indeed, **A** reacts with the *in situ* generated  $[Cy_2As]^+$  to form  $[(Cp^R Ta)_2(\mu_4, \eta^{2:2:2:2:1:1:1:1}-P_8)(1-AsCy_2)][BARF_{24}]$  (**3**,  $[BARF_{24}]^- = [B(3,5-(CF_3)_2C_6H_3)_4]^-$ ) in 46% crystalline yield. As redox-mediated aggregation has been observed for smaller  $P_n$  ligand complexes,<sup>[15,18]</sup> utilization of **A** would allow the preparation of extended polyphosphorus structures. Chemical oxidation of **A** affords the dimeric  $[(Cp^R Ta)_4(\mu_4, \eta^{2:2:2:2:2:2:2:2:1:1:1:1:1:1}-P_{16})][TEF]_2$  (**4**, 80%),  $[TEF]^- = [Al\{OC(CF_3)_3\}_4]^-$  which shows a newly formed P1–P1' bond. Notably, **4** displays the largest cationic polyphosphorus arrangement known to date. On the other hand, the reduction of **A** with  $KC_8$  also results in dimerization, furnishing  $[K@[2.2.2]cryptand]_2-[(Cp^R Ta)_4(\mu_4, \eta^{2:2:2:2:2:2:2:2:1:1:1:1:1:1}-P_{16})]$  (**5**, 80%, Scheme 2). **5**, however, reveals a bond formation via the more encumbered P4–P4' atoms, accompanied by the cleavage of the former P4–P4' bond within **A**. Thus, **5** features an unprecedented  $P_{16}$  chain, which is solely stabilized by the coordination to the  $\{Cp^R Ta\}$  moieties.

Crystallization of **A**, **1**, **3**, **4** and **5** allowed their X-ray crystallographic structure determination (Figure 1).<sup>[19]</sup> The central structural motif of **A** is a puckered *cyclo*- $P_8$  ligand coordinated by the two Ta atoms. The P–P bond lengths within the  $P_8$  cycle are roughly alternating in length (P1–P1' = 2.243(1) Å, P1–P2 = 2.145(1) Å, P2–P3 = 2.196(1) Å, P3–P4 = 2.170(1) Å, P4–P4' = 2.444(2) Å), reminiscent of the isolobal relationship to COT. Thus, the more



**Scheme 2.** Reactivity of **A** towards the Lewis acid  $[W(CO)_5(thf)]$ , its electrophilic functionalization with  $[AsCy_2]^+$ , and its redox chemistry.



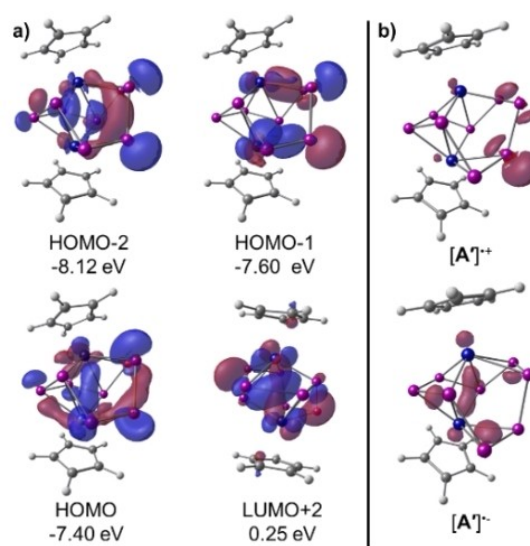
**Figure 1.** Molecular structures of **A**, **1**, **3**, **4** and **5** in the solid state. H atoms and counterions are omitted for clarity and ellipsoids are drawn at the 50% probability level.

coordinated P1–P2 and P3–P4 bonds are closer to the expected bond lengths for a P–P double bond than the residual P–P single bonds. The newly formed P–W bonds in **1** are in the expected range (2.510(2)–2.570(2) Å),<sup>[20]</sup> while the structural core remains intact upon coordination of the {W(CO)<sub>5</sub>} moieties. Similarly, the arsenium functionalization in **3** has only a minor impact on the structure of the *cyclo*-P<sub>8</sub> ligand with the newly formed P1–As bond length (2.301(4) Å) agreeing with a single bond.<sup>[20]</sup> The oxidized species **4** features a large bicyclic P<sub>16</sub> ligand, comprising two *cyclo*-P<sub>8</sub> moieties linked via a central P–P single bond (2.201(2) Å).<sup>[20]</sup> The P1–P2 bond in **4** is shortened (2.178(1) Å), while the residual P–P bonds remain similar in length upon oxidation. In contrast, the dianion in **5** also arises from the dimerization of **A**, however, the new P8–P9 bond (2.269(1) Å) is formed via the former P4 (in **A**) atoms. Additionally, the P1–P8 (3.222(1) Å) as well as the P9–P16 (3.263(2) Å) distances indicate complete P–P bond fission, thus leading to an unsubstituted P<sub>16</sub> chain. Notably, while long chain-type polyphosphides have been described,<sup>[21]</sup> the P<sub>16</sub> ligand in **5** is by far the longest linear polyphosphorus chain known to date.

