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Krachko, Tetiana

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

Tetiana Krachko,^[a] Andreas W. Ehlers,^[a, b] Martin Nieger,^[c] Martin Lutz,^[d] and J. Chris Slootweg*^[a]

Dedicated to Professor Koop Lammertsma

Abstract: The phosphorus analogues of cyclopentadienone, tricyclopentanone and housene were accessed from bis(cyclopropenyl)diphosphetanedione **3**, that 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 demetallation 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 to 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 housene **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} is reported. Incorporation of heteroatoms like phosphorus into these molecules is appealing due to their propensity to accommodate small angles and, at the same time, provide a coordination 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 monophospha-housene **I**⁹ are reported.

Scheme 1. Illustrative examples of strained ring systems.

We anticipated the phosphorus analogue of **C** (cyclopropenylphosphaketene **2**; Scheme 2)¹⁰ to be an ideal entry point into this chemistry, as both the needed 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** ($\delta^{31}\text{P}\{^1\text{H}\} = -231.7$ ppm) and **3** ($\delta^{31}\text{P}\{^1\text{H}\} = 119.0$ ppm; Scheme 2)¹³ that within 18 hours at 20 °C fully converts into 1,3-diphosphetane-2,4-dione **3**, which was isolated as a yellow powder in 97% yield ($\delta^{31}\text{P}\{^1\text{H}\} = 119.0$ ppm; $\delta^{13}\text{C}\{^1\text{H}\} = 224.8$ ppm, $^1J_{\text{C,P}} = 43.5$ Hz, CO; $\nu(\text{CO}) = 1627$ 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 calculations at the $\omega\text{B97X-D/6-31G(d,p)}$ level of theory ($\Delta E = -24.4$ kcal·mol^{−1}; $\Delta E^\ddagger = 10.6$ kcal·mol^{−1}; ZPE corrected).¹³

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

Diphosphetanedione **3** is stable under an inert atmosphere, but light sensitive. In daylight, it slowly releases CO, while irradiation with a xenon lamp quantitatively converts a bright yellow toluene solution of **3** to the orange diphosphene **4** (3 h, rt),

[a] T. Krachko, Dr. A. W. Ehlers, Assoc. 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

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

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

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

which was isolated after removal of all volatiles in 99% yield (Scheme 3; $\delta^{31}\text{P}\{^1\text{H}\} = 585.3$ 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 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, the related bis(pentamethylcyclopentadienyl) diphosphene ($\text{Cp}^*\text{P}=\text{PCp}^*$) has the cyclopentadienyl rings and P=P bond positioned *anti* to each other.¹⁹ $\omega\text{B97X-D/6-31G(d,p)}$ calculations¹³ revealed this difference is of steric nature. The bulky *tert*-butyl group at C1 in **4** destabilizes the *anti* conformation ($\Delta E_{\text{anti-syn}} = 8.0$ 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

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

Figure 1. Molecular structures of **4**, **5**, **7** and **8** (ellipsoids 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).

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), $^1J_{\text{P,P}} = 171.0$ 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** ($\text{P}_2\text{-E}$) 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 $\omega\text{B97X-D/6-31G(d,p)}$),^{13,22} and also found for triphosphahousene **H**.⁸

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

To gain more insight into the mechanism of the unusual **4**→**5** rearrangement, we resorted again to DFT calculations¹³ 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). **9** cannot undergo the classical bicyclo[1.1.0]butane–butadiene rearrangement to give diphosphacyclopentadiene **10** due 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 rearrangement²⁴ affording **10** ($\Delta E = 7.8$ kcal·mol^{−1}, $\Delta E^\ddagger = 38.8$ kcal·mol^{−1}), 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 diphosphetanedione **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), $^2J_{P,P} = 4.8$ Hz; 12%; Scheme 3) and an unidentified minor product ($\delta^{31}\text{P}\{^1\text{H}\} = -177.0$ ppm; 3%; 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 ω B97X-D/6-31G(d,p) calculations¹³ provided insight into the formation of **7** and revealed that phosphaketene **2** is an intermediate, that was also detected spectroscopically during the reaction (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 rearrangement²⁶ 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 phosphacyclobutadiene²⁷ and the rearranged phosphaketene **2**, in analogy to the chemistry of (phosphanyl)phosphaketenes recently reported by Grützmacher, Bertrand and co-workers.²⁸

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

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, $^1J_{P,Rh} = 171.2$ Hz, $J_{P,P} = 11.0$ Hz; P2), -24.9 (dd, $J_{P,Rh} = 30.3$ Hz, $J_{P,P} = 11.0$ 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).

Figure 2. Molecular structures of **11** and **13** (ellipsoids 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), $^1J_{C,P} = 31.4$ Hz; Scheme 5) together with a mixture of [Rh(triphos)_{*n*}Cl] and PPh₃, as confirmed by ³¹P, ¹H and ¹³C NMR spectroscopy (Figures S11–S13). Upon removal of the solvent, **12** rapidly dimerizes³¹ 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 ω 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.

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Entry for the Table of Contents

COMMUNICATION

The reaction of 1,2,3-tris-tert-butylcyclopropenium tetrafluoroborate with sodium phosphoethynolate (NaOCP) is presented. Photolytic decarbonylation of the resulting product affords bis(cyclopropenyl)diphosphene and after rearrangement diphosphahousene, while its thermolysis provides access to phosphatricyclo[2.1.0.0]pentanone and phosphacyclopentadienone.

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

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