Synthesis of a Complexed 2,2-Bisphosphirane**

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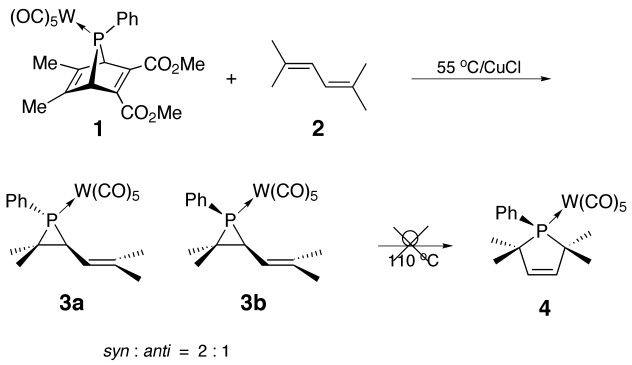
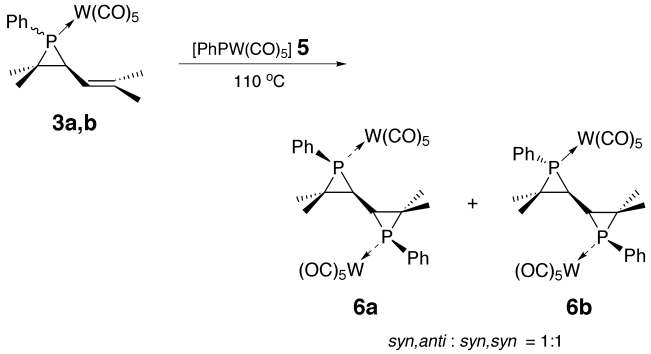
The past two decades saw an explosive growth in phosphorus-containing heterocycles of which the three-membered ring structure occupies a prominent place.[1] Even spiro-condensed systems containing this structural element have been synthesized.[2] Surprisingly absent in the plethora of heterocyclic organophosphorus structures are, however, the simple C–C-connected phosphiranes, in sharp contrast to the related bisoxiranes,[3] bisaziridines,[4] bissiliranes,[5] and bisthiiranes.[6] Even bisphosphirenes were described recently.[7] Here we report on the synthesis of a saturated analogue.

A convenient route to the three-membered phosphiranes is provided by the addition of in-situ-generated terminal-complexed phosphinidenes to olefins.[1b] As unencumbered reactive intermediates, phosphinidenes, such as [PhPW(CO)$_5$] (**5**), are considered to react as electrophilic singlet carbene-like species.[1b, 8] Double addition to conjugated dienes appears an obvious path to bisphosphiranes. However, after formation of the initial vinylphosphirane no second addition has yet been observed. Instead and in analogy to their hydrocarbon analogues, vinylphosphiranes with a *s-cisoid* conformation are subject both to a 1,3-sigmatropic shift yielding phospholenes and to epimerization at the phosphorus center.[1b, 9] Steric factors may contribute to the inability to add a second [RPW(CO)$_5$] unit in the systems studied thus far. We therefore decided to explore the double addition on a transoid noncyclic diene or more precisely the addition to a *s-trans* vinylphosphirane. A transoid conformation is preferred for 2,5-dimethyl-2,4-hexadiene (**2**)[10] and its methyl groups are considered small enough not to interfere with the second phosphinidene addition.

Reaction of [PhPW(CO)$_5$] (**5**), generated from the 7-phosphanorbornadiene complex **1**, with diene **2** at 55 °C in the presence of CuCl affords the *syn*- and *anti*-vinylphosphiranes **3a** and **3b**, respectively, in a 2:1 ratio in 76 % yield . In this case *syn* and *anti* refer to the orientation of the [W(CO)$_5$] with respect to the vinyl group. These isomers were distinguished based on their ^{31}P and ^{1}H NMR data. The major product isolated by crystallization is the *syn* isomer **3a**, whose olefinic proton is 0.25 ppm more deshielded ($\delta_H = 4.97$; no P-phenyl shielding), whose phosphorus atom is 18.2 ppm more deshielded ($\delta_P = -118.3$), and whose $^{1}J_{P,W}$ coupling is 7.8 Hz larger (256.2 Hz). All of these findings are in agreement with earlier assignments for cyclic *syn*-vinylphosphiranes.[11] The *cis*/*trans* and *E*/*Z* assignments of the methyl substituents are based on a combination of COSY and NOE NMR measurements. For example, for **3a** NOE interactions were observed between the phosphirane ring proton and the *trans*-methyl group and between the olefinic proton and the *E*-CH$_3$ group.



