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Reactivity of a kinetically stabilized 1,3,6-triphosphafulvene toward some nucleophiles

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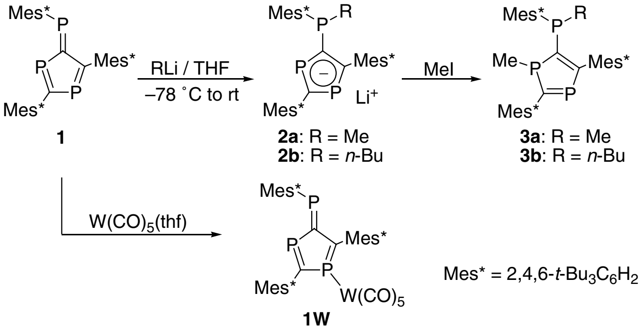
Abstract—A kinetically stabilized 1,3,6-triphosphafulvene displayed regioselective reactivity toward nucleophiles at the external phosphorus atom (position 6) to afford the corresponding phosphinodiphospholide anions, which gave phosphinodiphospholes after quenching with electrophiles, as well as being readily reduced by sodium naphthalenide suggesting properties similar to fulvenes.

We previously reported the formation and characterization of a sterically protected 1,3,6-triphosphafulvene **1** as a phosphorus congener of fulvene.[1] Compound **1** is a formal trimer of the phosphanylidene carbenoid [Mes*P=C(Br)Li],[2] resulting from the intermediary generation of phosphaalkyne [Mes*C≡P]. Fulvenes are a valence isomer of benzene and have widely been investigated as one of the most important cross-conjugated π-electron systems.[3] It is well established that the electrophilic fulvenes react with nucleophiles selectively at position 6 to afford the corresponding cyclopentadienides.[4] Moreover, fulvenes can readily be reduced by alkaline metals to afford the corresponding anionic species.[5,6] Taking the similarity between the phosphorus–carbon double bond and the carbon–carbon double bond into consideration,[7,8] **1** is expected to display reactivity toward nucleophiles as well as reducing reagents. In this paper, we report the reactions of **1** with alkyllithiums and lithium aluminum hydride followed by treatment with electrophiles. Additionally, reduction of **1** with sodium naphthalenide is described.

1,3,6-Triphosphafulvene **1**, prepared from 2,2-dibromo-1-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaethene [Mes*P=CBr$_2$],[9] was allowed to react with methyllithium to generate the corresponding phosphinodiphospholyl-anion **2a**. The formation of **2a** was monitored by ^{31}P NMR spectroscopy [δ_P = 223 (P1), 216 (P3), −31 (P6), $^2J_{P1P3}$ = 20 Hz, $^2J_{P1P6}$ = 15 Hz, $^3J_{P3P6}$ = 10 Hz] at room temperature.[10] Subsequently, the reaction mixture was treated with iodomethane and, after purification by silica-gel column chromatography, 5-phosphino-1*H*-[1,3]diphosphole **3a** (R = Me) was isolated in 51% yield.[11] In the ^{31}P NMR spectrum, peaks due to one sp^2 phosphorus atom and two phosphino groups were observed (Scheme 1).

The structure of **3a** was confirmed by X-ray crystallography and is displayed in Figure 1.[12] Two methyl groups are on P2 (position 1 according to IUPAC nomenclature) and P3, displaying (*R*,*R*) and (*S*,*S*) configurations probably as a result of steric congestion. The bulky Mes* groups are almost perpendicular, protecting the diphosphole ring effectively and thus, **3a** did not



Scheme 1.

Keywords: Phosphaalkenes; Conjugated system; Nucleophilic reaction; Reduction; Regioselectivity.

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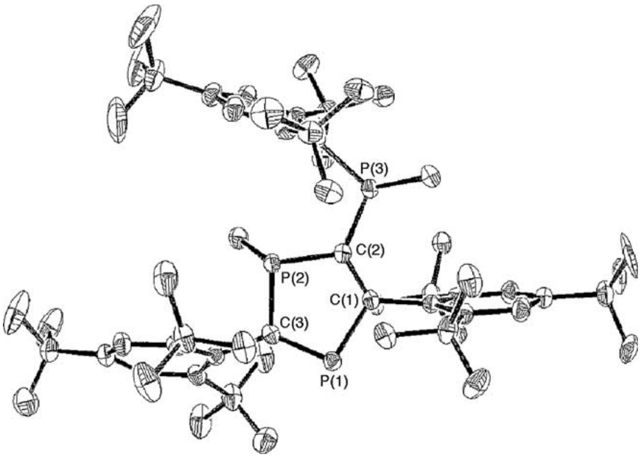

