

## Hot Paper

## Controlled Ring Opening of a Tetracyclic Tetraphosphane with Twofold Metallocene Bridging

Subhayan Dey,<sup>[a, b]</sup> Balázs Szathmári,<sup>[c]</sup> Roman Franz,<sup>[a]</sup> Clemens Bruhn,<sup>[a]</sup> Zsolt Kelemen,<sup>\*,[c]</sup> and Rudolf Pietschnig<sup>\*,[a]</sup>

A direct route to a doubly ferrocene bridged tetracyclic tetraphosphane **1** was developed via reductive coupling of Fe(CpPCL<sub>2</sub>)<sub>2</sub> (**2a**), where a chlorine terminated linear P<sub>4</sub>-compound **3** could be identified as an intermediate. Selective P–P bond activation was further achieved by reacting **1** with elemental selenium or [Cp\*Al]<sub>4</sub>, where regioselective insertion of Se or Al atoms resulted in ferrocenylene bridged [P<sub>4</sub>Se] (**4**) or [P<sub>4</sub>Al] (**7**) moieties. Compound **7** can be transformed to a hydrogen terminated linear P<sub>4</sub> species, **8**, with protic solvents.

Methylation of compound **1** with MeOTf, proceeds via intermediate formation of monomethylated species **5**, which gradually produced Me<sub>2</sub>-terminated dicationic **6**, again containing a linear P<sub>4</sub>-unit. Besides spectroscopic characterization, the structural details of compounds **1**, **4**, **6**, and **8** could be determined by SC-XRD. Moreover, DFT calculations were used to rationalize the reactivity of **1**, derived compounds and intermediates. As a key feature, **1** undergoes ring opening polymerization to a linear polyphosphane **9**.

## Introduction

Oligophosphanes or oligophosphines feature homoatomic chains or rings formally consisting of (>PR)<sub>n</sub> units, which is illustrative for an alternative formulation as oligophosphinidenes.<sup>[1]</sup> The closely related oligosilanes and their heavier germanium and tin analogs received considerable attention owing to their remarkable electronic properties.<sup>[2]</sup> In contrast to these homoatomic group 14 oligomers and polymers, in case of oligophosphanes the presence of a lone pair at each phosphorus atom usually leads to diastereomeric mixtures, which are difficult if not impossible to separate.<sup>[3]</sup> Moreover, oligophosphanes can be quite dynamic in ring size with planar inversion of the lone pairs,<sup>[4]</sup> and very recently Pringle and coworkers demonstrated spontaneous P–P bond metathesis even for diphosphanes.<sup>[5]</sup> There are some prominent examples of well-defined oligophosphanes, stabilized by sterically very demanding substituents,<sup>[6]</sup> or embedment into cyclic

scaffolds.<sup>[7]</sup> Being highly sensitive towards disproportionation, accompanied by rearrangements,<sup>[4,8]</sup> only a very limited number of catena-phosphanes with general formula X–(P<sub>n</sub>R<sub>n</sub>)–X (with X=H, SiMe<sub>3</sub>, SnMe<sub>3</sub>) have been reported till date: n=2 for R=Ph, 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub> (Mes),<sup>[9]</sup> n=3 for R=Ph,<sup>[10]</sup> and n=4 for R=<sup>t</sup>Bu, Ph, Mes,<sup>[6a,11]</sup> in contrast to more common cyclic tetraphosphanes A–D, complemented by rare 1,3-bridged or π-bonded P<sub>4</sub>-cycles as realized in the unique examples E–F (Figure 1). Recently we reported the formation of an isolable linear tetra- and polyphosphane, where the unique axial flexibility of the ferrocenylene substituent enabled all-*trans* conformation of the P<sub>4</sub>-chain.<sup>[12]</sup> Inspired by the configurational stability of some ferrocene based oligophosphorus compounds,<sup>[7c,13]</sup> we set out to explore the possibility of synthesizing a maximally condensed phosphoferrocenophane **1**. Herein, we report preparation and reactivity of such an unprecedented tetracyclic oligophosphane, **1**. Various methodologies for the synthesis of cyclooligophosphanes have been reported to date,<sup>[14]</sup> including Mg-mediated reductive coupling of substituted dihalophosphanes.<sup>[1a,12,15]</sup>

[a] S. Dey, R. Franz, C. Bruhn, R. Pietschnig  
Institut für Chemie und CINSaT, University of Kassel,  
Heinrich Plett-Straße 40, 34132 Kassel, Germany  
E-mail: pietschnig@uni-kassel.de

[b] S. Dey  
Current address: School of Advanced Sciences,  
Vellore Institute of Technology, Vandalur-Kelambakkam Road,  
Rajan Nagar, Chennai, Tamil Nadu 600127, India

[c] B. Szathmári, Z. Kelemen  
Department of Inorganic and Analytical Chemistry,  
Budapest University of Technology and Economics,  
Műegyetem Rkp 3, 1111 Budapest, Hungary  
E-mail: kelemen.zsolt@vbk.bme.hu

Supporting information for this article is available on the WWW under  
https://doi.org/10.1002/chem.202400194

© 2024 The Authors. Chemistry - A European Journal published by Wiley-VCH  
GmbH. This is an open access article under the terms of the Creative  
Commons Attribution License, which permits use, distribution and re-  
production in any medium, provided the original work is properly cited.