To explore whether the vinyl groups of **3a, b** are susceptible to a second phosphinidene addition they were treated with an additional equivalent of [PhPW(CO)$_5$] at 110 °C (without CuCl). Monitoring the reaction mixture by ^{31}P NMR spectroscopy showed indeed the formation in about 50 % yield of the diastereomeric bisphosphirane complexes (**6a**) (*syn*,*anti* isomer) and **6b** (*syn*,*syn* isomer) in a 1:1 ratio . The *syn*,*anti* isomer is easily recognized by its set of doublets ($\delta = -125.7$ and -135.0, $J_{P,P}$ 31.7 Hz) and the *syn*,*syn* form by its characteristic singlet ($\delta = -126.1$) in the ^{31}P NMR spectrum. Both products were isolated in 25 % yield and fully characterized by mass spectrometry, and ^{31}P, ^{13}C, and ^{1}H NMR spectroscopy. Interestingly, the ^{13}C NMR spectrum of the *syn*,*syn* isomer displays an AA′X system (A,A′ are P atoms) with a second-order line pattern (5 + 3) for the spiro-carbon atom (X).[12] The *anti*,*anti* isomer, if present, could not be detected.



Heating *syn*-vinylphosphirane **3a** in toluene (both with and without CuCl) at 110 °C for 1 h does not give detectable amounts of phospholene **4**, as expected, but instead leads to P-epimerization (yielding *anti* **3b**) and formation of bisphosphiranes **6a** and **6b** in a 1:1 ratio. Reaction of **3a** with [PhPW(CO)$_5$] at 110 °C also gives a 1:1 mixture of **6a** and **6b**.

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We attribute the equal formation of the *syn*,*anti*- and *anti*,*anti*-bisphosphiranes (and no *anti*,*anti*) from both the reaction of **3a** and the 2:1 mixture of **3a** and **3b** to occur thermodynamically as a result of P-epimerization and intermolecular transfer of the phosphinidene complex.

The *syn*,*syn* conformation of the C_2-symmetrical complex **6b** was established unequivocally by a single-crystal X-ray structure determination,[13] which revealed the expected geometrical features (Figure 1). The P–C2 and P–C3 bond

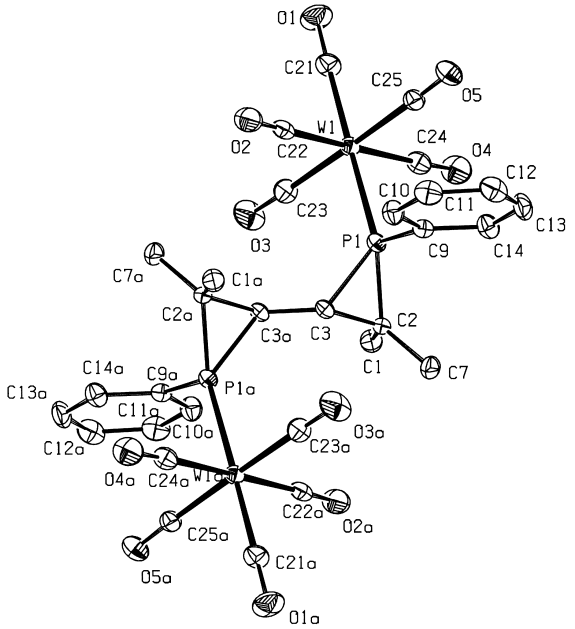

Figure 1. Structure of **6b**. Hydrogen atoms are omitted for clarity. Selected distances [Å] and angles [°]: P1-C2 1.848(5), P1-C3 1.842(5), C2-C3 1.537(7), C3-C3a 1.501(7), P1-W1 2.5031(13), P1-C9 1.809(5); W1-P1-C9 114.98(16), C2-P1-C3 49.2(2), P1-C3-C2 65.6(3), P1-C3-C3a 121.0(3), P1-C3-C3a-P1a 180.0(3).

