

UvA-DARE (Digital Academic Repository)

Synthesis and Reactivity of the Phosphorus Analogues of Cyclopentadienone, Tricyclopentanone, and Housene

Krachko, T.; Ehlers, A.W.; Nieger, M.; Lutz, M.; Slootweg, J.C.

DOI

[10.1002/ange.201711838](https://doi.org/10.1002/ange.201711838)

[10.1002/anie.201711838](https://doi.org/10.1002/anie.201711838)

Publication date

2018

Document Version

Final published version

Published in

Angewandte Chemie

License

Article 25fa Dutch Copyright Act

[Link to publication](#)

Citation for published version (APA):

Krachko, T., Ehlers, A. W., Nieger, M., Lutz, M., & Slootweg, J. C. (2018). Synthesis and Reactivity of the Phosphorus Analogues of Cyclopentadienone, Tricyclopentanone, and Housene. *Angewandte Chemie*, 130(6), 1699-1703. <https://doi.org/10.1002/ange.201711838>, <https://doi.org/10.1002/anie.201711838>

General rights

It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations

If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: <https://uba.uva.nl/en/contact>, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.

UvA-DARE is a service provided by the library of the University of Amsterdam (<https://dare.uva.nl>)

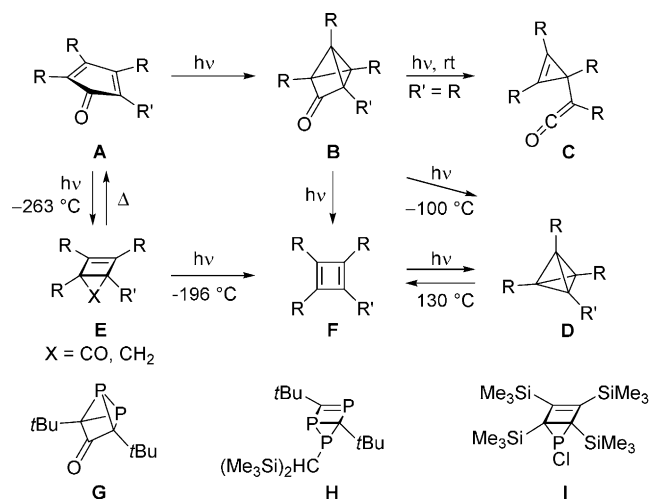
Synthesis and Reactivity of the Phosphorus Analogues of Cyclopentadienone, Tricyclopentanone, and Housene

Tetiana Krachko, Andreas W. Ehlers, Martin Nieger, Martin Lutz, and J. Chris Slootweg*

Dedicated to Professor Koop Lammertsma

Abstract: The phosphorus analogues of cyclopentadienone, tricyclopentanone, and housene were accessed from bis(cyclopropenyl)diphosphatenedione **3**, which was prepared by mixing 1,2,3-tris-*tert*-butylcyclopropenium tetrafluoroborate (**1**) and sodium phosphoethynolate [Na(OCP)(dioxane)_n]. While photolysis of **3** results in decarbonylation, yielding bis(cyclopropenyl)diphosphene **4** and after rearrangement diphosphahousene **5**, thermolysis of **3** leads to phosphatricyclo[2.1.0.0]pentanone **7**. Metal-mediated valence isomerization of **7** and subsequent demetalation provides access to phosphacyclopentadienone **12**.

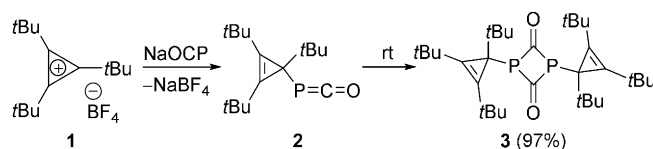
Pericyclic reactions are a powerful, atom-economical tool to provide access to strained ring systems with interesting topology. A striking example is the photoisomerization of tetra-*tert*-butylcyclopentadienone **A** (R, R' = *t*Bu; Scheme 1),^[1] a key cooperative ligand in Shvo's catalyst.^[2] Upon excitation (254 nm) **A** exclusively gives tricyclo[2.1.0.0^{2,5}]pentan-3-one **B**, which either converts into cyclopropenylketene **C** or releases carbon monoxide to afford the highly strained tetrahedrane **D**. On the other hand, irradiation of tris-*tert*-butyl-substituted dienone **A** (R = *t*Bu, R' = H) yields the thermally unstable housenone **E** (X = CO) that provides the antiaromatic cyclobutadiene **F** via CO elimination.^[3] To date, only one thermally stable, all-carbon housene **E** (X = CH₂, R = *t*Bu, R' = CO₂*t*Bu)^[4,5] has been reported. Incorporation of heteroatoms such as phosphorus into these molecules is appealing owing to their propensity to accommodate small angles and at the same time provide a coordi-



Scheme 1. Illustrative examples of strained ring systems.

nation site. So far, studies on the phosphorus analogues of **A**–**F** are scarce,^[6] and only Cowley's diphosphatricyclopentanone **G**,^[7] Nixon's triphospha analogue of housene **H**,^[8] and Sekiguchi's monophosphahousene **I**^[9] have been reported.

