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Bis-3-oxo-λ^5-phosphole: Isolation, Structural Analyses, and Synthesis of Phosphorus-ylide Containing Conjugated Heterocycle

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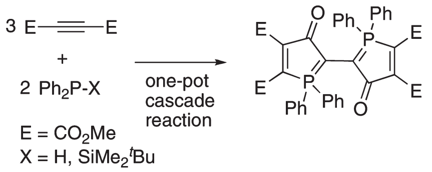

A new class of phosphorus-ylide containing conjugate heterocycle was isolated from a mixture of colored products of the reaction of a silylphosphine and dimethyl acetylenedicarboxylate. The structure was determined and the selective synthesis was developed. The indigo-like bis-phosphole structure appears a green to blue color, which is derived from the low energy-gap of the phosphole.

Conjugate heterocycles have been quite attractive because of their wide utilities in both electronic and optical functional materials.[1] Among them, phosphorus-containing conjugate heterocycles have received much attention. Thus, increasing numbers of reports have recently appeared concerning phospholes,[2,3] most of which are trivalent 1*H*-phospholes, or their oxides and sulfides. In contrast, phospholes with an ylide in a conjugate system have been rarely reported, although some examples of their synthesis had been reported in early 1970s.[4] Herein, we wish to report the first examples of a new class of conjugate heterocycles containing a phosphorus-ylide, 3-oxo-λ^5-phosphole (Figure 1a), isolated as a symmetrical bis-oxophosphole (Figure 1b).

On the course of our research using t-BuMe$_2$SiPPh$_2$ **1**,[5] we faced unexpected formation of a complex mixture of colored products in the reaction with dimethyl acetylenedicarboxylate (DMAD), when the reaction was conducted under rt.[6,7] Careful separation of the products by column chromatography afforded a number of colored materials, one of which was isolated as a green solid.[8] Conventional spectral analyses of the green compound gave only limited information about its detailed structure.[9] Careful assignments of ^{13}C signals with the aid of the 2D NMR spectra suggested the existence of one conjugate carbonyl carbon (166 ppm) and two alkenyl carbons (120 and 158 ppm) in addition to one ylidic carbon (90 ppm).[9] Characteristic multiple couplings of these carbon signals indicate that there are two phosphorus atoms with different connections around these carbons, in symmetrical position.[9] We speculated that the green compound might have a symmetrically connected bis-3-oxo-λ^5-phosphole **2a**, as depicted in Figure 1b.

Fortunately, recrystallization from ClCH$_2$CH$_2$Cl/MeOH gave a single crystal of **2a**·2ClCH$_2$CH$_2$Cl suitable for an X-ray diffraction study (Figure 2).[10] To the best of our knowledge, it is the first isolation of the phosphole ring with a 3-oxo-λ^5-phosphole structure.

The molecule has crystallographic C_i symmetry and comprises two 3-oxo-$\sigma^4\lambda^5$-phosphole ring fragments directly connected at each 2-position. It is in accordance with the presumption from the spectral analyses. Each phosphorus atom has a distorted tetrahedral environment: (C(1)−P−C(4) = 93.7(2)°, C(1)−P−C(15) = 119.3(2)°). Lengths of two C−P bonds are 1.744(5) Å (C(1)−P) and 1.821(6) Å

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(6) Selective 1:1 addition of **1** to DMAD proceeded at −78 °C.[5g] Silylphosphines also reacted with propiolates and alkynyl ketones to give the corresponding 1:1 adducts.[5g,7]

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(8) In this case, **2a** was isolated in only 7% yield. Most of the other separated colored materials still remained unidentified.

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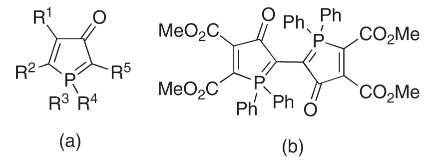

FIGURE 1. (a) 3-Oxo-λ^5-phosphole. (b) Bis-3-oxo-λ^5-phosphole **2a** (green material).