lengths of 1.848(5) and 1.842(5) Å, respectively, and the C-P-C bond angle of 49.2(2)° are typical for $[W(CO)_5]$-complexed phosphiranes. The connecting C3–C3a bond of 1.501(7) Å appears relatively short but its length is similar to that in biscyclopropane (1.517 Å).[14] The ab initio MP2/6-31G*-optimized geometry of uncomplexed *syn*,*syn*-bisphosphirane **7** (devoid of substituents, Figure 2) illustrates the stabilizing effect of the $[W(CO)_5]$ group and shows the interaction between the two rings to be minimal with a C–C bond length of 1.499 Å. Energy calculations at the G2MP2 level (to obtain ΔH_f values) in conjunction with an elaborate set of isodesmic

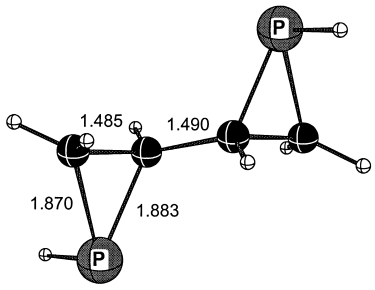

Figure 2. MP2/6-31G* structure of **7**.

reactions do not indicate an increment in strain energy of the phosphirane ring. Thus, even though the computed strain energy for **7** of 39.59 kcal mol^{-1} is slightly less than twice the value of 21.27 kcal mol^{-1} reported for C_2PH_5,[2d] the energy difference of 2.95 kcal mol^{-1} can be accounted for by the substituent effect. For example, the strain energy of the phosphirane already reduces by 1.05 kcal mol^{-1} (also at the G2MP2 level) on C-substituting the ring with a methyl group.

Experimental Section

NMR spectra were recorded on Bruker AC 200, MSL 400 (^{1}H, ^{13}C), and WM 250 (^{31}P) spectrometers using $SiMe_4$ (^{1}H, ^{13}C) or 85 % H_3PO_4 (^{31}P) as external standards. High-resolution mass spectra (HR-MS) were recorded on a Finnigan MAT 90 and FT-IR spectra on a Mattson 630 Galaxy spectrophotometer. Elemental analysis were performed by Micro-analytischer Labor Pascher, Remagen-Bandorf (Germany).