We anticipated the phosphorus analogue of **C** (cyclopropenylphosphaketene **2**; Scheme 2)^[10] to be an ideal entry



Scheme 2. Synthesis of 1,3-diphosphatane-2,4-dione **3**.

point into this chemistry, as both the required cyclopropenium cations and the phosphoethynolate anion (OCP⁻)^[11] are nowadays readily available. In this study, we focus on 1,2,3-tris-*tert*-butylcyclopropenium tetrafluoroborate (**1**).^[12] Addition of toluene to a mixture of [Na(OCP)(dioxane)_n] (n = 2.5–2.8) and **1** at –78 °C gave a 1:1 mixture of **2** (δ³¹P{¹H} = –231.7 ppm) and **3** (δ³¹P{¹H} = 119.0 ppm; Scheme 2)^[13] that within 18 hours at 20 °C fully converts into 1,3-diphosphatane-2,4-dione **3**, which was isolated as a yellow powder in 97% yield (δ³¹P{¹H} = 119.0 ppm; δ¹³C{¹H} = 224.8 ppm, ¹J_{CP} = 43.5 Hz, CO; ν(CO) = 1627 cm⁻¹).^[11b] Evidently, intermediate **2**, which we attribute to the phosphorus analogue of **C**,^[14] dimerizes via a facile head-to-tail [2+2] cycloaddition of the P=C bonds to yield **3**,^[15] which is also supported by DFT

[*] T. Krachko, Dr. A. W. Ehlers, Prof. Dr. J. C. Slootweg
Van 't Hoff Institute for Molecular Sciences
University of Amsterdam, Science Park 904
PO Box 94157, 1090 GD Amsterdam (The Netherlands)
E-mail: j.c.slootweg@uva.nl

Dr. A. W. Ehlers
Department of Chemistry, Science Faculty
University of Johannesburg
PO Box 254, Auckland Park, Johannesburg (South Africa)

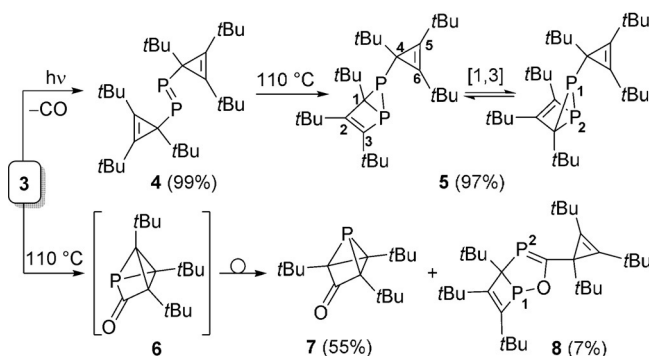
Dr. M. Nieger
Department of Chemistry University of Helsinki
A. I. Virtasen aukio 1, PO Box 55, Helsinki (Finland)

Dr. M. Lutz
Crystal and Structural Chemistry
Bijvoet Center for Biomolecular Research, Utrecht University
Padualaan 8, 3584 CH Utrecht (The Netherlands)

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:
<https://doi.org/10.1002/anie.201711838>.

calculations at the ω B97X-D/6-31G(d,p) level of theory ($\Delta E = -24.4$ kcal mol⁻¹; $\Delta E^\ddagger = 10.6$ kcal mol⁻¹; ZPE corrected).^[13]

Diphosphetanedione **3** is stable under an inert atmosphere, but is light-sensitive. In daylight, it slowly releases CO, while irradiation with a xenon lamp quantitatively converts a bright yellow toluene solution of **3** into the orange diphosphene **4** (3 h, RT), which was isolated after removal of all volatiles in 99% yield (Scheme 3; $\delta^{31}\text{P}\{^1\text{H}\} =$



Scheme 3. Photolysis and thermolysis of 1,3-diphosphetane-2,4-dione **3**.

