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Synthesis and Reactivity of the Phosphorus Analogues of Cyclopentadienone, Tricyclopentanone, and Housene
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Abstract: The phosphorus analogues of cyclopentadienone, tricyclopentanone, and housene were accessed from bis(cyclopropenyl)diphosphene 4, which was prepared by mixing 1,2,3-tris-tert-butycyclopropenium tetrafluoroborate (1) and sodium phosphaethynolate [Na(OCP)(dioxane)]. 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]pentanone. 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-butycyclopentadienone A (R, R' = tBu; Scheme 1)\(^{[1]}\) a key cooperative ligand in Shvo's catalyst.\(^{[12]}\)

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 tetrahehedral D. On the other hand, irradiation of tris-tert-butyl-substituted dienone A (R = tBu, 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 = CH\(_2\), R = tBu, R' = CO\(_2\)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 coordinate 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 point into this chemistry, as both the required cyclopropenium cations and the phosphaethynolate anion (OCP)\(^{[11]}\) are nowadays readily available. In this study, we focus on 1,2,3-tris-tert-butycyclopentadienonium tetrafluoroborate (1)\(^{[12]}\). Addition of toluene to a mixture of [Na(OCP)(dioxane)] (n = 2.5–2.8) and I at −78°C gave a 1:1 mixture of 2 (δ\(^{1}P[H] = −231.7 \text{ ppm}\)) and 3 (δ\(^{31}P[H] = 119.0 \text{ ppm}; \text{Scheme } 2)\(^{[13]}\) that within 18 hours at 20°C fully converts into 1,3-diphosphatene-2,4-dione 3, which was isolated as a yellow powder in 97% yield (δ\(^{31}P[H] = 119.0 \text{ ppm}; δ\(^{31}C[H] = 224.8 \text{ ppm}; \text{Scheme } 2)\(^{[13]}\). 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=O bonds to yield 3,\(^{[15]}\) which is also supported by DFT

\[\text{Scheme 1. Illustrative examples of strained ring systems.}\]

\[\text{Scheme 2. Synthesis of 1,3-diphosphatene-2,4-dione 3.}\]

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Diphosphatetanedione 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; \( \delta^{31}\text{P}[\text{H}]=585.3\text{ ppm}\)\[16,17\]). 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 that the related bis(pentamethylcyclopentadienyl)diphosphene (Cp*P=P=CP*) has the cyclopentadienyl rings and P=P bond positioned anti to each other.\[19\] \( \delta^{31}\text{P}[\text{H}]=8.0\text{ kcal mol}^{-1} \), while the anti conformer is favored for the corresponding methyl-C1 analogue (\( \Delta \delta^{31}\text{P}[\text{H}]=-1.1\text{ kcal mol}^{-1} \)).\[13\]

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 \( \delta^{31}\text{P}[\text{H}]=53.5\) (P1), -169.1 ppm (P2), \( J_{PP}=171.0\) Hz. Single-crystal X-ray structure determination provided unequivocally the molecular structure of 5 (Figure 1, top right),\[13\] 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 136(10)). Although diphosphahousene 5 (P=H) bears six inequivalent tert-butyl groups, only 4 different \( \delta^{1}\text{H} \) and \( \delta^{13}\text{C}[\text{H}] \) NMR resonances were found at room temperature. Upon cooling to -80°C, the expected 6 sets of \( \delta^{3}\text{Bu} \) 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 (\( \Delta \delta^{31}\text{P}[\text{H}]=17.5\text{ kcal mol}^{-1} \) at \( \delta^{31}\text{P}[\text{H}]=1.1\text{ kcal mol}^{-1} \) to \( \delta^{31}\text{P}[\text{H}]=8.0\text{ kcal mol}^{-1} \)).

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 phosphahyphorcycle[1.1.0]butane 9 as intermediate (\( \Delta \delta=2.7\text{ kcal mol}^{-1} \), \( \Delta \delta^{*}=31.4\text{ kcal mol}^{-1} \), Scheme 4). Compound 9 cannot undergo the classical bicyclo[1.1.0]butane-butaediene rearrangement to give diphosphacyclopentadiene 10 owing to geometrical constraints\[23\] but affords 5 instead via an unprecedented tricyclopropene-housene rearrangement\[24\] affording 10 (\( \Delta \delta=7.2\text{ kcal mol}^{-1} \), \( \Delta \delta^{*}=38.8\text{ kcal mol}^{-1} \)).
followed by an electrocyclic ring closure ($\Delta E^* = 36.6$ kcal mol$^{-1};$ Scheme 4), but this is a higher energy process.