3a, b: Complex **1** (0.51 g, 0.77 mmol) and 2,5-dimethyl-2,4-hexadiene (85 mg, 0.77 mmol) were heated at 60 °C for 3 h in toluene with CuCl (56 mg, 56 mmol). After evaporation of the solvent, the residue was chromotographed over silica with pentane/toluene (4/1) to yield a 2:1 isomeric mixture of **3a** and **3b** (0.32 g; 76 %) as determined by ^{31}P NMR spectroscopy. **3a**: m.p. 70–71 °C (pentane); ^{31}P NMR ($CDCl_3$): $\delta = -118.3$ (^1J(P,W) = 256.2 Hz); ^{13}C NMR ($CDCl_3$): $\delta = 198.0$ (d, ^2J(C,P) = 29.9 Hz; *cis*-CO), 195.6 (d, ^2J(C,P) = 8.1, ^1J(C,W) = 125.7 Hz; *trans*-CO), 138.3 (d, ^3J(C,P) = 8.9 Hz; C=*C*(CH$_3$)$_2$), 135.7 (d, ^1J(C,P) = 24.6 Hz; *ipso*-Ph), 132.1 (d, ^3J(C,P) = 10.2 Hz; *m*-Ph), 129.7 (d, ^4J(C,P) = 2.0 Hz; *p*-Ph), 128.6 (d, ^2J(C,P) = 9.1 Hz; *o*-Ph), 118.0 (d, ^2J(C,P) = 3.3 Hz; *C*=C(CH$_3$)$_2$), 35.5 (d, ^1J(C,P) = 15.4 Hz; PCH), 30.4 (d, ^1J(C,P) = 17.2 Hz; P*C*(CH$_3$)$_2$), 25.6 (d, ^2J(C,P) = 2.7 Hz; *trans*-PC(*C*H$_3$)$_2$), 25.5 (d, ^4J(C,P) = 3.1 Hz; (*E*)-C=C(*C*H$_3$)$_2$), 21.7 (d, ^2J(C,P) = 9.1 Hz; *cis*-PC(*C*H$_3$)$_2$), 19.1 (d, ^4J(C,P) = 2.6 Hz; (*Z*)-C=C(*C*H$_3$)$_2$); ^{1}H NMR ($CDCl_3$): $\delta = 7.44$–7.18 (m, 5H, Ph), 4.97 (m, ^3J(H,P) = 6.76, ^3J(H,H) = 8.10, ^4J(H,H) = 1.4 Hz, 1H; CH=C), 2.49 (pseudo-t, ^2J(H,P) = 8.10, ^3J(H,H) = 8.10 Hz, 1H; CHP), 1.86 (d, ^5J(H,P) = 3.68 Hz, 3H; (*Z*)-C=C(CH$_3$)), 1.74 (d, ^5J(H,P) = 5.53 Hz, 3H; (*E*)-C=C(CH$_3$)), 1.34 (d, ^3J(H,P) = 18.29 Hz, 3H; *cis*-CH$_3$), 1.13 (d, ^3J(H,P) = 12.19 Hz, 3H; *trans*-CH$_3$); HR-MS: calcd for $C_{19}H_{19}O_5PW$ (%): 542.04800, found: 542.04806. **3b**: ^{31}P NMR (toluene): $\delta = -136.5$ (^1J(P,W) = 248.4 Hz); ^{13}C NMR ($CDCl_3$): $\delta = 198.4$ (d, ^2J(C,P) = 29.7 Hz; *cis*-CO), 196.0 (d, ^2J(C,P) = 8.1, ^1J(C,W) = 125.7 Hz; *trans*-CO), 136.6 (d, ^3J(C,P) = 6.0 Hz; C=*C*(CH$_3$)$_2$), 133.3 (d, ^3J(C,P) = 9.9 Hz; *m*-Ph), 129.7 (d, ^4J(C,P) = 2.0 Hz; *p*-Ph), 128.4 (d, ^2J(C,P) = 9.1 Hz; *o*-Ph), 117.3 (d, ^2J(C,P) = 7.2 Hz; *C*=C(CH$_3$)$_2$), 36.7 (d, ^1J(C,P) = 16.7 Hz; PCH), 29.3 (d, ^1J(C,P) = 15.5 Hz; P*C*(CH$_3$)$_2$), 28.1 (d, ^2J(C,P) = 6.5 Hz; *cis*-PC(*C*H$_3$)$_2$), 25.7 (d, ^4J(C,P) = 2.4 Hz; (*E*)-C=C(*C*H$_3$)$_2$), 19.7 (d, ^2J(C,P) = 2.4 Hz; *trans*-PC(*C*H$_3$)$_2$), 18.7 (d, ^4J(C,P) = 1.9 Hz; (*Z*)-C=C(*C*H$_3$)$_2$); ^{1}H NMR ($CDCl_3$): $\delta = 7.12$–7.54 (m, 5H, Ph), 4.72 (m, CH=C), 2.32 (d, ^3J(H,H) = 8.90 Hz, 1H; CHP), 1.94 (m, 3H, (*Z*)-C=C(CH$_3$)), 1.77 (d, ^5J(H,P) = 4.02 Hz, 3H; (*E*)-C=C(CH$_3$)), 1.49 (d, ^3J(H,P) = 19.15 Hz, 3H; *cis*-CH$_3$), 1.29 (d, ^3J(H,P) = 11.54 Hz, 3H; *trans*-CH$_3$).

