

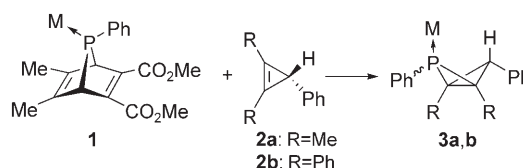
DOI: 10.1002/anie.200502248

 Valence Isomerization of 2-Phosphabicyclo-  
 [1.1.0]butanes\*\*

 J. Chris Slootweg, Steffen Krill, Frans J. J. de Kanter,  
 Marius Schakel, Andreas W. Ehlers, Martin Lutz,  
 Anthony L. Spek, and Koop Lammertsma\*

The unique electronic properties of the strained bicyclo[1.1.0]butanes<sup>[1]</sup> are enhanced by the heteroatoms in the molecular frame. Illustrative is the bond-stretch isomerization of the P<sub>2</sub>C<sub>2</sub> and P<sub>2</sub>B<sub>2</sub> bicycles.<sup>[2]</sup> However, very few systems are known with a single heteroatom,<sup>[3]</sup> probably because of their high reactivity, which is only moderated when the heteroatom occupies a bridgehead position as in the 1-aza derivatives.<sup>[4]</sup> The increased reactivity of the hetero systems is due to the valence isomerization to which the bicyclo[1.1.0]butanes are prone. We now report on the first 2-phospha derivatives.<sup>[4]</sup>

The carbene-like phosphinidene Ph-P=W(CO)<sub>5</sub><sup>[5]</sup> was generated in situ by cheletropic elimination from **1** at 110 °C in toluene and then allowed to react with cyclopropene **2a**<sup>[6]</sup> (Scheme 1). This led to the desired W(CO)<sub>5</sub>-complexed 2-phosphabicyclo[1.1.0]butanes *exo*-**3a** ( $\delta^{31}\text{P} = -85.1$  ppm) and *endo*-**3a** ( $\delta^{31}\text{P} = -36.7$  ppm)<sup>[7]</sup> in a 10:9 ratio, which were isolated in 69% yield as colorless solids. The remarkably



**Scheme 1.** Synthesis of the 2-phosphabicyclo[1.1.0]butanes **3**.  
 M = W(CO)<sub>5</sub>.

[\*] J. C. Slootweg, Dr. F. J. J. de Kanter, Dr. M. Schakel, Dr. A. W. Ehlers, Prof. Dr. K. Lammertsma  
 Department of Organic and Inorganic Chemistry  
 Faculty of Sciences  
 Vrije Universiteit  
 De Boelelaan 1083, 1081 HV, Amsterdam (The Netherlands)  
 Fax: (+31) 20-598-7488  
 E-mail: lammert@chem.vu.nl

Dr. S. Krill, Prof. Dr. K. Lammertsma  
 Formerly associated with the Department of Chemistry  
 University of Alabama at Birmingham  
 Birmingham, AL 35294 (USA)

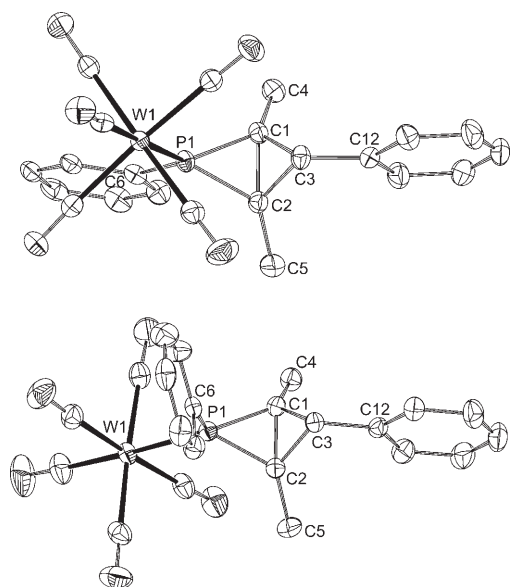
Dr. M. Lutz, Prof. Dr. A. L. Spek  
 Bijvoet Center for Biomolecular Research  
 Crystal and Structural Chemistry  
 Utrecht University  
 Padualaan 8, 3584 CH, Utrecht (The Netherlands)

[\*\*] This work was supported by the Council for Chemical Sciences of the Netherlands Organization for Scientific Research (NWO/CW).