585.3 ppm).^[16,17] The molecular structure of **4**, determined by a single-crystal X-ray structure determination (Figure 1, top left),^[18] reveals a centrosymmetric diphosphene with

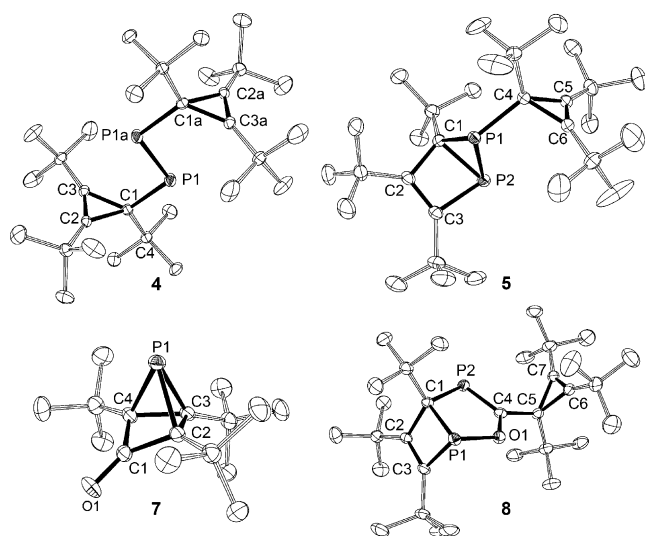
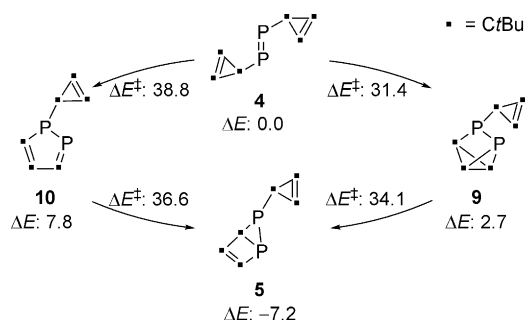


Figure 1. Molecular structures of **4**, **5**, **7**, and **8** (ellipsoids set at 50% probability, hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°] for **4**: P1–P1a 2.0210(6), P1–C1 1.8778(12), C1–C2 1.5209(16), C1–C3 1.5212(16), C2–C3 1.2938(17); P1a–P1–C1 102.88(4); P1a–P1–C1–C4 171.67(4). **5**: P1–P2 2.2080(6), P1–C1 1.8959(17), P1–C4 1.8909(16), P2–C1 1.8765(17), P2–C3 1.8487(17), C1–C2 1.548(2), C2–C3 1.362(2); P2–P1–C1 53.77(5); C3–P2–C1–C2 1.36(10). **7**: P1–C2 1.9198(12), P1–C3 1.8081(12), P1–C4 1.9293(13); C2–P1–C3 49.03(5), C3–P1–C4 48.77(5), C4–P1–C2 66.15(5); C2–P1–C3–C4 92.80(8). **8**: P1–O1 1.6896(12), C1–P1 1.8774(16), C1–C2 1.562(2), C2–C3 1.366(2), C3–P1 1.8110(17), P2–C1 1.8795(16), P2–C4 1.6926(17), C4–O1 1.3795(18); C3–P1–C1–C2 3.49(9), O1–P1–C1–P2 –1.66(8).

typical P1–P1a (2.0210(6) Å) and P1–C1 (1.8778(12) Å) bond lengths and a *syn* conformation (P1a–P1–C1–C4 171.67(4)°) of the cyclopropenyl groups and the P=P double bond. Note that the related bis(pentamethylcyclopentadienyl)diphosphene (Cp*P=PcP*) has the cyclopentadienyl rings and P=P bond positioned *anti* to each other.^[19] ω B97X-D/6-31G(d,p) calculations^[13] revealed this difference is of steric nature. The bulky *tert*-butyl group at C1 in **4** destabilizes the *anti* conformer ($\Delta E_{\text{anti-syn}} = 8.0$ kcal mol⁻¹), while the *anti* conformer is favored for the corresponding methyl-C1 analogue ($\Delta E_{\text{anti-syn}} = -1.1$ kcal mol⁻¹).^[13]