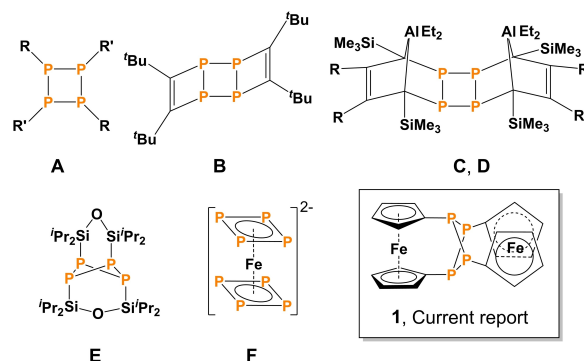


Figure 1. Title compound **1** and related cyclotetraphosphanes A (for R=R' and R≠R'),<sup>[17]</sup> B,<sup>[18]</sup> C (R=Me),<sup>[19]</sup> D (R=(CH<sub>2</sub>)<sub>4</sub>),<sup>[19]</sup> E,<sup>[20]</sup> and F.<sup>[21]</sup>

## Results and Discussion

To obtain oligophosphane **1**, we explored the straightforward reduction of the well-known 1,1'-bis(dichlorophosphanyl)ferrocene **2a** ( $\text{Fe}(\text{CpP}(\text{Cl})_2)_2$ ).<sup>[16]</sup> By reacting the latter with an excess of Mg in a 9:1 mixture of toluene and thf, compound **1** was obtained as the only observable product exclusively (Scheme 1, path I). Tracking the formation of **1** with  $^{31}\text{P}$  NMR at room temperature allowed us to identify resonances of an intermediate, which subsequently converts to product **1**. The resonances of the intermediate are consistent with a chloro-terminated tetraphosphane **3**, featuring an AA'BB' spin system in the solution-phase  $^{31}\text{P}$  NMR spectra, with resonances centered at  $\delta$  99.24 (terminal  $\text{Cl}-\text{P}(\text{C}_5\text{H}_4)-\text{P}(\text{C}_5\text{H}_4)-\text{P}(\text{C}_5\text{H}_4)-\text{P}(\text{C}_5\text{H}_4)-\text{Cl}$ ) position, Figure 3A, signal a) and  $-22.75$  ppm (inner  $\text{Cl}-\text{P}(\text{C}_5\text{H}_4)-\text{P}(\text{C}_5\text{H}_4)-\text{P}(\text{C}_5\text{H}_4)-\text{P}(\text{C}_5\text{H}_4)-\text{Cl}$ ) positions, Figure 3A, signal b).

The presence of intermediate **3** could also be corroborated by MALDI measurement, taken from an aliquot of the reaction mixture, where a molecular ion peak for [3-Cl] could be observed (Figure S16, ESI). With an authentic sample in hand, tetracyclic oligophosphane **1** could be identified as identical to a previously observed trace impurity in the thermal polymerization of [2]ferrocenophane **2b** ( $\text{Fe}(\text{CpP}^t\text{Bu})_2$ ) at high temperature (Scheme 1, path II), albeit in much lower yield (Figures S1–S4, ESI).<sup>[12]</sup>

X-ray crystallography revealed the molecular structure of compound **1** in the solid state (Figure 2), confirming the tetracyclic tetraphosphane core with ferrocenylene handles connecting the phosphorus atoms in the alternating positions. In contrast to most of its congeners **A** and **E** (Figure 1), **1** features a rectangular ( $\text{P}-\text{P}-\text{P}$  angle  $\varphi \approx 90^\circ$ ) and comparatively more planar (ring-fold angle  $\psi = 160.6^\circ$ ) geometry of the  $\text{P}_4$  moiety, similar to phosphalkyne cyclotetramer **B**, ate-complexes of aluminacyclopentadienes **C** and **D**, and inorganic ferrocene analogue **F** (Figure 1).<sup>[17–21]</sup> Investigating the Kohn-Sham orbitals of **1** (Figure S75, ESI), it can be established that