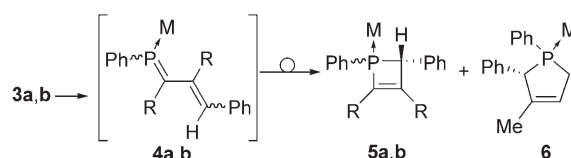
Supporting information for this article is available on the WWW under <http://www.angewandte.org> or from the author.

stable products were characterized by single-crystal X-ray analyses, which showed puckered geometries with P1-C1-C2-C3 folding angles of  $-114.66(15)^\circ$  for *exo-3a* and  $-120.65(14)^\circ$  for *endo-3a*, and transannular C1-C2 bonds of 1.516(3) and 1.550(3) Å, respectively (Figure 1). The flatter



**Figure 1.** The displacement ellipsoid plot of *exo-3a* (top) and *endo-3a* (bottom) with ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å], angles [°], and torsion angles [°] for *exo-3a*: W1–P1 2.5013(6), P1–C1 1.808(2), P1–C2 1.811(2), P1–C6 1.820(2), C1–C2 1.516(3), C1–C3 1.515(3), C1–C4 1.500(3), C2–C3 1.512(3), C2–C5 1.505(3), C3–C12 1.488(3); C1–P1–C2 49.52(10), P1–C1–C2 65.35(12), P1–C1–C3 96.79(15), C2–C1–C3 59.83(15), C2–C1–C4 139.6(2), P1–C2–C1 65.13(12), P1–C2–C3 96.78(15), C1–C2–C3 60.06(15), C1–C2–C5 141.4(2), C1–C3–C2 60.11(15); P1–C1–C2–C3  $-114.66(15)$ . *endo-3a*: W1–P1 2.4851(5), P1–C1 1.801(2), P1–C2 1.792(2), P1–C6 1.823(2), C1–C2 1.550(3), C1–C3 1.511(3), C1–C4 1.502(3), C2–C3 1.521(3), C2–C5 1.500(3), C3–C12 1.495(3); C1–P1–C2 51.11(9), P1–C1–C2 64.13(11), P1–C1–C3 100.05(14), C2–C1–C3 59.57(14), C2–C1–C4 135.80(19), P1–C2–C1 64.76(11), P1–C2–C3 100.08(13), C1–C2–C3 58.94(13), C1–C2–C5 136.7(2), C1–C3–C2 61.49(13); P1–C1–C2–C3  $-120.65(14)$ .

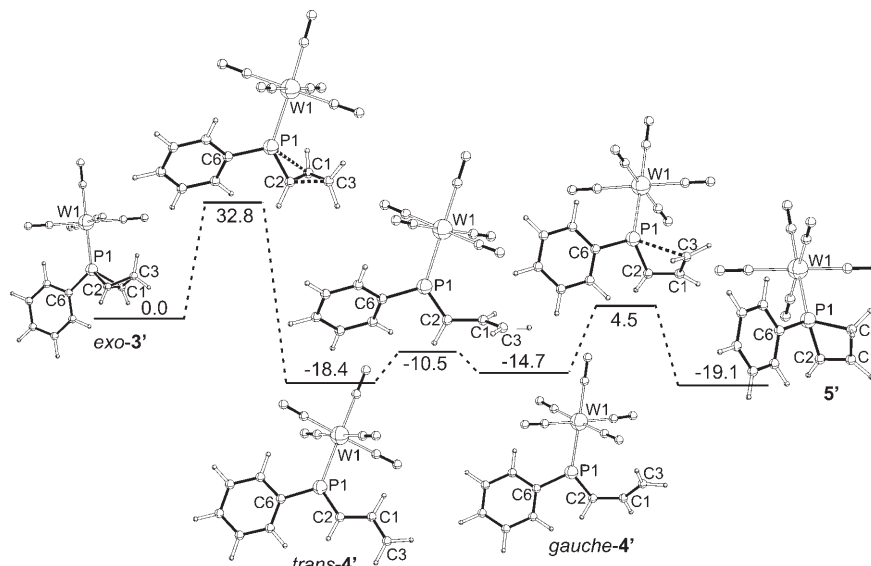
*endo* structure with the longer C1–C2 bond is the least stable of the two and decomposes at about 130 °C. At this temperature, the *exo* isomer undergoes valence isomerization to give 3-phosphacyclobutene complexes *cis-5a* ( $\delta^{31}\text{P} = 46.3$  ppm) and *trans-5a* ( $\delta^{31}\text{P} = 55.2$  ppm,  $^2J(\text{H},\text{P}) = 9.5$  Hz)<sup>[8]</sup> in a 4:1 ratio (35%) besides the phospholene complex **6** as the major product (41%,  $\delta^{31}\text{P} = 37.9$  ppm; Scheme 2). Formation of the phospholene was confirmed by crystal structure analysis.