Next, we studied the thermal stability of **4** and discovered a rare pericyclic rearrangement for a diphosphene.^[20] Heating **4** for 20 hours in refluxing toluene afforded **5**, which displays two different $^{31}\text{P}\{^1\text{H}\}$ NMR resonances and was isolated as a pale yellow solid in 97% yield (Scheme 3; $\delta^{31}\text{P}\{^1\text{H}\} = 53.5$ (P1), –169.1 ppm (P2), $^1J_{\text{PP}} = 171.0$ Hz). Single-crystal X-ray structure determination provided unequivocally the molecular structure of **5** (Figure 1, top right),^[18] which displays a diphosphahousene motif with a dihedral angle of 99.7° between the three-membered diphosphirane and the almost planar 4-membered phosphacyclobutene moiety (C3–P2–C1–C2 1.36(10)°). Although diphosphahousene **5** (P₂-E) bears six inequivalent *tert*-butyl groups, only 4 different ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR resonances were found at room temperature. Upon cooling to –80 °C, the expected 6 sets of *t*Bu signals were observed, indicating that **5** is dynamic at room temperature and undergoes a facile degenerate [1,3] sigmatropic shift (see Scheme 3),^[21] which was supported by theory ($\Delta E^\ddagger = 17.5$ kcal mol⁻¹ at ω B97X-D/6-31G(d,p)),^[13,22] and also found for triphosphahousene **H**.^[8]

To gain more insight into the mechanism of the unusual **4**–**5** rearrangement, we resorted again to DFT calculations^[13] and found that **4** undergoes a [2+2] cycloaddition between the P=P and C=C bonds affording P-bridged phosphabicyclo[1.1.0]butane **9** as intermediate ($\Delta E = 2.7$ kcal mol⁻¹, $\Delta E^\ddagger = 31.4$ kcal mol⁻¹; Scheme 4). Compound **9** cannot undergo the classical bicyclo[1.1.0]butane-butadiene rearrangement to give diphosphacyclopentadiene **10** owing to geometrical constraints,^[23] but affords **5** instead via an unprecedented tricyclopentane-housene rearrangement ($\Delta E = -7.2$ kcal mol⁻¹, $\Delta E^\ddagger = 34.1$ kcal mol⁻¹). In principle, **4** can also provide **5** via a vinylcyclopropene-cyclopentadiene rearrangement^[24] affording **10** ($\Delta E = 7.8$ kcal mol⁻¹, $\Delta E^\ddagger = 38.8$ kcal mol⁻¹),

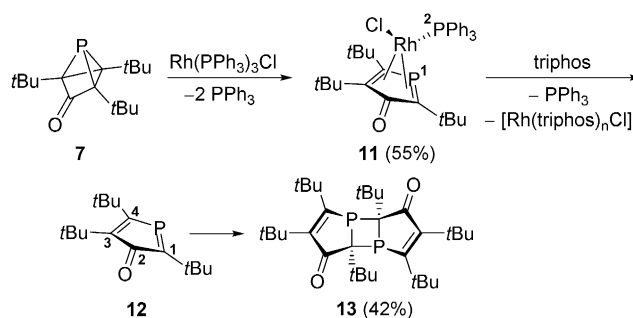


Scheme 4. Relative ω B97X-D/6-31G(d,p) energies (ZPE corrected, in kcal mol⁻¹) for the rearrangement of diphosphene **4** to give **5**. ■ = C*t*Bu.

followed by an electrocyclic ring closure ($\Delta E^\ddagger = 36.6$ kcal mol⁻¹; Scheme 4), but this is a higher energy process.

Next, we explored the thermal stability of diphosphatenedione **3** as a promising route to obtain the P analogues of **A** and **B** (Scheme 1). Heating **3** in the dark for 20 hours in refluxing toluene results in the formation of **7** ($\delta^{31}\text{P}\{^1\text{H}\} = -384.1$ ppm, $\nu(\text{CO}) = 1722$ cm⁻¹; 85%), **8** ($\delta^{31}\text{P}\{^1\text{H}\} = 134.5$ (P1), 153.9 ppm (P2), $^2J_{\text{P-P}} = 4.8$ Hz; 12%; Scheme 3) and an unidentified minor product ($\delta^{31}\text{P}\{^1\text{H}\} = -177.0$ ppm; 3%; Supporting Information, Figures S9, S10). Major product **7** was isolated as colorless crystals in 55% yield by recrystallization of the crude from Et₂O at -78°C and was characterized crystallographically (Figure 1, bottom left).^[18] The molecular structure of **7** reveals a 1-phosphatricyclo[2.1.0.0]pentan-3-one framework (P₁-**B**) with a remarkably small sum of angles at phosphorus (163.95(9)°), highlighting the tetrahedrane-type geometry. The transannular P1–C3 bond (1.8081(12) Å) of the bicyclobutane core is considerably shorter than the other two P–C bonds (P1–C2 1.9198(12), P1–C4 1.9293(13) Å), which points to a strongly bent σ -bond that was also reported for the all-carbon tricyclopentanones **B**.^[25] $\omega\text{B97X-D/6-31G(d,p)}$ calculations^[13] provided insight into the formation of **7** and revealed that phosphaketene **2** is an intermediate, that was also detected spectroscopically during the reaction (Supporting Information, Figures S7, S8), which forms 2-phosphatricyclopentan-3-one **6** via a [2+2] cycloaddition ($\Delta E = -11.8$ kcal mol⁻¹, $\Delta E^\ddagger = 25.9$ kcal mol⁻¹; Scheme 3). Subsequently, transient **6** undergoes a type I dyotropic rearrangement^[26] to alleviate steric strain of the three neighboring *tert*-butyl groups providing **7** ($\Delta E = -23.5$ kcal mol⁻¹, $\Delta E^\ddagger = 30.4$ kcal mol⁻¹). After separating **7** from the product mixture, column chromatography of the residue under an inert atmosphere afforded 2-oxa-1,4-diphosphabicyclo[3.2.0]hepta-3,6-diene **8** as a yellow crystalline solid in 7% yield (Scheme 3; Figure 1, bottom right),^[18] which formally results from a [2+3] cycloaddition of the putative phosphacyclobutadiene^[27] and the rearranged phosphaketene **2**, in analogy to the chemistry of (phosphanyl)-phosphaketenes recently reported by Grützmacher, Bertrand, and co-workers.^[28]