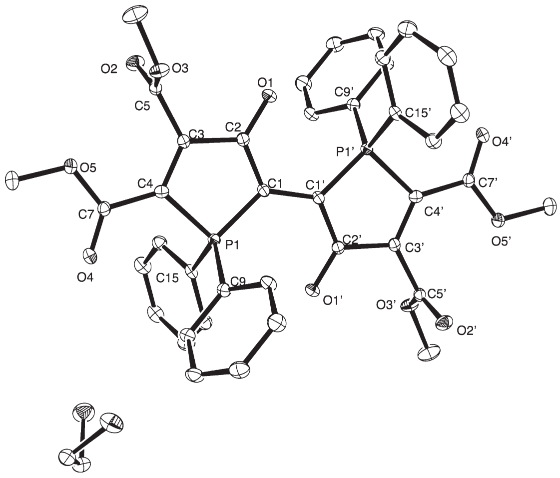

FIGURE 2. X-ray molecular structure of the bis-oxophosphole **2a** (primed atoms are generated by an inversion center).[10] H atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths [Å] and angles [deg]: C(1)−C(1)′ 1.439(7), P−C(1) 1.744(5), P−C(4) 1.821(6), C(1)−C(2) 1.396(6); C(1)−P−C(4) 93.7(2), C(1)−P−C(15) 119.3(2).[10]

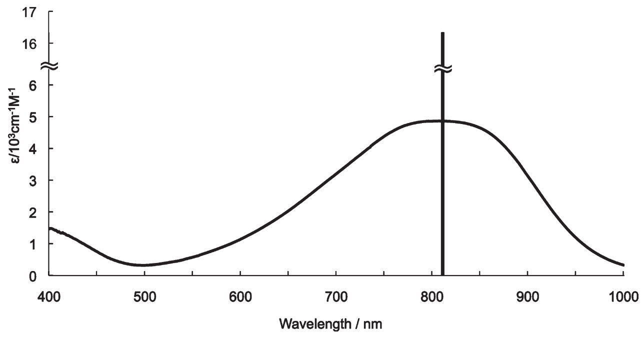

FIGURE 3. UV−vis spectrum of bis-oxophosphole (curve, observed for **2a** in $CHCl_3$ (9.3×10^{-5} M); perpendicular bar, calculated for **2d**.[9]

(C(4)−P), respectively, which clearly indicate an ylide structure of the C(1)−P bond. The shorter single bond (C(1)−C(2), 1.396(6) Å) shows a conjugation to the carbonyl group. Two oxophosphole rings are almost planar (torsion angles within ±1.1°). The slightly shorter C(1)−C(1)′ bond (1.439(7) Å) clearly shows the extension of conjugation through two rings. The broad absorption around the range of 500−1100 nm ($\lambda_{max} = 807$ nm, $\varepsilon = 4.9 \times 10^3$ dm^3 mol^{-1} cm^{-1}) also indicated the extended conjugation (Figure 3). A computational study using density functional theory methods (B3LYP/6-311G+(d,p)) gave an optimized structure for **2d** (R = R′ = Me) that was in excellent agreement with that obtained by the X-ray crystallography for **2a**.[9] The computed absorption maxima (λ_{max} = 811 nm) calculated by using TD-DFT methods correspond well with those determined experimentally (Figure 3). This result indicates that **2a** retains a planar structure in solution even though the central C−C single bond can rotate. A considerably small HOMO−LUMO gap (1.81 eV) is consistent with the π-conjugation extending across two oxophosphole moieties as expected from the X-ray structure. Low-lying HOMO and LUMO (−4.58 and −2.77 eV, respectively) are also characteristic properties of this new class of phospholes.[9]

This complicated condensation of five molecules into one most likely started from a nucleophilic attack of silylphosphane **1** to DMAD to give the 1:1 adduct **A**,[5g] plausibly followed by the multiple cascade reactions as proposed in Scheme 1.