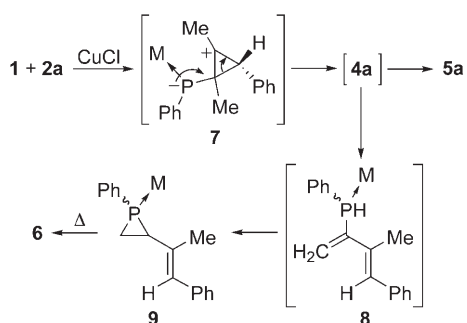
**Scheme 2.** Valence isomerization of **3** to form **5** and, for R=Me, **6**. M=W(CO)<sub>5</sub>.

The BP86/6-31G\*(LANL2DZ) calculations<sup>[9]</sup> on models (labeled with an apostrophe (')), no C substituents) did not demonstrate a direct path from **3** to **5**,<sup>[10]</sup> but instead the involvement of 1-phosphabutadiene **4** was established (see Scheme 2). Isomerization of *exo-3'* to give *trans-4'* proceeds by a concerted, asynchronous conrotatory ring opening ( $\Delta E = -18.4$ ,  $\Delta E^\ddagger = 32.8$  kcal mol<sup>-1</sup>; Figure 2). With subsequent conrotatory electrocyclic ring closure, via the *gauche* form of **4'** ( $\Delta E = 3.7$ ,  $\Delta E^\ddagger = 7.9$  kcal mol<sup>-1</sup>), the more stable phosphacyclobutene **5'** is formed ( $\Delta E = -4.4$ ,  $\Delta E^\ddagger = 19.2$  kcal mol<sup>-1</sup>). This route implies that 1-phosphabutadiene **4** is a reaction intermediate. The small energy difference between **4'** and 3-phosphacyclobutene **5'** is reflected in Tran Huy and Mathey's<sup>[11]</sup> use of derivatives of **5** as masked 1-phosphabutadienes.<sup>[12]</sup> These results highlight that the stability order  $\mathbf{3}' \ll \mathbf{4}' < \mathbf{5}'$  of the three valence isomers differs from the established values for the hydrocarbons ( $\mathbf{3}'' \ll \mathbf{5}'' \ll \mathbf{4}''$ ).<sup>[13]</sup>

To gain more insight into the formation of phospholene **6**, we resorted to the more gentle CuCl-catalyzed reaction of **1**<sup>[5,14]</sup> with **2a** (55 °C, 15 h; Scheme 3). This reaction gave, with the exception of **6**, the same products as the noncatalyzed



**Figure 2.** The relative BP86/6-31G\*(LANL2DZ for W) energies (ZPE corrected, in kcal mol<sup>-1</sup>) for the rearrangement of *exo-3'* into **5'**. Selected bond lengths [Å], angles [°], and torsion angles [°] of *exo-3'* (C<sub>2</sub>): W1–P1 2.536, P1–C1 1.833, P1–C6 1.846, C1–C2 1.527, C1–C3 1.506; C1–P1–C2 49.2, C1–C3–C2 60.9, P1–C1–C2–C3 120.2; **TS***exo-3'-trans-4'*: W1–P1 2.541, P1–C1 2.709, P1–C2 1.801, P1–C6 1.820, C1–C2 1.474, C1–C3 1.446, C2–C3 1.595; *trans-4'* (C<sub>2</sub>): W1–P1 2.515, P1–C2 1.703, P1–C6 1.830, C1–C2 1.441, C1–C3 1.359; **TS***trans-4'-gauche-4'*: P1–C2–C1–C3 95.2; *gauche-4'*: P1–C2–C1–C3 31.0; **TS***gauche-4'-5'*: W1–P1 2.568, P1–C2 1.774, P1–C3 2.558, C1–C2 1.391, C1–C3 1.419, P1–C2–C1–C3 26.4; **5'**: W1–P1 2.539, P1–C2 1.838, P1–C3 1.915, P1–C6 1.848, C1–C2 1.355, C1–C3 1.518.