To access the P₁-**A**, we targeted the metal-mediated valence isomerization of phosphatricyclopentanone **7**.^[29] Satisfyingly, treatment of **7** with 1.0 equivalent of RhCl(PPh₃)₃ in refluxing dichloromethane afforded rhodium complex **11**, which was isolated as brown crystals in 55% yield by recrystallization from Et₂O at -78°C ($\delta^{31}\text{P}\{^1\text{H}\}$: 32.9 (dd, $^1J_{\text{P,Rh}} = 171.2$ Hz, $J_{\text{P-P}} = 11.0$ Hz; P2), -24.9 (dd, $^1J_{\text{P,Rh}} = 30.3$ Hz, $J_{\text{P-P}} = 11.0$ Hz; P1) ppm; $\nu(\text{CO}) = 1644$ cm⁻¹; Scheme 5). The molecular structure of **11** (Figure 2, left)^[18] revealed the formation of a unique (η^4 -phosphacyclopentadienone)rhodium(I) complex, which is the phosphorus analogue of [(Ph₄C₄CO)MCl(PPh₃)Cl] (M = Rh, Ir), a key pre-catalyst for the acceptorless dehydrogenation by metal–ligand cooperation.^[30] The PPh₃ ligand in **11** shows a strong *trans*-influence (P2–Rh1–C4 169.20(5)°, which leads to elongation of the Rh1–C4 bond (2.2595(16) Å) versus the shorter Rh1–C2 (2.2011(17) Å) and Rh1–C5 bonds (2.1773(17) Å).



Scheme 5. Valence isomerization of tricyclopentanone **7** in the coordination sphere of Rh^I and synthesis and dimerization of the uncomplexed diphosphacyclopentadienone **12**. Triphos = CH₃C(CH₂PPh₂)₃, *n* = 1 or 2.

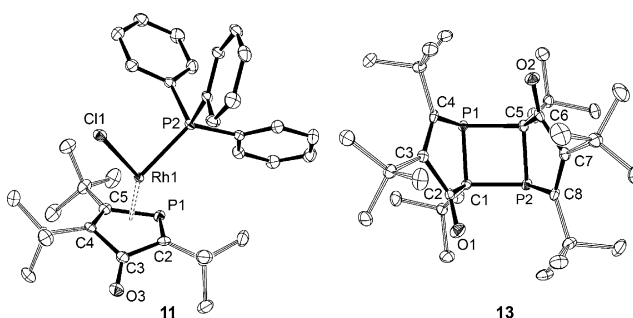


Figure 2. Molecular structures of **11** and **13** (ellipsoids set at 50% probability, hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°] for **11**: Rh1–P1 2.3297(5), Rh1–C2 2.2011(17), Rh1–C4 2.2595(16), Rh1–C5 2.1773(17), Rh–C3 2.5917(18), Rh1–P2 2.3678(4), P1–C2 1.7616(19), P1–C5 1.8416(19); C4–Rh1–P2 169.20(5); C2–P1–C5–C4 -3.27(13). **13**: P1–C1 1.858(2), P1–C5 1.916(3), C1–C2 1.513(3), C2–C3 1.515(3), C3–C4 1.361(3), C4–P1 1.857(2); P2–C1–P1 92.82(11), C1–P1–C5 85.64(11); P2–C1–P1–C5 -12.36(10), C4–P1–C1–C2 -7.13(17).