the HOMO and HOMO-1 are degenerate orbitals involving the lone pairs of all phosphorus atoms. The same energy level of these orbitals can be attributed to the high symmetry of the system with four equivalent phosphorus atoms and indeed the lone pairs of them are combined with each other (HOMO and HOMO-1). Spurred by the synthetic access in acceptable yield and purity, we set out to explore the reactivity of the  $\text{P}_4$  moiety in **1**. Owing to the unusual arrangement and degeneracy of the phosphorus lone-pairs in tetracyclic tetraphosphane **1**, we wanted to assess their donor properties, for which the  $^1J_{\text{PSe}}$  coupling of the corresponding selenophosphorane is a convenient measure.<sup>[22]</sup> To this end, **1** was reacted with grey selenium, however, instead of forming the corresponding selenophosphorane as in related cases,<sup>[23]</sup> the Se atom inserted between two adjacent P atoms, giving rise to compound **4** as a sole isolable product in nearly quantitative yield (Scheme 2a) with the structural motif corroborated by SC-XRD (cf. Figure 2). Similar to previously reported P–P bond activated species  $[(\text{CyP})_4\text{AsLi}]$ ,<sup>[24]</sup>  $[\text{D}^{\text{ipp}}\text{BDISi}]_4\text{P}_4$ ,<sup>[25]</sup> and  $[\text{D}^{\text{ipp}}\text{BDIMg}]_2[\text{Bu}_2\text{P}_4]$ ,<sup>[26]</sup> (where  $\text{D}^{\text{ipp}}\text{BDI} = \text{HC}(\text{C}(\text{Me})_2\text{N}(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3))_2$ ), compound **4** showed an AA'BB'X spin system in the  $^{31}\text{P}$  NMR spectra with resonances centered at  $\delta$  55.82 (for  $\text{Se}-\text{P}(\text{C}_5\text{H}_4)-\text{P}(\text{C}_5\text{H}_4)-\text{P}(\text{C}_5\text{H}_4)-\text{P}(\text{C}_5\text{H}_4)-\text{Se}$ ) and 31.96 ppm (for  $\text{Se}-\text{P}(\text{C}_5\text{H}_4)-\text{P}(\text{C}_5\text{H}_4)-\text{P}(\text{C}_5\text{H}_4)-\text{P}(\text{C}_5\text{H}_4)-\text{Se}$ ), Figure S25, ESI). To illustrate the unique reaction behavior of our tetracyclic tetraphosphane scaffold, we additionally subjected literature known  $[\text{P}^t\text{Bu}]_4$  to the same reactions for the sake of comparison.<sup>[27]</sup> However, in this case only the  $^t\text{Bu}$ -substituted variation of the Woolin's type reagent was observed and identified by crystallographic means (Figure S35, ESI).<sup>[28]</sup> In order to understand the selectivity of the reaction with selenium, DFT calculations were carried out at  $\omega\text{B97X-D/def2-TZVP}$  level of theory (more details in ESI). Since modeling the direct reaction with grey selenium is challenging, a different (hypothetical) selenium transfer reaction was calculated to evaluate the thermodynamic stability of **4** (Scheme S1, ESI). The common motif of these processes is that most of the reactions are thermoneutral or slightly exergonic. Therefore, the



Scheme 1. Synthetic approaches to tetracyclic oligophosphane **1**.

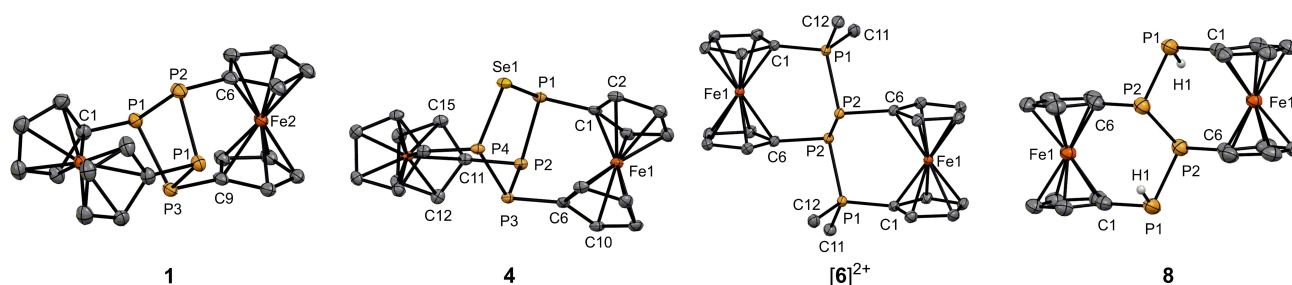
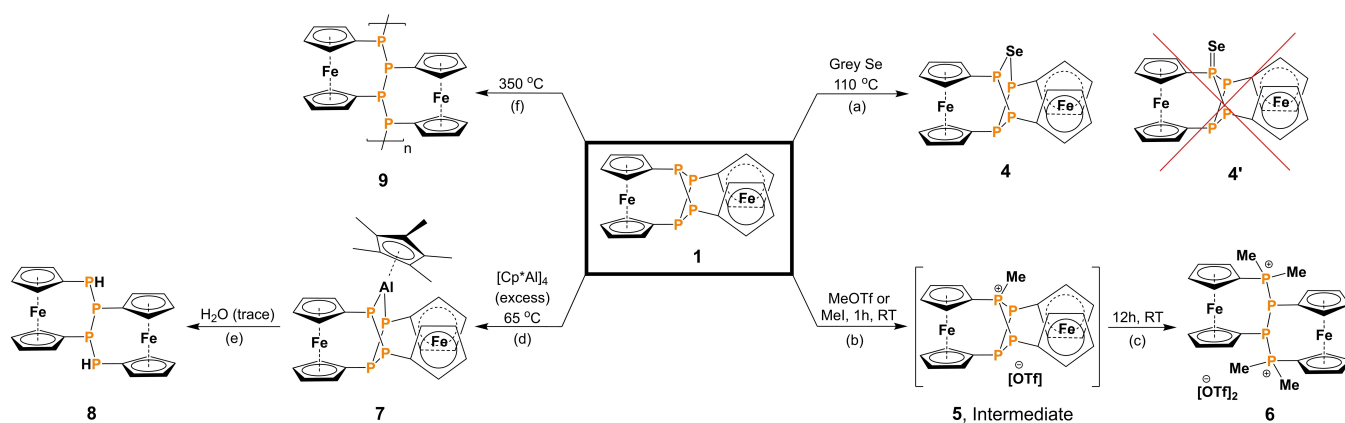