**Scheme 3.** The CuCl-catalyzed formation of **5a** and **9**. M = W(CO)<sub>5</sub>.

reaction, that is, *exo*- and *endo*-**3a** (4:1 ratio, 16%) and *cis*- and *trans*-**5a** (7:8 ratio, 30%). Additionally, the vinyl-phosphirane complexes *anti*-**9** ( $\delta^{31}\text{P} = -157.1$  ppm) and *syn*-**9** ( $\delta^{31}\text{P} = -150.2$  ppm) were also produced in a 3:1 ratio (6%). The vinyl-phosphiranes formed in this milder process (55°C vs. 110°C) corroborates the role of phosphabutadienes as reaction intermediates. Heating of isolated *anti*-**9** at 110°C effected epimerization of the phosphorus center to give the *syn*-**9** isomer, which underwent the established [1,3]-sigmatropic shift<sup>[15]</sup> to phospholene complex **6**. The presumed reagent, the [PhP(Cl)W(CO)<sub>5</sub>]-Cu-alkene complex,<sup>[14]</sup> is more sensitive than Ph-P=W(CO)<sub>5</sub> to steric congestion in the 1,2-cycloaddition, which is reflected in the lower yield of the 2-phosphabicyclobutanes **3a**. The competitive reaction is, in our opinion, the formation of zwitterion **7**, for which there is computational support on related systems.<sup>[16]</sup> Compound **7** can also rearrange to phosphabutadiene **4a** in analogy to the addition of dichlorocarbene to cyclopropenes.<sup>[17]</sup> Ring closure then gives **5a**,<sup>[8]</sup> while two known hydride shifts<sup>[18]</sup> lead, via the secondary vinylphosphane complex **8**, to vinyl-phosphirane **9** (Scheme 3). The **4**'→**9**' process is exothermic by  $-1.8$  kcal mol<sup>-1</sup> for the parent system (no phenyl substituent on the diene).<sup>[9]</sup>

Valence isomerization is sensitive to the nature of the bridgehead substituents, and this also applies to **3**→**4**→**5**. Reaction of cyclopropene **2b**, which has phenyl instead of methyl substituents, with the phosphinidene precursor **1** at 110°C gave as sole products the 3-phosphacyclobutene complexes *cis*-**5b** ( $\delta^{31}\text{P} = 43.8$  ppm,  $^2J(\text{H},\text{P}) = 6.2$  Hz) and *trans*-**5b** ( $\delta^{31}\text{P} = 53.4$  ppm,  $^2J(\text{H},\text{P}) = 9.6$  Hz)<sup>[8]</sup> (5:1 ratio, 95%); *cis*-**5b** was characterized by X-ray crystallography. Apparently, **3b** isomerizes faster than **3a**. In this case, phospholene **6** cannot be formed because the phenyl substituents render a hydride shift (to give **8**) impossible.

2-Phosphabicyclo[1.1.0]butanes *exo*-**3b** ( $\delta^{31}\text{P} = -70.5$  ppm) and *endo*-**3b** ( $\delta^{31}\text{P} = 3.8$  ppm)<sup>[7]</sup> could be obtained (4:1 ratio, 33%) by the milder CuCl-catalyzed reaction (2 equiv of **1**, 55°C, 0.5 h). The X-ray crystal structure of the *exo* isomer revealed two different triclinic polymorphs with  $Z = 2$  and  $Z = 6$ , respectively, and very similar molecular structures. Polymorph I shows a folding angle (113.27(10)°) and a transannular bond length (1.510(2) Å) that are similar to those of *exo*-**3a**. Heating of isolated **3b** (*exo* + *endo*, 4:1) in toluene at 50°C for 60 h gave the favored phosphacyclobutene *cis*-**5b**, indicating that

valence isomerization of the novel 2-phosphabicyclo[1.1.0]butanes is indeed directed by the bridgehead substituents (**3b** 50°C; **3a** 130°C). This behavior parallels that observed for the all-carbon analogue 2,2-dimethyl-bicyclo[1.1.0]butane, where the 1,3-diphenyl derivative isomerizes at 130°C and the 1,3-dimethyl derivative at temperatures above 280°C.<sup>[19]</sup>

In conclusion, W(CO)<sub>5</sub>-complexed 2-phosphabicyclo[1.1.0]butanes are remarkably stable compounds that valence-isomerize to 3-phosphacyclobutenes via 1-phosphabutadienes at elevated temperatures. In contrast to the hydrocarbon analogues, the diene can be trapped as a phospholene due to rearrangements that are specific for the phosphorus compounds.

