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

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Dedicated to Professor Koop Lammersma

Abstract: The phosphorus analogues of cyclopentadienone, tricyclopentanone, and housene were accessed from bis(cyclopropenyl)diposphetedione 3, which was prepared by mixing 1,2,3-tris-tert-butylcyclopropenium tetrafluoroborates (1) and sodium phosphoethynolate [Na(OCP)(dioxane)]. While photoysis of 3 results in decarbonylation, yielding bis(cyclopropenyl)diphosphene 4 and after rearrangement diphosphahousene 5, thermolysis of 3 leads to phosphatriacyclo[2.1.0.02,5]pentanone, 6. 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[2.1.0.02,5]pentan-3-one B, which either converts into cyclopropylketene 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 houseone E (X = CO) that provides the antiaromatic cyclobutadiene F via CO elimination.[3] To date, only one thermally stable, all-carbon houseone E (X = CH3, R = t-Bu, R′ = CO2Bu)[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 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 houseone H,[8] and Sekiguchi’s monophosphahousene I[9] have been reported.

We anticipated the phosphorus analogue of C (cyclopropenylphosphaketene 2; Scheme 2) to be an ideal entry point into this chemistry, as both the required cyclopropenium cations and the phosphoethynolate anion (OCP) are nowadays readily available. In this study, we focus on 1,2,3-tris-tert-butylcyclopropenium tetrafluoroborat (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 (δ3[P][H] = -231.7 ppm) and 3 (δ3[P][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 79% yield (δ3[P][H] = 119.0 ppm; δ3[C][H] = 224.8 ppm, JCP = 43.5 Hz, CO; ν(CO) = 1627 cm⁻¹).[14] Evidently, intermediate 2, which we attribute to the phosphorus analogue of C,[15] dimerizes via a facile head-to-tail [2+2] cycloaddition of the P=C bonds to yield 3,[16] which is also supported by DFT
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 it to 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; $\delta^{31}$P[1H] = 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 a planar 4-membered phosphacyclobutene moiety (C3-P2-C1-C8). Although diphosphahousene 5 (P-E-E) bears six inequivalent tert-butyl groups, only four different 1H and 31P[H] NMR resonances 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 ($\Delta E_{\text{anti}} - \Delta E_{\text{syn}} = 17.5 \text{ kcal mol}^{-1}$ at oB97X-D/6-31G(d,p)).[13,22] and also found for triphosphahousene H.[9]

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 phosphacyclo[1.1.0]butane 9 as intermediate ($\Delta E = 2.7 \text{ kcal mol}^{-1}$, $\Delta E_{\text{syn}} = 31.4 \text{ kcal mol}^{-1}$; Scheme 4). Compound 9 cannot undergo the classical bicyclo[1.1.0]butane-buteni diene rearrangement to give phosphacyclopentadiene 10 owing to geometrical constraints,[23] but affords 5 instead via an unprecedented tricyclopentene-housene rearrangement ($\Delta E = -7.2 \text{ kcal mol}^{-1}$, $\Delta E_{\text{syn}} = 34.1 \text{ kcal mol}^{-1}$). In principle, 4 can also provide 5 via a vinylcyclopropene-cyclopentadiene rearrangement[24] affording 10 ($\Delta E = 7.8 \text{ kcal mol}^{-1}$, $\Delta E_{\text{syn}} = 38.8 \text{ kcal mol}^{-1}$),
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 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 resulted in the formation of 7 ($\delta^{13}$P[H] = −384.1 ppm, ν(CO) = 1722 cm$^{-1}$; 85 %). 8 ($\delta^{13}$P[H] = 134.5 (P1), 153.9 ppm (P2), $\delta_{J_{p-p}}$ = 4.8 Hz; 12 %; Scheme 3) and an unidentified minor product ($\delta^{13}$P[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).[38] The molecular structure of 7 reveals a 1-phosphatricycl[2.1.0]pentan-3-one framework (P1–B) with a remarkably small sum of angles at phosphorus (163.95(9)°), highlighting the tetrahedral-like 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 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$^{-1}$, $\Delta E^* = 25.9$ kcal mol$^{-1}$; Scheme 3). Subsequently, transient 6 undergoes a type I 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-diphosphabicyclo[3.2.0]hepta-3,6-diene 8 as a yellow crystaline solid in 7 % yield (Scheme 3; Figure 1, bottom right)[39] which formally results from a [2+3] cycloaddition of the putative phosphacyclobutadiene[7,27] and the rearranged phosphaketene 2, in analogy to the chemistry of (phosphonyl)phosphaketenes recently reported by Grützmacher, Bertrand, and co-workers.[28]

To access the P$_2$-A, we targeted the metal-mediated valence isomerization of phosphatricyclopentanone 7.[7,27] Satisfyingly, treatment of 7 with 1.0 equivalent of RhCl$_2$(PP$_3$)$_2$, in refluxing dichloromethane afforded bridgehead complex 11, which was isolated as brown crystals in 55 % yield by recrystallization from Et$_2$O at −78°C ($\delta^{13}$P[H]: 32.9 (dd, $J_{p-p}$ = 171.2 Hz, $J_{p-p}$ = 11.0 Hz; P2), −24.9 (dd, $J_{p-p}$ = 30.3 Hz, $J_{p-p}$ = 11.0 Hz; P1) ppm, ν(CO) = 1644 cm$^{-1}$; Scheme 5). The molecular structure of 11 (Figure 2, left)[39] revealed the formation of a unique ($\eta^1$-phosphacyclopentadienone)rhodium(I) complex, which is the phosphorus analogue of [(Ph$_3$C)$_2$COMCl(PP$_3$)$_2$](M = Rh, Ir), a key pre-catalyst for the acceptorless dehydrogenation by metal–ligand cooperation.[30] The P$_3$H$_2$ ligand in 11 shows a strong trans-influence (P$_2$-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).

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 phosphacyclopentadiene 12 ($\delta^{31}$P = 303.1 ppm; $\delta^{31}$C = 195.4 ppm (P = C), $\delta_{J_{p-p}}$ = 31.4 Hz; Scheme 5) together with a mixture of [Rh(triphos),Cl] and PPh$_3$, as confirmed by $^{31}$P, $^1$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 ($\delta^{31}$P = −13.4 ppm; Scheme 5) and characterized crystallographically (Figure 2, right).[38] 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$^{-1}$, respectively), which can be attributed to secondary orbital interactions in the transition state leading to the endo adduct.[32] In summary, cyclopropenylphosphaketene 2 and its dimer, 1,3-diphosphethane-2,4-dione 3 grant access to the phosphorus...
analogues of houseine, tricyclopentanone, and cyclopentadiene, all of which display intriguing pericyclic reactions. Currently, we are developing decarbonylation strategies for phosphatricyclopentanone \( \text{OCP} \) ultimately leading to the elusive phosphacyclobutadiene and phosphatetetrahedran.

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**Conflict of interest**

The authors declare no conflict of interest.

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[14] See the Supporting Information for further details.


The full “walk” of the \( \text{P}_1\text{C}_3(\text{tBu})_3 \) moiety over the phosphacyclobutadiene ring in 5 is prohibited, since the [1,3] sigmatropic shift from P2 to C2 is endothermic (\( \Delta \text{E} = 23.0 \text{ kcal mol}^{-1} \)) due to the formation of an intermediate with a P=C instead of a C=C bond.


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.


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