Figure 2. Molecular structures of **1**, **4**,  $[\text{6}]^{2+}$ , and **8** based on SC-XRD.<sup>[30]</sup> Coordinates for the hydrogen atoms on the terminal P atoms in **8** are freely refined with fixed isotropic thermal parameters.



Scheme 2. Reactions of  $[\text{Fe}(\text{CpP})_2]_2$  (1) with grey Se (a), MeOTf (b and c) and  $[\text{Cp}^*\text{Al}]_4$  (d) followed by quenching (e), or heating (f).

selenium incorporation is favored thermodynamically, similar to other phosphanes. Despite the selenophosphorane isomer of 4 (i.e. 4') was not detected, its relative stability was determined (Figure S76, ESI) and our calculations revealed that reaction  $4' \rightarrow 4$  is exergonic ( $\Delta G = -9.1$  kcal/mol), but the corresponding barrier of the monomolecular transformation is high (63.3 kcal/mol). For comparison, the thermodynamic driving force of the related transformation is lower in case of diphospha[2]ferrocenophane ( $\Delta G = -2.1$  kcal/mol), but the corresponding reaction barrier is lower (34.4 kcal/mol) as well (for better comparison values were recomputed at  $\omega\text{B97X-D/def2-TZVP}$ ).<sup>[29]</sup> The question arises why only 4 is formed exclusively and no other selenium containing species could be detected. Different possible products were investigated (Scheme S1, ESI) and based on our computational results it can be established that introducing a second selenium atom is less favoured thermodynamically, with the transfer reactions being endergonic. It seems that the formed five-membered ring in 4 has significant thermodynamic stability, which is likely complemented by the steric hindrance of the ferrocene unit. Since the proclivity to undergo quaternization is a prototypic reactivity feature of phosphanes, we set out exploring the methylation of 1. To this end we reacted 1 with MeOTf, where stoichiometric and sub-stoichiometric amount of the reagent produced mono-methylated 5, as a mixture with unreacted 1, and 6 (Scheme 2b; Figures S41, S42, S49, and S50, ESI). Reaction of 1 with an excess

of MeOTf (7 eq.) resulted selectively and quantitatively in compound 6 (Scheme 2). Tracking the formation of 6 by  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR, we were able to identify the resonances of an intermediate, consistent with mono-methylated 5, which over long standing eventually produces crystals of compound 6. In its  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra, compound 5 shows an ABCB' type spin system, where three different multiplets at  $\delta$  61.62 (for  $\langle >P-P(\text{C}_5\text{H}_4)-\text{PMe}$ , signals c), 46.90 (for  $\langle >P-P(\text{C}_5\text{H}_4)-\text{PMe}$ , signals d) and 27.61 (for  $\langle >P-P(\text{C}_5\text{H}_4)-\text{PMe}$ , signals e) were observed (Figure 3B). The identity of compound 5 could further be confirmed with MALDI-MS, which showed a molecular ion peak for  $[1 + \text{Me}]^+$  (Figure S40, ESI). The solid-state structure of 6 was analyzed by X-ray crystallography, where a linear all-*trans*  $\text{P}_4$  chain could be observed terminated by two methyl units on each side (Figure 2), entailing two positive charges. Two triflate anions further compensate the positive charges of the  $[\text{Fc}'_2\text{P}_4\text{Me}_4]$  scaffold.<sup>[30]</sup>

As monovalent aluminum complexes have previously been used to access rare Al-P cages and clusters by reducing highly reactive white phosphorus and its derivatives,<sup>[31]</sup> the reactivity of compound 1 was then explored with  $[\text{Cp}^*\text{Al}]_4$ . Similar to the reaction of  $\text{P}_4$  with complexes of monovalent group 13 elements,<sup>[31d]</sup> the reaction resulted in regioselective insertion yielding Al(III)-species 7 as product (Scheme 2d). The latter shows an AA'BB'X spin system in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra with two multiplets, centered at  $\delta -251.21$  (for  $\text{AlP}(\text{C}_5\text{H}_4)-\text{P} \langle$ ) and