6a, b: Complex **1** (0.88 g, 1.3 mmol) was heated at 110 °C for 20 h with a 2:1 mixture of *syn*:*anti* isomers of vinylphosphirane (**3**) (0.98 g, 1.8 mmol) in toluene (5 mL). The solution was concentrated to a volume of 3 mL and pentane (6 mL) was added. Complex **6b** precipitated as a white solid (0.33 g, 25 %). The extract was evaporated to dryness and the residue was chromatographed over silica, starting with pentane as eluent, and slowly converting to toluene to give complex **6a** (0.29 g, 22 %). **6a** (*syn*, *anti* isomer): m.p.:179–180 °C (decomp); ^{31}P NMR ($CDCl_3$): $\delta = -125.7$ (d, ^1J(W,P) = 256.9, ^3J(P,P) = 31.7 Hz), -135.0 (d, ^1J(W,P) = 256.0, ^3J(P,P) = 31.5 Hz); ^{13}C-NMR: $\delta = 197.9$ (d, ^2J(P,C) = 30.3 Hz; *trans*-CO), 197.1 (d, ^2J(P,C) = 27.1 Hz; *trans*-CO), 195.6 (d, ^2J(P,C) = 8.0 Hz; *cis*-CO), 195.5 (d, ^2J(P,C) = 7.8 Hz; *cis*-CO), 135.5 (^1J(P,C) = 26.7 Hz; *ipso*-Ph), 133.3 (d, ^3J(P,C) = 9.7 Hz, *m*-Ph), 131.8 (^1J(P,C) = 27.5 Hz; *ipso*-Ph), 131.8 (d, ^3J(P,C) = 10.4 Hz; *m*-Ph), 130.4 (d, ^4J(P,C) = 1.8 Hz; *p*-Ph), 130.1 (d, ^4J(P,C) = 1.0 Hz; *p*-Ph), 129.1 (d, ^2J(P,C) = 9.0 Hz; *o*-Ph), 128.9 (d, ^2J(P,C) = 9.3 Hz; *o*-Ph), 36.0 (dd, ^1J(P,C) = 19.3, ^2J(P,C) = 3.6 Hz; *anti*-PCH), 35.2 (dd, ^1J(P,C) = 18.4, ^2J(P,C) = 4.5 Hz; *syn*-PCH), 28.8 (d, ^1J(P,C) = 15.4 Hz; *syn*-P*C*(CH$_3$)$_2$), 28.4 (dd, ^1J(P,C) = 13.3, ^3J(P,C) = 1.4 Hz; *anti*-P*C*(CH$_3$)$_2$), 28.2 (d, ^2J(P,C) = 6.7 Hz; *cis*(*anti*)-PC(*C*H$_3$)$_2$),