Finally, we focused on the demetallation of **11**. Addition of 1,1,1-tris(diphenylphosphinomethyl)ethane (triphos) to a dichloromethane solution of **11** at room temperature afforded within minutes selectively phosphacyclopentadienone **12** ($\delta^{31}\text{P} = 303.1$ ppm; $\delta^{13}\text{C} = 195.4$ ppm (P = C), $^1J_{\text{C-P}} = 31.4$ Hz; Scheme 5) together with a mixture of [Rh(triphos)_{*n*}Cl] and PPh₃, as confirmed by ³¹P, ¹H, and ¹³C NMR spectroscopy (Supporting Information, Figures S11–S13). Upon removal of the solvent, **12** rapidly dimerizes^[31] to bis(phosphole)-3,7-dione **13** as a single (*endo*) stereoisomer, which was isolated after column chromatography as a yellow solid in 42% yield ($\delta^{31}\text{P} = -13.4$ ppm; Scheme 5) and characterized crystallographically (Figure 2, right).^[18] The facile head-to-tail [2+2] dimerization of **12** was supported by DFT calculations, again at the $\omega\text{B97X-D/6-31G(d,p)}$ level of theory, which revealed *endo*-**13** to be thermodynamically and kinetically favored over *exo*-**13** ($\Delta E = -50.8$ versus -36.3 kcal mol⁻¹; $\Delta E^\ddagger = 21.9$ versus 25.2 kcal mol⁻¹, respectively), which can be attributed to secondary orbital interactions in the transition state leading to the *endo* adduct.^[13]

In summary, cyclopropenylphosphaketene **2** and its dimer 1,3-diphosphetane-2,4-dione **3** grant access to the phosphorus

analogues of housene, tricyclopentanone, and cyclopentadienone, all of which display intriguing pericyclic reactions. Currently, we are developing decarbonylation strategies for phosphatricyclopentanone **7**^[29] ultimately leading to the elusive phosphacyclobutadiene and phosphatetrahedrane.

Acknowledgements

This work was supported by the European Union (Marie Curie ITN SusPhos, Grant Agreement No. 317404) and the Council for Chemical Sciences of The Netherlands Organization for Scientific Research (NWO/CW) by a VIDI grant (J.C.S.). Prof. Dr. Hansjörg Grützmacher and Dr. Riccardo Suter are gratefully acknowledged for providing [Na(OCP)(dioxane)_n].

Conflict of interest

The authors declare no conflict of interest.

Keywords: main-group elements · pericyclic reactions · phosphorus · small ring systems · valence isomerization

How to cite: *Angew. Chem. Int. Ed.* **2018**, *57*, 1683–1687
Angew. Chem. **2018**, *130*, 1699–1703