Multinuclear NMR studies of **A** in CD<sub>2</sub>Cl<sub>2</sub> reveal the preservation of its C<sub>2</sub> symmetry in solution. Moreover, the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **A** features an AA'MM'QQ'XX' spin system for the symmetrical *cyclo*-P<sub>8</sub> ligand. In contrast, this symmetry is revoked within the {W(CO)<sub>5</sub>} coordinated species **1**, **2a** and **2**. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **1** reveals the presence of two species in solution at –80 °C which, however, coalesce at room temperature (see Supporting Information). As both species feature similar ABMNOQX spin systems, this behavior is attributed to rotationally hindered Cp''' ligands consistent with the presence of two diastereomers (see Supporting Information), which are in rapid exchange at room temperature. Additional <sup>1</sup>J<sub>P,W</sub> coupling for P<sub>A</sub> and P<sub>X</sub> corroborates the structural integrity

of **1** in solution. Similarly, the <sup>31</sup>P{<sup>1</sup>H} NMR spectra of **2a** and **2** show complex ACGMNSTX and AMNQRSTU spin systems, respectively, yet with only one <sup>1</sup>J<sub>P,W</sub> coupling each. This allows the determination of **2a** as the respective 1-{W(CO)<sub>5</sub>} and **2** as the 4-{W(CO)<sub>5</sub>} isomer. Analogously, the arsenium functionalization in **3** leads to an AMNOPQRX spin system in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum, bearing the {AsCy<sub>2</sub>} substituent at P<sub>M</sub>. The much larger dicationic complex **4** reveals broad and overlapping signals in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum as well as a set of signals consistent with rotationally fixed Cp''' ligands in the <sup>1</sup>H NMR spectrum. This is in line with a rapid exchange between two diastereomers formed by rotationally hindered Cp''' ligands as in **1** (see Supporting Information). However, this exchange process cannot be resolved for **4**, not even at low temperatures (–80 °C, see Supporting Information). In contrast, **5** rapidly decomposes upon dissolution in common solvents, hampering its spectroscopic characterization. However, the combustion analysis of crystalline **5** confirms its composition.

To obtain insight into the electronic structure and reactivity of **A**, DFT calculations on the model system [(CpTa)<sub>2</sub>(μ,η<sup>2:2:2:2:1:1</sup>-P<sub>8</sub>)] (**A'**) were performed (see Supporting Information). The WBIs for the P–P bonds in **A'** (0.85–1.06) corroborate its formulation as a *cyclo*-P<sub>8</sub> ligand complex, with only the P4–P4' bond exhibiting slightly lower values (0.51). The HOMOs of **A'** demonstrate a strong p(P1/1') contribution (Figure 2a), explaining the reactivity of **A** towards Lewis acids and cationic electrophiles. On the other hand, the P4–P4' character of the LUMO + 2 of **A'** as well as the calculated spin density for the initial reduction product [**A'**]<sup>–</sup> (Figure 2, right) reveal a tendency for the cleavage of the latter bond. Thus, both the oxidation and the reduction of **A'** lead to a dimerization via P–P bond formation involving P1 or P4, and the newly formed P–P bonds



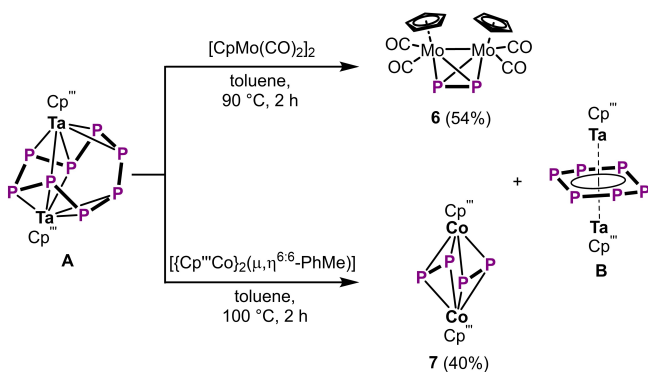
**Figure 2.** a) Molecular frontier orbitals of **A'**; b) Spin densities of [**A'**]<sup>•+</sup> and [**A'**]<sup>•–</sup>; calculated at the ωB97X-D3/def2-TZVP level of theory, surfaces are drawn at isovalues of 0.005 (MOs) and 0.008 (spin densities).