## Experimental Section

**3a** and **6**: Compounds **1**<sup>[5]</sup> (591 mg, 0.90 mmol) and **2a**<sup>[6]</sup> (156 mg, 1.08 mmol) were heated in toluene (3 mL) at reflux for 17 h. Removal of the solvents under vacuum and chromatography of the residue over silica with pentane/toluene (9:1) as eluent gave *endo*-**3a** (155 mg, 30%) and *exo*-**3a** (200 mg, 39%) as colorless solids as well as **6** (20 mg, 4%) as a pale yellow solid together with minor amounts of *cis*-**5a** (10 mg, 2%) and *trans*-**5a** (5 mg, 1%). *exo*-**3a**: m.p.: 115–116°C;  $^{31}\text{P}\{^1\text{H}\}$  NMR (101.3 MHz, CDCl<sub>3</sub>):  $\delta = -85.1$  ( $^1J(\text{P},\text{W}) = 263.7$  Hz). *endo*-**3a**: m.p.: 79–82°C;  $^{31}\text{P}\{^1\text{H}\}$  NMR (101.3 MHz, CDCl<sub>3</sub>):  $\delta = -36.7$  ppm ( $^1J(\text{P},\text{W}) = 260.3$  Hz); HRMS (EI, 70 eV):  $m/z$  (%): 576 (9) [ $M$ ]<sup>+</sup>; calcd for C<sub>22</sub>H<sub>17</sub>O<sub>5</sub>PW: 576.0323; found: 576.0325. **6**: m.p.: 107°C;  $^{31}\text{P}\{^1\text{H}\}$  NMR (101.3 MHz, CDCl<sub>3</sub>):  $\delta = 37.9$  ppm ( $^1J(\text{P},\text{W}) = 240.4$  Hz); HRMS (EI, 70 eV):  $m/z$  (%): 576 (30) [ $M$ ]<sup>+</sup>; calcd for C<sub>22</sub>H<sub>17</sub>O<sub>5</sub>PW: 576.0323; found: 576.0329.

**3b**: Compounds **2b** (122.6 mg, 0.46 mmol), **1** (598 mg, 0.91 mmol), and CuCl (10 mg, 0.1 mmol) in toluene (2 mL) were heated at 55°C for 30 min. The reaction was stopped at incomplete conversion to ensure maximum yield of **3b**. Removal of the solvents under vacuum and chromatography of the residue over silica with pentane/toluene (9:1) as eluent gave a 4:1 mixture of *exo*-**3b** and *endo*-**3b** (107 mg, 33%) as a pale yellow solid. *exo*-**3b**: m.p.: 124°C (decomp.);  $^{31}\text{P}\{^1\text{H}\}$  NMR (101.3 MHz, CDCl<sub>3</sub>):  $\delta = -70.5$  ppm ( $^1J(\text{P},\text{W}) = 262.0$  Hz); HRMS (EI, 70 eV):  $m/z$  (%): 700 (22) [ $M$ ]<sup>+</sup>; calcd for C<sub>32</sub>H<sub>21</sub>O<sub>5</sub>PW: 700.0636; found: 700.0634. *endo*-**3b**:  $^{31}\text{P}\{^1\text{H}\}$  NMR (101.3 MHz, CDCl<sub>3</sub>):  $\delta = 3.8$  ppm ( $^1J(\text{P},\text{W}) = 271.8$  Hz).