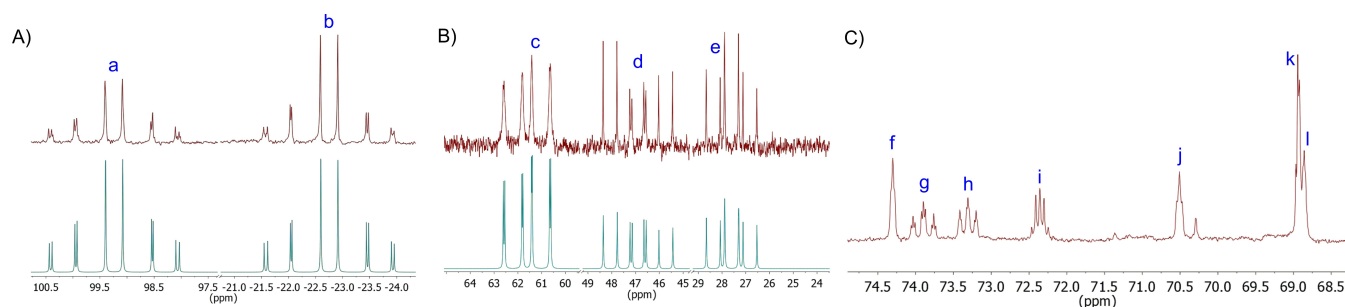


Figure 3. Experimental (red) and simulated (teal)  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of compounds 3 (A) and 5 (B);  $\delta$  ca. 68–75 ppm view of  $^{13}\text{C}$  NMR spectrum of compound 7 (C).

–56.87 ppm (for  $\text{AlP}(\text{C}_5\text{H}_4)\text{-P}<$ ) (Figures S56 and S60, ESI). The  $\alpha$  and  $\beta$  carbon atoms of the  $\text{C}_5\text{H}_4$ -rings with P–Al bonds exhibit complex multiplets (signals g–i, and l in Figure 3C), whereas similar carbon atoms of the other half of ferrocene units are showing simpler resonances (signals f, j, and k in Figure 3C), which is an agreeable pattern for the  $\text{C}_2$  symmetric nature of  $[\text{AlP}_4]$  core. On the other hand, monocyclic  $[\text{P}^t\text{Bu}]_4$  showed no reaction with  $[\text{Cp}^*\text{Al}]_4$  even with an excess of the Al(I)-reagent, as confirmed by  $^{31}\text{P}$  and  $^{27}\text{Al}$  NMR (Figures S65–S67, ESI). The reaction of **1** with equimolar amounts of  $[\text{Cp}^*\text{Al}]_4$  remained incomplete (Figures S51 and S52, ESI), even at  $110^\circ\text{C}$ , over several days. Using an excess (2.5 eq.) of  $[\text{Cp}^*\text{Al}]_4$  allowed full conversion (Figures S55 and S56, ESI) and selective formation of **7** which could be isolated in 81% yield along with unreacted  $[\text{AlCp}^*]_4$  (Figures S58 and S60, ESI). The reaction of **1** with  $[\text{AlCp}^*]_4$  was investigated by DFT calculations. As expected, the reaction of **1** with the  $\text{AlCp}^*$  monomer is exergonic ( $\Delta G = -22.2$  kcal/mol), and the brutto process ( $4 \text{ eq. } \mathbf{1} + [\text{AlCp}^*]_4 \rightarrow \mathbf{7}$ ) has significant thermodynamic driving force ( $\Delta G = -79.0$  kcal/mol) as well. Similar to the reaction with selenium, the introduction of the second  $\text{AlCp}^*$  unit is endergonic  $\Delta G = 3.1$  kcal/mol (Scheme S2, ESI).

Aluminumphosphanide **7** is highly reactive and protic solvents like water lead to its selective conversion to the ring opened hydrogen-terminated linear tetraphosphane **8** (Scheme 2e). The molecular structure of **8** in the solid-state shows a linear all-*trans*  $\text{P}_4$  moiety with terminal P–H bonds (Figure 2), which in the ATR-IR spectrum shows a characteristic band for the P–H stretching mode (ca.  $2360 \text{ cm}^{-1}$ , Figure S72, ESI). The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of **8**, show an AA'BB' spin system, with two multiplets, centered at  $\delta -66.71$  (for  $\text{HP}(\text{C}_5\text{H}_4)\text{-P}<$ ) and  $-36.37$  ppm (for  $\text{HP}(\text{C}_5\text{H}_4)\text{-P}<$ ), similar to the pattern observed for previously published  $[\text{Fc}'_2\text{P}_4^t\text{Bu}_2]$  (Figure S68, ESI).<sup>[12]</sup>

The geometric parameters of the  $\text{Me}_2$ - and hydrogen terminated dicationic and neutral linear  $\text{P}_4$ -species **6** and **8** are mostly comparable to those of their cyclic analog **1** (Figure 2).<sup>[30]</sup> The P–P–P or  $\varphi$  angle, is closest to  $90^\circ$  in **1** [ $89.15(4)^\circ$ – $89.24(5)^\circ$ ] which increases by ca.  $6$ – $8.5^\circ$  in ring-opened **6** [ $97.58(9)^\circ$ ] and **8** [ $95.14(8)^\circ$ ].<sup>[30]</sup> Although many cyclic  $\text{P}_4$  systems with even lower  $\varphi$  angles are reported in the literature, their molecular strain around the  $\text{P}_4$  core are compensated by low ring fold angles  $\psi$ , making the ring more puckered than planar.<sup>[17]</sup> When both  $\varphi$  and  $\psi$  angles simultaneously increase,<sup>[32]</sup> rigid equatorial orientations of the substituents at the P atoms get conformationally disfavored. With respect to the distortion of the cyclopentadienyl moieties from coplanarity,<sup>[33]</sup> **1** ( $\alpha = 3.8^\circ$ ) shows a slightly higher tilt angle than  $[\text{Fc}'_2\text{P}_4^t\text{Bu}_2]$  ( $\alpha = 0^\circ$ ) and other phosphatrimers,<sup>[29b]</sup> but nevertheless indicates negligible ring strain of the ferrocenophane scaffold. However, both **1** and  $[\text{Fc}'_2\text{P}_4^t\text{Bu}_2]$  feature twist angles of  $\tau = 0^\circ$  highlighting the directional rigidity of the linear P–P backbone.<sup>[33]</sup>