The trivalent phosphorus atom of the initially formed 1:1 adduct **A** attacked the alkynyl carbon of DMAD to give the zwitter ionic intermediate **B**, followed by a nucleophilic acyl substitution at the ester group resulting in the formation of phosphonium intermediate **C**. This was then attacked by another **1** followed by desilylation to give the half ylide intermediate **D**. A similar cyclization process was then repeated with another DMAD to afford bis-oxophosphole **2a**. Since a bulky silyl group would interfere in each reaction (such as the addition of **1** to C), the use of a less hindered secondary phosphine gave the bis-oxophosphole **2** in relatively selective manner (Scheme 2).[11]

In summary, we have isolated a new phosphorus-ylide containing conjugate heterocycle, 3-oxo-λ^5-phosphole, as bis-oxophosphole. A selective approach by a five-molecule condensation was also established. Since oxophospholes

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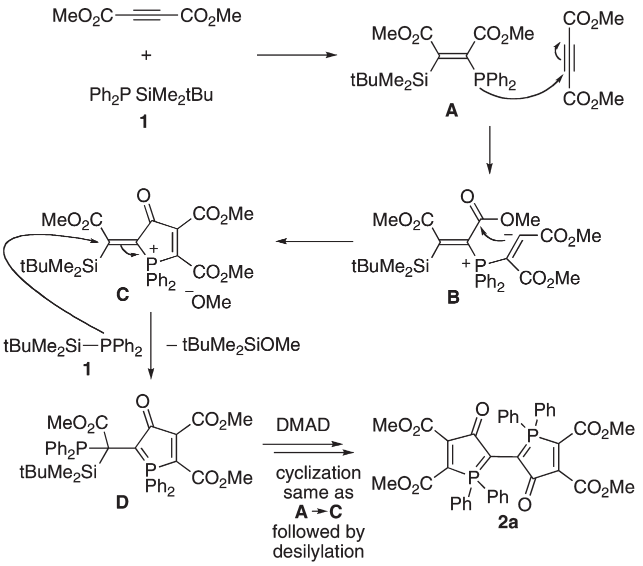
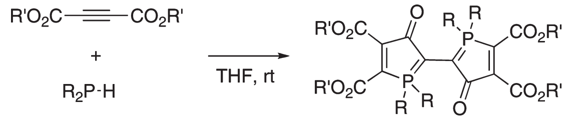
(9) Conventional spectral analyses (^{1}H, ^{13}C, ^{31}P NMR, IR, and FABMS) of **2a** gave only limited information about its detailed structure. However, its symmetrical structure was confirmed in addition to its composition (two phosphane parts and three alkynes). FABMS spectrum of **2a** showed the molecular ion peak at $m/z = 734$, which was a little (may be two MeO parts, vide infra) smaller than the sum of two phosphine parts (PPh_2) and three DMAD parts. However, ^{31}P NMR spectrum showed one singlet signal at 27 ppm, which suggested that the molecule has a symmetrical structure in which two phosphines are placed under magnetical equivalence. That only two methyl signals appeared in the ^{1}H NMR spectrum also supported a symmetric structure. No TBDMS group was observed in the ^{1}H NMR spectrum, which is in accordance with the result of the FABMS spectrum. The ratio of integrals of the methyl esters and the aromatic parts was 3:5, which should be 12:20 on the basis of FABMS. It is also in accordance with four methyl esters in the molecule, although three DMAD were embedded (two MeO groups were eliminated). Further information from careful assignments of ^{13}C signals with the aid of the 2D NMR spectra (HMQC, HMBC) suggested the existence of one conjugate carbonyl carbon (166 ppm) and two alkenyl carbons (120 and 158 ppm) in addition to one ylidic carbon (90 ppm). The carbon signals at 163 and 160 ppm gave cross peaks with Me ester singlets in the HMBC spectrum, which showed that these signals are the ester carbonyl carbons. The proton signal at 8.0 ppm (*ortho*-H) gave a cross peak with 166 ppm (conjugate ketone), 120 ppm (alkenyl), 118 ppm (Ph-*ipso*) and 90 ppm (ylide-C), which suggested a cyclic conjugate ylide structure. The carbon signals with characteristic multiple couplings, especially the ABX spin system of the signals at 90 and 120 ppm, indicate that there are two phosphorus atoms with different connections around those carbons, in a symmetrical position. The IR absorption (1693 cm^{-1}), assigned as conjugate carbonyls, also supported the above NMR analysis.This speculation was strongly supported by spectral analyses of the C4−C5 reduced 3-oxo-4,5-dihydro-$\sigma^4\lambda^5$-phosphole **3** obtained by hydride reduction of **2** as a pair of diastereomers.

