

Phosphorus Compounds

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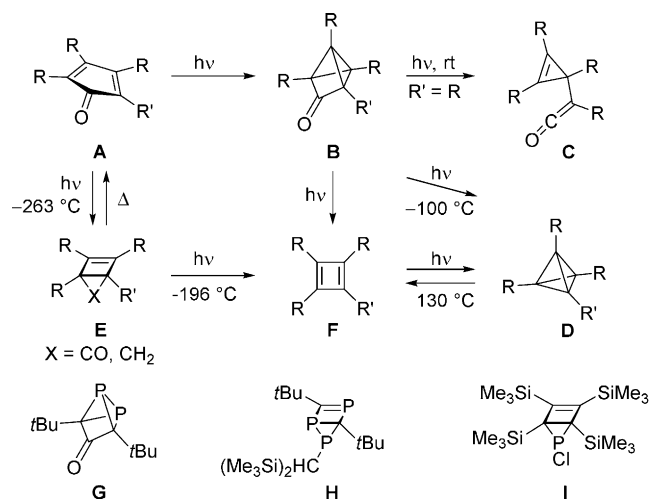
Synthesis and Reactivity of the Phosphorus Analogues of Cyclopentadienone, Tricyclopentanone, and Housene

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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**.

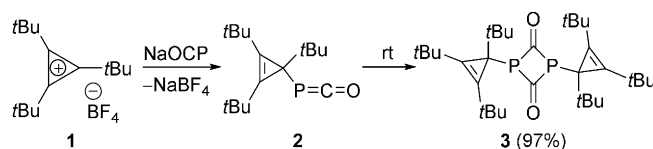
Pericyclic reactions are a powerful, atom-economical tool to provide access to strained ring systems with interesting topology. A striking example is the photoisomerization of tetra-*tert*-butylcyclopentadienone **A** (R, R' = *t*Bu; Scheme 1),^[1] a key cooperative ligand in Shvo's catalyst.^[2] Upon 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

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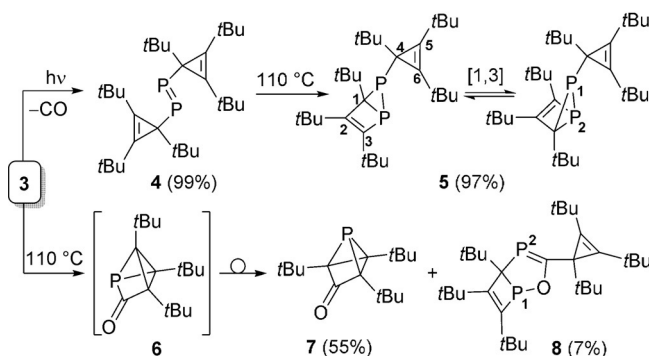
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calculations at the ω B97X-D/6-31G(d,p) level of theory ($\Delta E = -24.4$ kcal mol⁻¹; $\Delta E^\ddagger = 10.6$ kcal mol⁻¹; ZPE corrected).^[13]

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

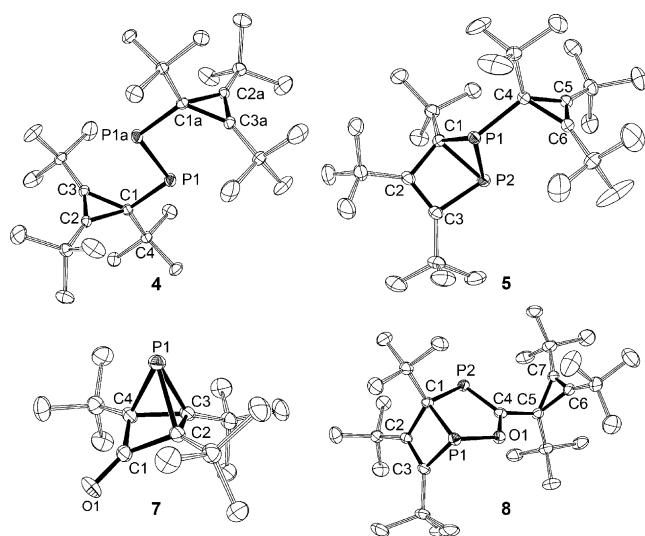
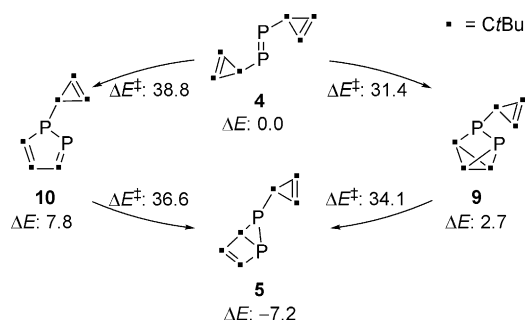