Next, we explored the thermal stability of diphospheta-

dione 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 ($8\text{P}^\text{H} = -384.1$ ppm, $\nu(\text{CO}) = 1722$ cm$^{-1};$ 85 %), 8 ($6\text{P}^\text{H} = 134.5$ (P1), 153.9 ppm (P2), $J_{PP} = 4.8$ Hz; 12 %; Scheme 3) and an unidentified minor product ($9\text{P}^\text{H} = -170.0$ ppm; 3 %; Supporting Information, Figures S9, S10). Major product 7 was isolated as colorless crystals in 55 % yield by recrystal-

ization of the crude from Et$_2$O at $-78^\circ$C and was charac-

terized crystallographically (Figure 1, bottom left). The molecular structure of 7 reveals a 1-phosphatricyclo-

[2.1.0]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 o-bond that was also reported for the all-carbon tricyclopentanones B$^{[29]}$ oB97X-D/6-31G(d,p) calculations$^{[30]}$ 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-phosphatricylo-pentan-3-one 6 via a [2+2] cycloaddition ($\Delta E = -11.8$ kcal mol$^{-1}$, $\Delta E^* = 25.9$ kcal mol$^{-1}$; Scheme 3). Subsequently, transient 6 undergoes a type 1 dyotropic rearrangement$^{[20]}$ to alleviate steric strain of the three neighboring tert-butyl groups providing 7 ($\Delta E = -23.5$ kcal mol$^{-1}$, $\Delta E^* = 30.4$ kcal mol$^{-1}$). After separating 7 from the product mixture, column chromatography of the residue under an inert atmosphere afforded 2-oxa-1,4-

diphasphacyclo[3.2.0]hepta-3,6-diene 8 as a yellow crystal-

linal solid in 7% yield (Scheme 3; Figure 1, bottom right)$^{[30]}$ which formally results from a [2+3] cycloaddition of the putative phosphacylobutadiene$^{[27]}$ and the rearranged phosphaketene 2, in analogy to the chemistry of (phosphanyl)-phosphaketenes recently reported by Grützmacher, Bertrand, and co-workers.$^{[19]}$

To access the P$_2$A, we targeted the metal-mediated valence isomerization of phosphatricyclopentadione 7$^{[29]}$ Satisfyingly, treatment of 7 with 1.0 equivalent of RhCl[(triphos)$_2$], in refluxing dichloromethane afforded rhodium complex 11, which was isolated as brown crystals in 55 % yield by recrystallization from Et$_2$O at $-78^\circ$C ($8\text{P}^\text{H}$: 32.9 (dd, $J_{PP} = 171.2$ Hz, $J_{PP} = 11.0$ Hz; P2), $-24.9$ (dd, $J_{PP} = 30.3$ Hz, $J_{PP} = 11.0$ Hz; P1), $\nu(\text{CO}) = 1644$ cm$^{-1}$; Scheme 5). The molecular structure of 11 (Figure 2, left)$^{[30]}$ revealed the formation of a unique ($\eta^1$-

phosphacyclopentadienone)rhodium(I) complex, which is the phosphorus analogue of [[Ph,C(=C)O)]MCl(triphos)]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)°), which leads to elongation of the Rh1-C4 bond (2.2595(16) Å) versus the shorter Rh1-C2 bond (2.2011(17) Å) and Rh1-C5 bond (2.1773(17) Å).

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 phosphacyclopenta-

dione 12 ($8\text{P} = 303.1$ ppm; $\delta^{13}$C = 195.4 ppm (P = C), $J_{PP} = 31.4$ Hz; Scheme 5) together with a mixture of [Rh(triphos),]Cl and PPh$_3$, as confirmed by $31^P$, H, 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 ($8\text{P} = -13.4$ ppm; Scheme 5) and characterized crystallographically (Figure 2, right).$^{[30]}$ The facile head-to-tail [2+2] dimerization of 12 was supported by DFT calculations, again at the oB97X-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$^{-1}$; $\Delta E^* = 21.9$ versus 25.2 kcal mol$^{-1}$), 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-diphasphetane-2,4-dione 3 grant access to the phosphorus
analouges of houseine, tricyclopentanone, and cyclopentadie-one, all of which display intriguing pericyclic reactions. Currently, we are developing decarbonylation strategies for phosphatricyclopentanone \[\text{7}^{(9)}\] ultimately leading to the elusive phosphacyclobutadiene and phosphatetrahedran.

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**Conflict of interest**

The authors declare no conflict of interest.

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The full “walk” of the P$_3$(t-Bu)$_3$ moiety over the phosphacyclobutadiene ring in 5 is prohibited, since the [1,3] sigmatropic shift from P$_2$ to C$_2$ is endothermic ($\Delta E = 23.0$ kcal mol$^{-1}$) due to the formation of an intermediate with a P=C instead of a C=C bond.