- [1] a) G. Maier, S. Pfriem, *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 519–520; *Angew. Chem.* **1978**, *90*, 551–552; b) G. Maier, S. Pfriem, U. Schäfer, R. Matusch, *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 520–521; *Angew. Chem.* **1978**, *90*, 552–553; c) G. Maier, S. Pfriem, U. Schäfer, K.-D. Malsch, R. Matusch, *Chem. Ber.* **1981**, *114*, 3965–3987.
- [2] a) R. Karvembu, R. Prabhakaran, K. Natarajan, *Coord. Chem. Rev.* **2005**, *249*, 911–918; b) B. L. Conley, M. K. Pennington-Boggio, E. Boz, T. J. Williams, *Chem. Rev.* **2010**, *110*, 2294–2312.
- [3] a) G. Maier, A. Alzérreca, *Angew. Chem. Int. Ed. Engl.* **1973**, *12*, 1015–1016; *Angew. Chem.* **1973**, *85*, 1056–1057; b) G. Maier, U. Schäfer, W. Sauer, H. Hartan, R. Matusch, G. F. M. Oth, *Tetrahedron Lett.* **1978**, *19*, 1837–1840.
- [4] U.-J. Vogelbacher, P. Eisenbarth, M. Regitz, *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 708–710; *Angew. Chem.* **1984**, *96*, 691–693.
- [5] Housene **E** (X = C(Me)CO₂Me, R = H, R' = Me) undergoes a “walk” rearrangement at 0 °C, in which the bridgehead group CMe(CO₂Me) migrates via [1,3]-sigmatropic shifts along the 4-membered ring with inversion of configuration at the bridgehead carbon, see: a) F.-G. Klärner, F. Adamsky, *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 674–675; *Angew. Chem.* **1979**, *91*, 738–739; b) R. F. Childs, *Tetrahedron* **1982**, *38*, 567–608; c) F.-G. Klärner, F. Adamsky, *Chem. Ber.* **1983**, *116*, 299–322; d) F. Jensen, *J. Am. Chem. Soc.* **1989**, *111*, 4643–4647.
- [6] For metal-complexed diphospha-analogues of **A**, see: a) M. H. A. Benvenuti, P. B. Hitchcock, J. L. Kiplinger, J. F. Nixon, T. G. Richmond, *Chem. Commun.* **1997**, 1539–1540; b) M. Scheer, J. Krug, *Z. Anorg. Allg. Chem.* **1998**, *624*, 399–405; c) U. Vogel, M. Eberl, M. Eckhardt, A. Seitz, E.-M. Rummel, A. Y. Timoshkin, E. V. Peresykina, M. Scheer, *Angew. Chem. Int. Ed.* **2011**, *50*, 8982–8985; *Angew. Chem.* **2011**, *123*, 9144–9148. For metal-complexed phospho-derivatives of **F**, see: d) V. Lyaskovskyy, N. Elders, A. W. Ehlers, M. Lutz, J. C. Slootweg, K. Lammertsma, *J. Am. Chem. Soc.* **2011**, *133*, 9704–9707; For a antimony-diphospha analogue of housene **E**, see: e) C. Fish, M. Green, J. C. Jeffery, R. J. Kilby, J. M. Lynam, J. E. McGrady, D. A. Pantazis, C. A. Russell, C. E. Willans, *Angew. Chem. Int. Ed.* **2006**, *45*, 6685–6689; *Angew. Chem.* **2006**, *118*, 6837–6841.
- [7] A. R. Barron, A. H. Cowley, S. W. Hall, C. M. Nunn, *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 837–838; *Angew. Chem.* **1988**, *100*, 873–874.
- [8] a) V. Caliman, P. B. Hitchcock, J. F. Nixon, *Chem. Commun.* **1998**, 1537–1538; b) S. M. Bachrach, V. Caliman, J. F. Nixon, *J. Chem. Soc. Chem. Commun.* **1995**, 255, 2395–2396.
- [9] V. Y. Lee, H. Sugawara, O. A. Gapurenko, R. M. Minyaev, V. I. Minkin, H. Gornitzka, A. Sekiguchi, *Chem. Eur. J.* **2016**, *22*, 17585–17589.
- [10] For phosphaketenes created from the OCP anion, see: a) S. Alidori, D. Heift, G. Santiso-Quinones, Z. Benkő, H. Grützmacher, M. Caporali, L. Gonsalvi, A. Rossin, M. Peruzzini, *Chem. Eur. J.* **2012**, *18*, 14805–14811; b) L. Liu, D. A. Ruiz, F. Dahcheh, G. Bertrand, R. Suter, A. M. Tondreau, H. Grützmacher, *Chem. Sci.* **2016**, *7*, 2335–2341; c) N. Del Rio, A. Baceiredo, N. Saffon-Merceron, D. Hashizume, D. Lutters, T. Müller, T. Kato, *Angew. Chem. Int. Ed.* **2016**, *55*, 4753–4758; *Angew. Chem.* **2016**, *128*, 4831–4836; d) Y. Xiong, S. Yao, T. Szilvási, E. Ballester-Martínez, H. Grützmacher, M. Driess, *Angew. Chem. Int. Ed.* **2017**, *56*, 4333–4336; *Angew. Chem.* **2017**, *129*, 4397–4400.
- [11] Synthesis of [Na(OCP)(dioxane)_n], see: a) F. F. Puschmann, D. Stein, D. Heift, C. Hendriksen, Z. A. Gal, H.-F. Grützmacher, H. Grützmacher, *Angew. Chem. Int. Ed.* **2011**, *50*, 8420–8423; *Angew. Chem.* **2011**, *123*, 8570–8574; b) D. Heift, Z. Benkő, H. Grützmacher, *Dalton Trans.* **2014**, *43*, 831–840; c) I. Krummenacher, C. C. Cummins, *Polyhedron* **2012**, *32*, 10–13.
- [12] **1** has been successfully applied in the synthesis of cyclobutadienes **F**, see: a) S. Masamune, N. Nakamura, M. Suda, H. Ona, *J. Am. Chem. Soc.* **1973**, *95*, 8481–8483; b) H. Wingert, M. Regitz, *Chem. Ber.* **1986**, *119*, 244–256.
- [13] See the Supporting Information for further details.
- [14] For phosphaketenes, see: a) R. Appel, W. Paulen, *Tetrahedron Lett.* **1983**, *24*, 2639–2642; b) R. Appel, W. Paulen, *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 785–786; *Angew. Chem.* **1983**, *95*, 807–808; c) Z. Li, X. Chen, M. Bergeler, M. Reiher, C.-Y. Su, H. Grützmacher, *Dalton Trans.* **2015**, *44*, 6431–6438.
- [15] U. Salzner, S. M. Bachrach, *J. Am. Chem. Soc.* **1994**, *116*, 6850–6855.
- [16] For reviews, see: a) L. Weber, *Chem. Rev.* **1992**, *92*, 1839–1906; b) M. Yoshifuji, *Eur. J. Inorg. Chem.* **2016**, 607–615.
- [17] Note that carbon monoxide release from phosphaketenes to form diphosphenes has been recently observed, see: a) L. Liu, D. A. Ruiz, D. Munz, G. Bertrand, *Chem* **2016**, *1*, 147–153; b) M. M. Hansmann, R. Jazzar, G. Bertrand, *J. Am. Chem. Soc.* **2016**, *138*, 8356–8359; c) Ref. [10b]; d) Ref. [10d]; For a theoretical study on the coordination of CO to low-valent phosphorus centers, see: e) G. von Frantzius, A. Espinosa Ferao, R. Streubel, *Chem. Sci.* **2013**, *4*, 4309–4322.
- [18] CCDC 1583606 (**4**), 1583607 (**5**), 1584611 (**7**), 1584612 (**8**), 1583608 (**11**), 1584613 (**13**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre. For the experimental details of the X-ray crystal structure determinations, see the Supporting Information.
- [19] a) P. Jutzi, U. Meyer, B. Krebs, M. Dartmann, *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 919–921; *Angew. Chem.* **1986**, *98*, 894–895; b) P. Jutzi, U. Meyer, *J. Organomet. Chem.* **1987**, *333*, C18–C20.
- [20] An intramolecular electrocyclozation product has been proposed only as an intermediate in a dimerization reaction; see Ref. [16a].
- [21] R. E. Bulo, H. Jansen, A. W. Ehlers, F. J. J. de Kanter, M. Schakel, M. Lutz, A. L. Spek, K. Lammertsma, *Angew. Chem. Int. Ed.* **2004**, *43*, 714–717; *Angew. Chem.* **2004**, *116*, 732–735.