Figure 1. Molecular structure of **3a** (30% probability ellipsoids). Hydrogen atoms are omitted for clarity. The *o*- and *p*-*tert*-butyl groups in the C1–Mes* group and the *p*-*tert*-butyl group in the C3–Mes* group are disordered and atoms with predominant occupancy factors are shown. Selected bond lengths (Å) and angles (°): P1–C1 1.815(3), P1–C3 1.685(3), P2–C2 1.799(3), P2–C3 1.794(4), P2–Me 1.823(5), P3–C2 1.822(3), P3–Me 1.832(4), P3–Mes* 1.870(3), C1–C2 1.376(4), C1–Mes* 1.521(4), C3–Mes* 1.511(4), C1–P1–C3 98.2(2), C2–P2–C3 98.4(1), C2–P2–Me 110.8(2), C3–P2–Me 105.0(2), C2–P3–Mes* 105.9(1), C2–P3–Me 108.4(2), Mes*–P3–Me 111.9(2), P1–C1–C2 117.1(2), P1–C1–Mes* 118.6(2), C2–C1–Mes* 124.3(3), P2–C2–P3 121.5(2), P2–C2–C1 112.3(2), P3–C2–C1 125.8(2), P1–C3–P2 112.6(2), P1–C3–Mes* 134.9(3), P2–C3–Mes* 112.3(2).

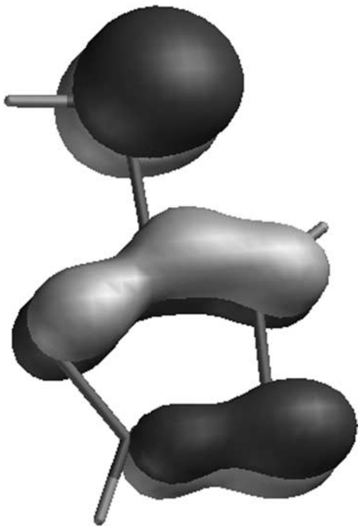

Figure 2. Drawing of LUMO of 1,3,6-triphosphafulvene **1′** (HF/6-31G*).

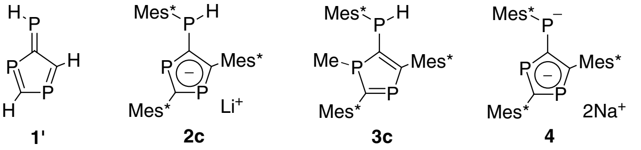

Chart 1.

decompose at room temperature in air. The P1–C3 distance indicates a phosphorus–carbon double bond, and the structural parameters of the 1*H*-[1,3]diphosphole ring are close to the reported 3,3′-1,1′-biphospholyl compound.[13] The reaction of iodomethane on P2 is consistent with the softness of the phosphorus and the iodomethane.[14,15] Although the bulk around P2 seems to be larger than that around P1 (position 3) as indicated by formation of **1W**,[1] the regioselective methylation might be due to formation of a thermodynamically favored (Me)P–C═P–C═C[P(Me) Mes*]–P skeleton.

Similar to fulvene, the external phosphorus atom (position 6) of **1** reacts with the employed nucleophile, revealing the electron-withdrawing effect of the [1,3]diphosphole ring. An ab initio calculation for 1,3,6-triphosphafulvene **1′** (HF/6-31G*) as a model indicates that the LUMO has the largest coefficient at the external phosphorus atom in agreement with the regioselective attack of nucleophile as shown in Figure 2.

In the reaction of **1** with butyllithium, the regioselective attack of butyllithium at the external phosphorus atom occurred to give the corresponding diphospholyl anion **2b** [$\delta_P = 223, 216, -2$] and, after the treatment with iodomethane, **3b** was obtained. The structure of **3b** was confirmed by NMR spectra[11] as well as X-ray crystallographic analysis (CCDC-236714, see Supporting information). Moreover, **1** was allowed to react with LAH (= lithium aluminum hydride) to generate diphospholyl anion **2c**, which afforded **3c** by quenching with iodomethane (60% yield) (Chart 1).[16]