showing WBIs of 0.86 and 0.94, respectively. However, the comparably low calculated bond dissociation energy for **5** ( $\Delta G = -74.55 \text{ kJ mol}^{-1}$ , see Supporting Information) corroborates its labile character.

Moreover, the large *cyclo*-P<sub>8</sub> ligand in **A** was hypothesized to potentially serve as a source of an extremely reactive P<sub>2</sub> unit via ring contraction to **B**. Although P<sub>2</sub> is a highly versatile building block in organophosphorus chemistry, only a handful of compounds are known to liberate molecular P<sub>2</sub> under certain conditions,<sup>[22]</sup> while remaining stable enough to be stored. Indeed, the mild thermolysis of **A** with [CpMo(CO)<sub>2</sub>]<sub>2</sub><sup>[23]</sup> or [[Cp<sup>'''</sup>Co]<sub>2</sub>(μ,η<sup>6:6</sup>-PhMe)]<sup>[24]</sup> proceeds rapidly affording [[CpMo(CO)<sub>2</sub>]<sub>2</sub>(μ,η<sup>2:2</sup>-P<sub>2</sub>)]<sup>[8a]</sup> (**6**, 54 % by NMR)<sup>[25]</sup> or [[Cp<sup>'''</sup>Co]<sub>2</sub>(μ,η<sup>2:2</sup>-P<sub>2</sub>)]<sup>[12c]</sup> (**7**, 40 % by NMR), respectively (Scheme 3). Accordingly, the formation of **B** is observed spectroscopically, indicating the clean release of P<sub>2</sub> from **A**.

In summary, the synthesis and characterization of [[Cp<sup>'''</sup>Ta]<sub>2</sub>(μ,η<sup>2:2:2:2:1:1</sup>-P<sub>8</sub>)] (**A**) is reported. **A** is the first compound featuring a *cyclo*-P<sub>8</sub> ligand, which is the largest monocyclic polyphosphorus species known to date revealing a COT-like arrangement and bonding character. Reaction of **A** with [W(CO)<sub>5</sub>(thf)] combined with computational studies discloses the energetically most accessible P-centered lone pairs. These findings allowed the selective electrophilic functionalization of **A** yielding [[Cp<sup>'''</sup>Ta]<sub>2</sub>(μ,η<sup>2:2:2:2:1:1</sup>-P<sub>8</sub>(1-AsCy<sub>2</sub>))][BArF<sub>24</sub>] (**3**). Exploiting the redox reactivity of **A** allowed the isolation of dicationic [[Cp<sup>'''</sup>Ta]<sub>4</sub>(μ<sub>4</sub>,η<sup>2:2:2:2:2:2:2:2:1:1:1:1</sup>-P<sub>16</sub>)] [TEF]<sub>2</sub> (**4**) as well as dianionic [K@ [2.2.2]cryptand]<sub>2</sub> [[Cp<sup>'''</sup>Ta]<sub>4</sub>(μ<sub>4</sub>,η<sup>2:2:2:2:2:2:2:2:1:1:1:1</sup>-P<sub>16</sub>)] (**5**) compounds. While **4** represents the largest cationic polyphosphorus cage species reported to date, the P<sub>16</sub> chain in **5** constitutes the longest unsubstituted polyphosphorus chain so far. This highlights the synthetic utility of **A** as a building block for even larger polyphosphorus architectures. Completing this synthetic survey, **A** was demonstrated to be an efficient precursor transferring molecular P<sub>2</sub> units upon ring contraction.



**Scheme 3.** Thermolysis of **A** with [CpMo(CO)<sub>2</sub>]<sub>2</sub> and [[Cp<sup>'''</sup>Co]<sub>2</sub>(μ,η<sup>6:6</sup>-PhMe)], respectively, demonstrating the potential of **A** as a P<sub>2</sub> synthon.

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

**Keywords:** *Cyclo*-P<sub>8</sub> · DFT Calculations · Phosphorus · Polyphosphorus · Tantalum

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