- [22] The full “walk” of the $P_1C_3(tBu)_3$ moiety over the phosphacyclobutadiene ring in **5** is prohibited, since the [1,3] sigmatropic shift from P2 to C2 is endothermic ($\Delta E = 23.0 \text{ kcal mol}^{-1}$) due to the formation of an intermediate with a P=C instead of a C=C bond.
- [23] a) J. C. Slootweg, S. Krill, F. J. J. de Kanter, M. Schakel, A. W. Ehlers, M. Lutz, A. L. Spek, K. Lammertsma, *Angew. Chem. Int. Ed.* **2005**, *44*, 6579–6582; *Angew. Chem.* **2005**, *117*, 6737–6740; b) J. C. Slootweg, A. W. Ehlers, K. Lammertsma, *J. Mol. Model.* **2006**, *12*, 531–536.
- [24] H. E. Zimmerman, D. W. Wilson, *J. Org. Chem.* **1995**, *60*, 692–697.
- [25] H. Irngartinger, A. Goldmann, *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 775–776; *Angew. Chem.* **1982**, *94*, 786–787.
- [26] a) I. Fernández, F. P. Cossío, M. A. Sierra, *Chem. Rev.* **2009**, *109*, 6687–6711; b) H. V. Pham, A. S. Karns, C. D. Vanderwal, K. N. Houk, *J. Am. Chem. Soc.* **2015**, *137*, 6956–6964.
- [27] We speculate that phosphacyclobutadiene forms through elimination of CO from **6** or **7**, akin to their hydrocarbon derivatives **B**; see: H. Ona, H. Yamaguchi, S. Masamune, *J. Am. Chem. Soc.* **1970**, *92*, 7495–7497.
- [28] Z. Li, X. Chen, Z. Benkő, L. Liu, D. A. Ruiz, J. L. Peltier, G. Bertrand, C.-Y. Su, H. Grützmacher, *Angew. Chem. Int. Ed.* **2016**, *55*, 6018–6022; *Angew. Chem.* **2016**, *128*, 6122–6126.
- [29] H. Ona, M. Sakai, M. Suda, S. Masamune, *J. Chem. Soc. Chem. Commun.* **1973**, 45–46.
- [30] S. Kusumoto, M. Akiyama, K. Nozaki, *J. Am. Chem. Soc.* **2013**, *135*, 18726–18729.
- [31] L. N. Markovski, V. D. Romanenko, *Tetrahedron* **1989**, *45*, 6019–6090.

Manuscript received: November 17, 2017

Accepted manuscript online: December 15, 2017

Version of record online: January 12, 2018