As pointed out earlier, **1** had been observed as byproduct in trace amounts during the thermal ring expansion polymerization of [2]ferrocenophane ( $\text{Fe}(\text{CpP}^t\text{Bu})_2$ ). We were wondering, whether **1** could be ring-opened thermally to an all-*trans* linear polyphosphinidene, as well. To solve this question, we heated neat **1** in vacuum at  $350^\circ\text{C}$  which likewise resulted in the

formation of polymer **9** (Scheme 2f), as confirmed by identical IR and elemental analysis compared with an authentic sample (Figure S74, ESI). The latter findings might point at a role of **1** as potential intermediate in the formation of this polymer for the thermally driven dealkylative ring-expansion polymerization of [2]ferrocenophane ( $\text{Fe}(\text{CpP}^t\text{Bu})_2$ ).<sup>[12]</sup> We speculate that the only moderate strain as documented in the above-mentioned geometrical parameters of **1**, together with the torsional flexibility of the ferrocene moiety allow for a controlled ring-opening by various reagents or just thermally. By contrast, a less flexible tetraphosphane such as **C**, disintegrates with reducing and methylating reagents, leading to complete fragmentation of the  $\text{P}_4$  moiety to P-containing small molecules.<sup>[19]</sup>

## Conclusions

In summary, straightforward access to a unique tetracyclic tetraphosphane **1** with twofold metallocene bridging has been demonstrated. Despite the degeneracy of the lone-pairs at all four phosphorus atoms, functionalization with electrophilic and ambiphilic reagents occurs exclusively at a single P–P bond. The resulting linear tetraphosphane **8** and its closely related analog **3** with opposite polarity are attractive building blocks for larger catena polyphosphanes. Likewise, P–P bond activation in **1** can be effected thermally transforming **1** into all-*trans* catena polyphosphane **9**, for which it may have been the actual intermediate in a previously reported approach. We anticipate that the only moderate strain of **1**, together with the torsional flexibility of the ferrocene moiety allow for a controlled ring-opening. This is in contrast to less flexible tetraphosphanes such as **C** which disintegrate with reducing and methylating reagents, leading to complete fragmentation of the  $\text{P}_4$  moiety.<sup>[19]</sup>

## Supporting Information

The data that support the findings of this study are available in the Electronic Supporting Information (ESI) of this article.

## Acknowledgements

Z. K. is grateful for the general support of János Bolyai Research Scholarship, Project UNKP-23-5-BME-419 and TKP2021-EGA-02 provided by the Ministry of Innovation and Technology of Hungary. R.P. and S.D. are further thankful to ZFF for their generous contribution in funding this research. R.P. thanks the DFG for continued support and funding. Open Access funding enabled and organized by Projekt DEAL.

## Conflict of Interests

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:** Ferrocene · Cyclic Oligophosphine · Regioselective Ring-expansion · P-Catenation · Monovalent Aluminum