(10) Crystal data. **2a**·$2ClCH_2CH_2Cl$: $C_{40}H_{32}O_{10}P_2 \cdot 2(C_2H_4Cl_2)$; MW = 932.50; monoclinic; space group $P2_1/c$ (No. 14); a = 13.15(3), b = 12.75(3), c = 14.29(3); b = 114.524(15); V = 2180(8) Å^3; Z = 2; m(Mo Kα) = 0.402 mm^{-1}; T = 150 K; 16357 reflections collected; R_{int} = 0.0582; $R(F)$ = 0.0847 for 3659 data with $I > 2\sigma(I)$, $wR(F^2)$ = 0.2438 for all 4966 independent data. CCDC-759535 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Date Centre via www.ccdc.cam.ac.uk/data_request/cif.

SCHEME 1. **Plausible Formation Mechanism of 2a**



SCHEME 2. **Selective Synthesis of Bis-oxophosphole 2**



2a-c

2a (R = Ph, R' = Me) 54%
2b (R = Ph, R' = Et) 33%
2c (R = c-Hex, R' = Me) 14%

having other substituents could not be accessed by this approach, generally applicable synthetic methods are now being developed in our lab and will appear elsewhere.

Experimental Section

Bis[4,5-bis(methoxycarbonyl)-3-oxo-1,1-diphenyl-$\sigma^4\lambda^5$-phosphole] 2a. A THF solution (3 mL) of DMAD (280 μL, 2.3 mmol, 4.0 equiv.) was added diphenylphosphine (107 mg, 0.57 mmol) at rt under N_2. After stirring for 3 h, a green precipitate was formed. After the mixture was concentrated to dryness, a small amount of MeOH was added to the residue. Pure **2a** was obtained by a simple filtration (54%). Alternatively, the product could be isolated by column chromatography on silica gel ($CHCl_3$/AcOEt = 3:1 to 1:1) despite low solubility of the compounds requiring a large amount of eluent. ^{1}H NMR ($CDCl_3/CF_3CO_2D$) δ 3.59 (s, 6 H, $CH_3\times2$), 3.79 (s, 6 H, $CH_3\times2$), 7.54−7.61 (m, 8 H, Ph-*meta*), 7.65−7.73 (m, 4 H, Ph-*para*), 7.92−7.99 (m, 8 H, Ph-*ortho*); ^{13}C NMR δ 52.8 (s, $CH_3\times2$), 53.1 (s, $CH_3\times2$), 90.1 (ABX, ylide-C × 2), 118.1 (ABX, Ph-*ipso*-C × 4), 119.8 (ABX, alkenyl-C × 2), 129.5 (t, J = 7.0 Hz, Ph-*meta*-C × 4), 133.3 (t, J = 5.6 Hz, Ph-*ortho*-C × 4), 134.1 (s, Ph-*para*-C × 2), 157.6 (t, J = 4.4 Hz, alkenyl-C × 2), 160.3 (t, J = 6.0 Hz, ester-C=O × 2), 163.1 (t, J = 8.7 Hz, ester-C=O × 2), 165.6 (t, J = 17.6 Hz, 3-C=O × 2); ^{31}P NMR δ 25.8; IR 1743, 1693 cm^{-1}; FABMS 734 [M]$^+$; HRMS calcd for $C_{40}H_{32}O_{10}P_2$ 734.1470, found 734.1443. Mp 210 °C (dec).