Reduction of **1** with a single-electron reducing reagent showed the characteristic features of the triphosphafulvene structure. Compound **1** was allowed to react with sodium naphthalenide (ca. 3 equiv) and subsequently quenched with iodomethane at −78 °C to generate **3a** together with **3c** in a 2:1 ratio through an anionic intermediate **4**. Compound **3c** might be afforded due to the formation of the sodium salt of a **2c** equivalent in the reaction mixture.[17] The electron-accepting ability of **1** was measured by cyclic voltammetry, revealing that the reduction potential ($E_{1/2}$) was observed at −0.68 V versus Ag/AgCl (Fig. 3). The electron-accepting property of **1** corresponds to fulvene,[3–6] and the reduction potential of **1** is similar to that of phosphaalkenes.[2,7] The reversible redox wave in Figure 3 indicates that the anionic species generated from **1** is stable to some extent.

In summary, it has been verified that 1,3,6-triphosphafulvene **1** regioselectively reacts with nucleophiles at the external phosphorus atom to generate phosphinodiphospholyl anions **2**. The LUMO calculation of 1,3,6-triphosphafulvene is consistent with this reactivity. Diphospholyl anions **2** were allowed to react with iodomethane to give 5-phosphino-1*H*-[1,3]diphospholes **3** and the structure was analyzed by X-ray crystallography. As indicated by the CV measurement, **1** was readily reduced by sodium naphthalenide to generate the dianionic intermediate. These results suggest not only the correspondence of **1** with fulvenes, the carbon congeners, but also the usefulness of novel organophosphorus

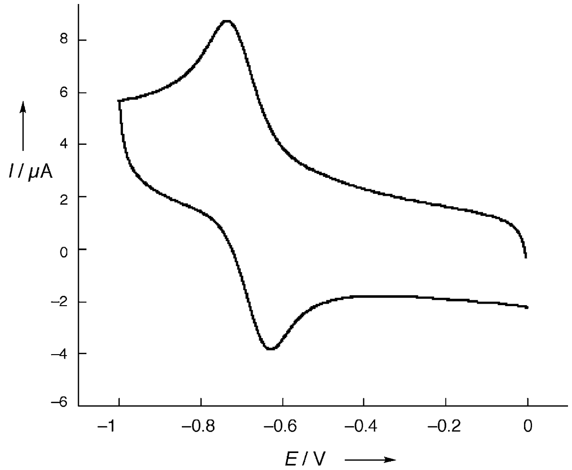

Figure 3. Cyclic voltammogram of **1**. Conditions: 1 mM in dichloromethane; supporting electrolyte: 0.1 M $n\text{Bu}_4\text{NClO}_4$ (TBAP); working electrode: glassy carbon; counter electrode: platinum wire; reference electrode: Ag/AgCl at 20 °C; scan rate: $50\,\text{mV}\,\text{s}^{-1}$; *E* = potential, *I* = current.

ring compounds, which can be applicable to materials such as ligands of metal complexes.[7] Attempts to isolate several anionic species of **2** as well as observation of radical anions generated from **1** are underway.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2004.07.144.