- [1] a) W. A. Henderson, M. Epstein, F. S. Seichter, *J. Am. Chem. Soc.* **1963**, *85*, 2462–2466; b) U. Schmidt, R. Schröder, H. Achenbach, *Angew. Chem. Int. Ed.* **1966**, *5*, 316–316; c) R. Ahlrichs, D. Fenske, H. Oesen, U. Schneider, *Angew. Chem.* **1992**, *104*, 312–314; d) C. A. Dyker, S. D. Riegel, N. Burford, M. D. Lumsden, A. Decken, *J. Am. Chem. Soc.* **2007**, *129*, 7464–7474.
- [2] a) R. D. Miller, J. Michl, *Chem. Rev.* **1989**, *89*, 1359–1410; b) J. R. Koe, D. R. Powell, J. J. Buffy, R. West in *Octachlorocyclotetrasilane, perchloropolysilane and new dialkoxy- and diamino polysilanes*, Eds.: N. Auner, J. Weis, **2000**, pp. 323–330; c) M. L. Amadoruge, C. S. Weinert, *Chem. Rev.* **2008**, *108*, 4253–4294; d) V. Y. Lu, T. D. Tilley, *Macromolecules* **2000**, *33*, 2403–2412.
- [3] R. Wolf, M. Finger, C. Limburg, A. C. Willis, S. B. Wild, E. Hey-Hawkins, *Dalton Trans.* **2006**, 831–837.
- [4] M. Baudler, K. Glinka, *Chem. Rev.* **1994**, *94*, 1273–1297.
- [5] C. Branfoot, T. A. Young, D. F. Wass, P. G. Pringle, *Dalton Trans.* **2021**, *50*, 7094–7104.
- [6] a) R. Wolf, S. Gomez-Ruiz, J. Reinhold, W. Boehlmann, E. Hey-Hawkins, *Inorg. Chem.* **2006**, *45*, 9107–9113; b) I. Jevtovikj, P. Lönnecke, E. Hey-Hawkins, *Chem. Commun.* **2013**, *49*, 7355–7357.
- [7] a) J. D. Masuda, A. J. Hoskin, T. W. Graham, C. Beddie, M. C. Fermin, N. Etkin, D. W. Stephan, *Chem. Eur. J.* **2006**, *12*, 8696–8707; b) A. J. Hoskin, D. W. Stephan, *Angew. Chem. Int. Ed.* **2001**, *40*, 1865–1867; c) C. Moser, F. Belaj, R. Pietschnig, *Chem. Eur. J.* **2009**, *15*, 12589–12591; d) P. Kilian, H. L. Milton, A. M. Z. Slawin, J. D. Woollins, *Inorg. Chem.* **2004**, *43*, 2252–2260.
- [8] M. Baudler, *Angew. Chem. Int. Ed.* **1987**, *26*, 419–441.
- [9] a) K. Issleib, K. Krech, *Chem. Ber.* **1966**, *99*, 1310–1315; b) M. Baudler, M. Hallab, A. Zarkadas, E. Tolls, *Chem. Ber.* **1973**, *106*, 3962–3969; c) M. Baudler, B. Carlsohn, D. Koch, P. K. Medda, *Chem. Ber.* **1978**, *111*, 1210–1216; d) M. Baudler, C. Gruner, H. Tschäbunin, J. Hahn, *Chem. Ber.* **1982**, *115*, 1739–1745; e) A. H. Cowley, J. E. Kilduff, N. C. Norman, M. Pakulski, *J. Chem. Soc. Dalton Trans.* **1986**, 1801–1808; f) J. T. Yeh, L. R. Avens, J. L. Mills, *Phosphorus Sulfur Relat. Elem.* **1990**, *47*, 319–323; g) S. Kurz, H. Oesen, J. Sieler, E. Hey-Hawkins, *Phosphorus Sulfur Relat. Elem.* **1996**, *117*, 189–196.
- [10] a) M. Baudler, D. Koch, B. Carlsohn, *Chem. Ber.* **1978**, *111*, 1217–1220; b) M. Baudler, G. Reuschenbach, *Phosphorus Sulfur Relat. Elem.* **2006**, *9*, 81–85; c) M. Baudler, J. Hellmann, G. Reuschenbach, *Z. Anorg. Allg. Chem.* **1984**, *509*, 38–52.
- [11] a) M. Baudler, G. Reuschenbach, J. Hahn, *Z. Anorg. Allg. Chem.* **1981**, *482*, 27–39; b) M. Baudler, G. Reuschenbach, J. Hellmann, J. Hahn, *Z. Anorg. Allg. Chem.* **1983**, *499*, 89–98; c) M. Baudler, G. Reuschenbach, J. Hahn, *Chem. Ber.* **1983**, *116*, 847–855; d) F. Fritz, T. Vaahs, *Z. Anorg. Allg. Chem.* **1987**, *552*, 18–33.
- [12] S. Dey, D. Kargin, M. V. Höfler, B. Szathmári, C. Bruhn, T. Gutmann, Z. Kelemen, R. Pietschnig, *Polymer* **2022**, *242*, 124589.
- [13] a) C. Moser, M. Nieger, R. Pietschnig, *Organometallics* **2006**, *25*, 2667–2672; b) N. Nagahora, T. Sasamori, N. Takeda, N. Tokitoh, *Organometallics* **2005**, *24*, 3074–3080.