Bis[4,5-bis(ethoxycarbonyl)-3-oxo-1,1-diphenyl-$\sigma^4\lambda^5$-phosphole] 2b. By the same procedure for **2a**, **2b** was obtained as a green solid in 33% (813 mg) from Ph_2PH (4.4 mmol). ^{1}H NMR (C_6D_6/CF_3CO_2D) δ 0.54 (t, J = 7.1 Hz, 6 H, $CH_3\times2$), 1.07 (t, J = 7.1 Hz, 6 H, $CH_3\times2$), 3.55 (q, J = 7.1 Hz, 4 H, $CH_2\times2$), 4.26 (q, J = 7.1 Hz, 4 H, $CH_2\times2$), 7.18−7.30 (m, 12 H, Ph-*meta,para*), 8.14−8.22 (m, 8 H, Ph-*ortho*); ^{13}C NMR δ 13.1 (s, $CH_3\times2$), 13.2 (s, $CH_3\times2$), 62.2 (s, $CH_2\times2$), 63.6 (s, $CH_2\times2$), 93.1 (ABX, ylide-C × 2), 116.9 (ABX, Ph-*ipso*-C × 4), 121.3 (ABX, alkenyl-C × 2), 129.7 (t, J = 7.1 Hz, Ph-*meta*-C × 4), 133.4 (t, J = 5.9 Hz, Ph-*ortho*-C × 4), 134.5 (s, Ph-*para*-C × 2), 156.7 (t, J = 4.7 Hz, alkenyl-C × 2), 159.5 (t, J = 6.0 Hz, ester-C=O × 2), 162.8 (t, J = 8.6 Hz, ester-C=O × 2), 165.1 (t, J = 18.0 Hz, 3-C=O × 2); ^{31}P NMR δ 27.6; IR 1732, 1686, 1531, 1269, 1249, 1110, 1041 cm^{-1}; FABMS 791 [M+H]$^+$; HRMS calcd for $C_{44}H_{41}O_{10}P_2$ 791.2175, found 791.2156. Mp 245 °C (dec.).

Bis[4,5-bis(methoxycarbonyl)-3-oxo-1,1-dicyclohexyl-$\sigma^4\lambda^5$-phosphole] 2c. By the same procedure for **2a**, **2c** was obtained as a deep-blue solid in 14% (27 mg) from *c*-Hex_2PH (0.51 mmol) by a column chromatography on silica gel ($CHCl_3$/AcOEt = 3:1). ^{1}H NMR ($CDCl_3$) δ 1.07−2.11 (m, 40 H, $CH_2\times20$), 3.25−3.39 (br, 4 H, CH × 4), 3.77 (s, 6 H, $CH_3\times2$), 3.92 (s, 6 H, $CH_3\times2$); ^{13}C NMR δ 25.7 (s, $CH_2\times4$), 26.5 (t, J = 6.5 Hz, $CH_2\times4$), 26.5 (s, $CH_2\times4$), 26.7 (t, J = 7.2 Hz, $CH_2\times4$), 28.2 (s, $CH_2\times4$), 34.6 (t, J = 22.4 Hz, P-CH × 4), 52.4 (s, $CH_3\times2$), 52.8 (s, $CH_3\times2$), 83.0 (ABX, ylide-C × 2), 111.9 (ABX, alkenyl-C × 2), 162.8 (br, ester-C=O × 2), 164.5 (br, alkenyl-C × 2), 165.6 (t, J = 7.3 Hz, ester-C=O × 2), 168.0 (t, J = 14.8 Hz, 3-C=O × 2); ^{31}P NMR δ 47.2; FABMS 758 [M]$^+$; HRMS calcd for $C_{40}H_{56}O_{10}P_2$ 758.3348, found 758.3365. Mp 232−234 °C.

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Supporting Information Available: Experimental details and characterization data for **2a**−**2c**; ^{1}H, ^{13}C, ^{31}P NMR and 2D NMR spectra of **2a**−**2c**; CIF file of **2a**; and computational details of **2d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) A reaction of Ph_2PH with DMAD was reported to give 2,3-diphosphinosuccinate in ether,[12] but we could not reproduce the result; **2a** was formed instead as the main product in CH_2Cl_2, THF, and other solvents at rt in various ratios of Ph_2PH and DMAD. Although the reactions in Scheme 2 were conducted under optimized conditions, they also gave a number of colored materials probably because of the multiple mode of additions which occurred simultaneously in these reactions. Therefore, we could not identified the intermediates C, D, and others in the reaction mixture even when Ph_2PH and DMAD were reacted in a 1:2 ratio.

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