Figure 1. Molecular structures of **4**, **5**, **7**, and **8** (ellipsoids set at 50% probability, hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°] for **4**: P1–P1a 2.0210(6), P1–C1 1.8778(12), C1–C2 1.5209(16), C1–C3 1.5212(16), C2–C3 1.2938(17); P1a–P1–C1 102.88(4); 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 ³¹P{¹H} 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_{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 ¹³C{¹H} 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),

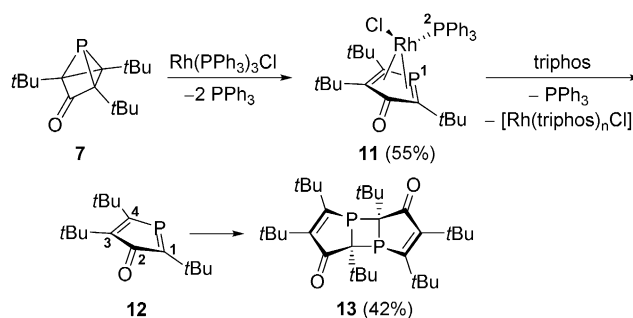


Scheme 4. Relative ω B97X-D/6-31G(d,p) energies (ZPE corrected, in kcal mol⁻¹) for the rearrangement of diphosphene **4** to give **5**. ■ = C*t*Bu.

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 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), $^2J_{\text{P-P}} = 4.8$ 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 Et $_2$ O 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 (P $_1$ -**B**) with a remarkably small sum of angles at phosphorus (163.95(9) $^\circ$), 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 P $_1$ -**A**, we targeted the metal-mediated valence isomerization of phosphatricyclopentanone **7**.^[29] Satisfyingly, treatment of **7** with 1.0 equivalent of RhCl(PPh $_3$) $_3$ in refluxing dichloromethane afforded rhodium complex **11**, which was isolated as brown crystals in 55% yield by recrystallization from Et $_2$ O 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, $J_{\text{P,Rh}} = 30.3$ 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 [(Ph $_4$ C $_4$ CO)MCl(PPh $_3$)Cl] (M = Rh, Ir), a key pre-catalyst for the acceptorless dehydrogenation by metal–ligand cooperation.^[30] The PPh $_3$ ligand in **11** shows a strong *trans*-influence (P2–Rh1–C4 169.20(5) $^\circ$), 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 phosphacyclopentadienone **12**. Triphos = CH $_3$ C(CH $_2$ PPh $_2$) $_3$, $n = 1$ or 2 .

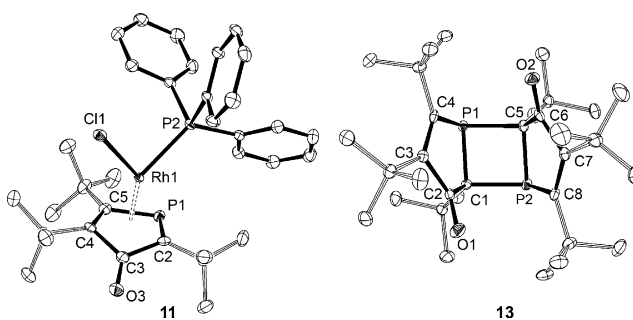


Figure 2. Molecular structures of **11** and **13** (ellipsoids set at 50% probability, hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [$^\circ$] for **11**: Rh1–P1 2.3297(5), Rh1–C2 2.2011(17), Rh1–C4 2.2595(16), Rh1–C5 2.1773(17), Rh–C3 2.5917(18), Rh1–P2 2.3678(4), P1–C2 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 PPh $_3$, as confirmed by ^{31}P , ^1H , and ^{13}C 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.

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Conflict of interest

The authors declare no conflict of interest.

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

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