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26.4 (d, ^2J(P,C) = 2.4 Hz; *trans*(*syn*)-PC(CH_3)$_2$), 21.7 (d, ^2J(P,C) = 8.6 Hz; *cis*(*syn*)-PC(CH_3)$_2$), 20.0 (d, ^2J(P,C) = 2.7 Hz; *trans*(*anti*)-PC(CH_3)$_2$); ^{1}H NMR ($CDCl_3$): δ = 7.2 – 7.4 (m, 10H, Ph), 1.72 (d, ^3J(H,P) = 17.45 Hz, 3H; *cis*(*syn*)-PC(CH_3)$_2$), 1.66 (d, ^3J(H,P) = 19.23 Hz, 3H; *cis*(*anti*)-PC(CH_3)$_2$), 1.64 (d, ^3J(H,P) = 10.65 Hz, 3H; *trans*(*anti*)-PC(CH_3)$_2$), 1.39 (m, 2H; PCH), 1.27 (d, ^3J(H,P) = 12.01 Hz, 3H; *trans*(*syn*)-PC(CH_3)$_2$). **6b** (*syn*,*syn* isomer): m.p. 179 – 180 °C (decomp); ^{31}P NMR: ($CDCl_3$): δ = – 126.1 (^1J(P,W) = 217.2 Hz); ^{13}C NMR: δ = 197.1 (m, $^{(2+5)}J$ = 29.6 Hz; *trans*-CO), 195.6 (m, $^{(2+5)}J$(P,C) = 7.6 Hz; *cis*-CO), 134.9 (m, $^{(1+4)}J$ = 27.7 Hz; *ipso*-Ph), 131.8 (m, $^{(3+6)}J$ = 11.6 Hz; *m*-Ph), 130.2 (s, *p*-Ph), 128.8 (m, $^{(2+5)}J$ = 9.4 Hz; *o*-Ph), 34.5 (m, $^{(1+2)}J$ = 13.2 Hz; PCH), 29.2 (m, $^{(1+3)}J$ = 14.0 Hz; P*C*(CH_3)$_2$), 25.5 (s, *trans*-PC(CH_3)$_2$), 21.5 (m, $^{(2+4)}J$ = 8.4 Hz; *cis*-PC(CH_3)$_2$); ^{1}H NMR ($CDCl_3$): δ = 7.2 – 7.4 (m, 10H, Ph), 1.78 (s, 2H, CHP), 1.69 (m, ^3J(H,P) = 17.50 Hz, 6H; *cis*-CH_3), (m, ^3J(H,P) = 12.15 Hz, 6H; *trans*-CH_3); HR-MS: calcd for $C_{30}H_{24}O_{10}P_2W_2$ (%): 973.98645; found: 973.98637; IR (KBr): $\tilde{\nu}$ = 2073, 1950 cm^{-1} (CO).

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[13] Crystal structure determination of $C_{30}H_{24}O_{10}P_2W_2$, M_r = 974.11, colorless, space group $P\bar{1}$ (no. 2), a = 8.9501(7), b = 12.4181(6), c = 15.7582(10) Å, α = 88.342(4), β = 83.656(6), γ = 71.097(5)°, V = 1646.8(2) Å^3, Z = 2, ρ = 1.964 g cm^{-3}, μ(Mo$_{K\alpha}$) = 7.13 mm^{-1}. A total of 10787 reflections were measured at 150 K on a CAD4T/rotating anode diffractometer (λ = 0.71073 Å) and averaged in a unique set of 7569 reflections (R_{av} = 0.036). The structure was solved by Patterson methods (DIRDIF-96) and refined on F^2 (SHELXL97) to a final $R1$ = 0.0312 (6350 reflections with $I > 2\sigma(I)$; $wR2$ = 0.072; S = 1.045). The data ware corrected for absorption using PLATON/DELABS. Hydrogen atoms were taken into account at calculated positions. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-138219. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Micellization versus Cyclodextrin – Surfactant Complexation**

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Upon addition of cyclodextrin (CD) to a surfactant solution, a considerable change in the physicochemical properties can be observed, that is, the surface tension of the surfactant solution usually increases.[1] When a concentration of cyclodextrin well in excess of the surfactant concentration is reached, the surface tension approaches that of pure water, indicating that neither surfactant – cyclodextrin complexes nor cyclodextrins themselves are surface active. Other properties such as cloud point, molar conductance, sodium ion activity, ultrasonic properties, spectral behavior, and hydrophobicity are modified by the addition of CD's. It has traditionally been assumed that the cyclodextrin molecules complex the monomers of the surfactant in such a way that the process of micellization will only begin once the surfactant monomers have saturated the cyclodextrin capacity for complexation. The strength of CD – hydrocarbon chain interactions increases for the common water-soluble ionic surfactants as the length of the alkyl chains increases.[2] The large diameter of β-cyclodextrin allows the hydrocarbon chain to coil inside the cavity.[3]

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