- [14] a) M. Schmitz, S. Leininger, U. Bergsträßer, M. Regitz, *Heteroat. Chem.* **1998**, *9*, 453–460; b) C. Frenzel, E. Hey-Hawkins, *Phosphorus Sulfur Relat. Elem.* **2006**, *143*, 1–17; c) V. Naseri, R. J. Less, R. E. Mulvey, M. McPartlin, D. S. Wright, *Chem. Commun.* **2010**, *46*, 5000–5002; d) L. Wu, V. T. Annibale, H. Jiao, A. Brookfield, D. Collison, I. Manners, *Nat. Commun.* **2019**, *10*, 2786; e) R. Schoemaker, P. Kossatz, K. Schwedtmann, F. Hengersdorf, J. J. Weigand, *Chem. Eur. J.* **2020**, *26*, 11734–11741; f) A. N. Barrett, C. R. Woof, C. A. Gault, D. Gasperini, M. F. Mahon, R. L. Webster, *Inorg. Chem.* **2021**, *60*, 16826–16833; g) Z. Han, D. P. Gates, *Chem. Eur. J.* **2021**, *27*, 14594–14599; h) Y. Mei, Z. Yan, L. L. Liu, *J. Am. Chem. Soc.* **2022**, *144*, 1517–1522.
- [15] a) J. P. Albrand, A. Cogne, J. B. Robert, *J. Am. Chem. Soc.* **1978**, *100*, 2600–2604; b) A. H. Cowley, M. J. S. Dewar, M. Lattman, J. L. Mills, M. McKee, *J. Am. Chem. Soc.* **1978**, *100*, 3349–3354; c) Y. Tanimoto, Y. Ishizu, K. Kubo, K. Miyoshi, T. Mizuta, *J. Organomet. Chem.* **2012**, *713*, 80–88.
- [16] C. Moser, A. Orthaber, M. Nieger, F. Belaj, R. Pietschnig, *Dalton Trans.* **2006**, *32*, 3879–3885.
- [17] Table S1 (ESI) for further detail.
- [18] B. Geissler, S. Barth, U. Bergsträsser, M. Slany, J. Durkin, P. B. Hitchcock, M. Hofmann, P. Binger, J. F. Nixon, P. von Ragué Schleyer, M. Regitz, *Angew. Chem. Int. Ed.* **1995**, *34*, 484–487.
- [19] S. Du, J. Yang, J. Hu, Z. Chai, G. Luo, Y. Luo, W.-X. Zhang, Z. Xi, *J. Am. Chem. Soc.* **2019**, *141*, 6843–6847.
- [20] A. Kracke, C. von Hänisch, *Eur. J. Inorg. Chem.* **2011**, *2011*, 3374–3380.
- [21] Z.-C. Wang, L. Qiao, Z.-M. Sun, M. Scheer, *J. Am. Chem. Soc.* **2022**, *144*, 6698–6702.
- [22] S. Dey, R. Pietschnig, *Coord. Chem. Rev.* **2021**, *437*, 213850.
- [23] R. Franz, S. Nasemann, C. Bruhn, Z. Kelemen, R. Pietschnig, *Chem. Eur. J.* **2021**, *27*, 641–648.
- [24] A. Bashall, F. García, A. A. Hopkins, J. A. Wood, M. McPartlin, A. D. Woods, D. S. Wright, *Dalton Trans.* **2003**, 1143–1147.
- [25] Y. Xiong, S. Yao, M. Brym, M. Driess, *Angew. Chem. Int. Ed.* **2007**, *46*, 4511–4513.
- [26] M. Arrowsmith, M. S. Hill, A. L. Johnson, G. Kociok-Köhn, M. F. Mahon, *Angew. Chem. Int. Ed.* **2015**, *54*, 7882–7885.
- [27] C. A. Dyker, N. Burford, G. Menard, M. D. Lumsden, A. Decken, *Inorg. Chem.* **2007**, *46*, 4277–4285.
- [28] a) G. Hua, J. D. Woollins, *Angew. Chem. Int. Ed.* **2009**, *48*, 1368–1377; b) J. T. Shore, W. T. Pennington, M. C. Noble, A. W. Cordes, *Phosphorus Sulfur Relat. Elem.* **1988**, *39*, 153–157.
- [29] a) S. Dey, F. Roesler, C. Bruhn, Z. Kelemen, R. Pietschnig, *Inorg. Chem. Front.* **2023**, *10*, 3828–3843; b) R. Franz, B. Szathmári, C. Bruhn, Z. Kelemen, R. Pietschnig, *Inorg. Chem.* **2023**, *62*, 4341–4350.
- [30] Table S2 (ESI) for further comparison between **6**, **8**, other related species. Tables S3, S4, S5, S6 (ESI) for further detail on crystals **1** (CCDC deposition number 2287309), **4** (CCDC deposition number 2294958), **6** (CCDC deposition number 2287311), **8** (CCDC deposition number 2287310), respectively. Table S7 (ESI) for crystal refinement data.
- [31] a) Y. Peng, H. Fan, H. Zhu, H. W. Roesky, J. Magull, C. E. Hughes, *Angew. Chem. Int. Ed.* **2004**, *43*, 3443–3445; b) C. Dohmeier, H. Schnöckel, C. Robl, U. Schneider, R. Ahlrichs, *Angew. Chem. Int. Ed.* **1994**, *33*, 199–200; c) R. Yadav, T. Simler, B. Goswami, C. Schoo, R. Koppe, S. Dey, P. W. Roesky, *Angew. Chem. Int. Ed.* **2020**, *59*, 9443–9447; d) M. Haimerl, M. Piesch, R. Yadav, P. W. Roesky, M. Scheer, *Chem. Eur. J.* **2023**, *29*, e202202529; e) S. Nees, T. Wellnitz, F. Dankert, M. Härterich, S. Dotzauer, M. Feldt, H. Braunschweig, C. Hering-Junghans, *Angew. Chem. Int. Ed.* **2023**, *62*, e202215838.
- [32]  $\psi$  = ring-fold angle,  $\phi$  = P–P–P bond angle.
- [33]  $\alpha$  = tilt angle,  $\tau$  = twist angle.

Manuscript received: January 19, 2024

Accepted manuscript online: February 19, 2024

Version of record online: March 5, 2024