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9. The yield of **1** was improved up to 59% by using a 1:1 mixture of THF and hexane as the solvent.
10. Aromaticity of the 1,3-diphospholyl anion, indicating the stability of **2**, was verified by theoretical calculations: Dransfeld, A.; Nyulászi, L.; Schleyer, P. v. R. *Inorg. Chem.* **1998**, *37*, 4413.
11. **3a**: Yellow prisms ($\text{EtOH/CH}_2\text{Cl}_2$), mp 229–231 °C; $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3) δ 272 (dd, $^2J_{\text{P1P3}} = 43\,\text{Hz}$, $^3J_{\text{P3P6}} = 21\,\text{Hz}$, P3), 66 (dd, $^2J_{\text{P1P3}} = 43\,\text{Hz}$, $^2J_{\text{P1P6}} = 32\,\text{Hz}$, P1), −21 (dd, $^2J_{\text{P1P6}} = 32\,\text{Hz}$, $^3J_{\text{P3P6}} = 21\,\text{Hz}$, P6); ^1H NMR (400 MHz, CDCl_3) δ 7.51 (2H, s, arom), 7.37 (4H, s, arom), 1.51 (18H, s, *o*-*t*Bu), 1.48 (18H, s, *o*-*t*Bu), 1.39 (18H, s, *o*-*t*Bu), 1.39 (9H, s, *p*-*t*Bu), 1.29 (9H, s, *p*-*t*Bu), 1.23 (9H, s, *p*-*t*Bu), 0.93 (3H, d, $^2J_{\text{PH}} = 7.0\,\text{Hz}$, Me) (one methyl group was not determined due to overlap with peaks of the *t*-butyl groups); UV (hexanes) λ_{max}/nm (ε) 390 (5800), 290 (sh, 12,000); SIMS found: 895.6590; calcd for $\text{C}_{59}\text{H}_{93}\text{P}_3\text{+H}$: 895.6563. **3b**: $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3) δ 265 (dd, $^2J_{\text{P1P3}} = 50\,\text{Hz}$, $^3J_{\text{P3P6}} = 19\,\text{Hz}$, P3), 67 (dd, $^2J_{\text{P1P3}} = 50\,\text{Hz}$, $^2J_{\text{P1P6}} = 50\,\text{Hz}$, P1), −8 (dd, $^2J_{\text{P1P6}} = 50\,\text{Hz}$, $^3J_{\text{P3P6}} = 19\,\text{Hz}$, P6); ^1H NMR (400 MHz, CDCl_3, selected) δ 7.5 (6H, m, arom), 1,49 (36H, s, *t*Bu), 1.39 (18H, s, *t*Bu), 1.38 (9H, s, *t*Bu), 1.30 (9H, s, *t*Bu), 1.25 (9H, s, *t*Bu), 0.66 (3H, t, $^3J_{\text{HH}} = 7\,\text{Hz}$, Me in the butyl group), the methylene protons and the PMe protons were not assignable due to the overlap with those of the *t*-butyl groups; SIMS found: 937.7034; calcd for $\text{C}_{62}\text{H}_{99}\text{P}_3$: 937.7032.
12. Crystallographic data of **3a**: $\text{C}_{59}\text{H}_{93}\text{P}_3$, $M = 895.31$, triclinic $P\bar{1}$ (no 2), $a = 10.725(3)$, $b = 13.974(3)$, $c = 20.493(4)\,\text{Å}$, $\alpha = 96.711(4)$, $\beta = 91.820(4)$, $\gamma = 108.574(4)°$, $V = 2883.7(1)\,\text{Å}^3$, $Z = 2$, $D_{\text{calc}} = 1.031\,\text{g}\,\text{cm}^{-3}$, $\mu(\text{Mok}\alpha) = 0.136\,\text{mm}^{-1}$, $T = 243\,\text{K}$, $R = 0.084$ ($I > 2\sigma(I)$), $wR = 0.225$ (all data), $S = 1.10$ (608 parameters). Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Date Centre as supplementary publication numbers CCDC-236713. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk.
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15. Reaction of **2a** with ethanol resulted in giving an unidentified mixture.
16. ^{31}P NMR (162 MHz, C_6D_6) data: **2c**: δ 224 (ddd, $^2J_{\text{PP}} = 73\,\text{Hz}$, $^2J_{\text{PP}} = 15\,\text{Hz}$, $^3J_{\text{PH}} = 15\,\text{Hz}$, ring-P), 211 (dd, $^2J_{\text{PP}} = 15\,\text{Hz}$, $^3J_{\text{PP}} = 8\,\text{Hz}$, ring-P), −59 (ddd, $^2J_{\text{PP}} = 73\,\text{Hz}$, $^3J_{\text{PP}} = 8\,\text{Hz}$, $^1J_{\text{PH}} = 232\,\text{Hz}$, PH); **3c**: δ 260 (dd, $^2J_{\text{P1P3}} = 52\,\text{Hz}$, $^3J_{\text{P3P6}} = 12\,\text{Hz}$, P3), 64 (dddm, $^2J_{\text{P1P3}} = 52\,\text{Hz}$, $^2J_{\text{P1P6}} = 12\,\text{Hz}$, $^3J_{\text{PH}} = 10\,\text{Hz}$, P1), −64 (ddd, $^2J_{\text{P1P6}} = 12\,\text{Hz}$, $^3J_{\text{P3P6}} = 12\,\text{Hz}$, $^1J_{\text{PH}} = 240\,\text{Hz}$, P6) [$\delta_{\text{H}}$ 5.70 (PH)].
17. The PH proton of **3c** might have come from moisture in the reaction mixture or from the solvent itself (THF). Reduction of **1** with an excess amount of sodium naphthalenide followed by quenching with methanol gave unidentified products.