**3a**, **5a**, and **9**: Compounds **1** (1.24 g, 1.90 mmol), **2a** (410 mg, 2.84 mmol), and CuCl (10 mg, 0.1 mmol) in toluene (8 mL) were heated at 55°C for 15 h. Removal of the solvents under vacuum and chromatography of the residue (an insoluble black residue remains) over silica with pentane/toluene (9:1) as eluent gave *endo*-**3a** (40 mg, 4%), *cis*-**5a** (160 mg, 14%), *exo*-**3a**, and *trans*-**5a** in a 10:8 ratio (310 mg, 28%), and *syn*- and *anti*-**9** in a 3:1 ratio (65 mg, 6%) as colorless oils. *cis*-**5a**:  $^{31}\text{P}\{^1\text{H}\}$  NMR (101.3 MHz, CDCl<sub>3</sub>):  $\delta = 46.3$  ppm ( $^1J(\text{P},\text{W}) = 221.4$  Hz). Crystallization of the mixture of *exo*-**3a** and *trans*-**5a** from pentane at  $-80^\circ\text{C}$  afforded the pale yellow crystals of *trans*-**5a**: M.p. 111°C;  $^{31}\text{P}\{^1\text{H}\}$  NMR (101.3 MHz, CDCl<sub>3</sub>):  $\delta = 55.2$  ppm ( $^1J(\text{P},\text{W}) = 237.5$  Hz); HRMS (EI, 70 eV):  $m/z$  (%): 576 (39) [ $M$ ]<sup>+</sup>; calcd for C<sub>22</sub>H<sub>17</sub>O<sub>5</sub>PW: 576.0323; found: 576.0318. *syn*-**9**:  $^{31}\text{P}\{^1\text{H}\}$  NMR (101.3 MHz, CDCl<sub>3</sub>):  $\delta = -157.1$  ppm ( $^1J(\text{P},\text{W}) = 255.2$  Hz); HRMS (EI, 70 eV):  $m/z$  (%): 576 (20) [ $M$ ]<sup>+</sup>; calcd for C<sub>22</sub>H<sub>17</sub>O<sub>5</sub>PW: 576.0323; found: 576.0318. *anti*-**9**:  $^{31}\text{P}\{^1\text{H}\}$  NMR (101.3 MHz, CDCl<sub>3</sub>):  $\delta = -150.2$  ppm ( $^1J(\text{P},\text{W}) = 263.3$  Hz).

**5b**: Compounds **1** (261 mg, 0.40 mmol), **2b** (118 mg, 0.44 mmol), and CuCl (10 mg, 0.1 mmol) in toluene (2 mL) were heated at 55°C for 38 h or, alternatively (without CuCl), at reflux for 16 h. Removal of the solvents under vacuum and chromatography of the residue over silica with pentane/toluene (4:1) as eluent gave *cis*-**5b** (215 mg, 77%) as a pale yellow solid together with a trace of *trans*-**5b** ( $\approx 2\%$ ).

Removal of the solvents under vacuum and chromatography of the residue over silica with pentane/toluene (4:1) as eluent gave a 5:1 mixture of *cis*-**5b** and *trans*-**5b** (300 mg, 95%) as a pale yellow oil. Crystallization from pentane at  $-20^{\circ}\text{C}$  afforded colourless crystals of *cis*-**5b**: m.p.:  $117\text{--}118^{\circ}\text{C}$ ;  $^{31}\text{P}\{^1\text{H}\}$  NMR (101.3 MHz,  $\text{CDCl}_3$ ):  $\delta = 43.8$  ppm ( $^1J(\text{P,W}) = 230.9$  Hz); HRMS (EI, 70 eV):  $m/z$  (%): 700 (23) [ $M$ ] $^{+}$ ; calcd for  $\text{C}_{32}\text{H}_{21}\text{O}_5\text{PW}$ : 700.0636; found: 700.06486. *trans*-**5b**:  $^{31}\text{P}\{^1\text{H}\}$  NMR (101.3 MHz,  $\text{CDCl}_3$ ):  $\delta = 53.4$  ppm ( $^1J(\text{P,W}) = 247.0$  Hz).

Crystal structure data (see Supporting Information): *exo*-**3a** ( $\text{C}_{22}\text{H}_{17}\text{O}_5\text{PW}$ ):  $P2_1/c$  (no. 14);  $a = 6.8439(1)$ ,  $b = 21.3415(2)$ ,  $c = 14.4400(1)$  Å,  $\beta = 95.2844(3)^{\circ}$ ,  $V = 2100.13(4)$  Å $^3$ ;  $Z = 4$ ;  $R$  [ $I > 2\sigma(I)$ ]:  $R1 = 0.0178$ ,  $wR2 = 0.0406$ . *endo*-**3a** ( $\text{C}_{22}\text{H}_{17}\text{O}_5\text{PW}$ ):  $P2_1/c$  (no. 14);  $a = 8.2108(1)$ ,  $b = 15.0945(1)$ ,  $c = 17.8628(2)$  Å,  $\beta = 99.0907(3)^{\circ}$ ,  $V = 2186.07(4)$  Å $^3$ ;  $Z = 4$ ;  $R$  [ $I > 2\sigma(I)$ ]:  $R1 = 0.0175$ ,  $wR2 = 0.0403$ . **6** ( $\text{C}_{22}\text{H}_{17}\text{O}_5\text{PW}$ ):  $C2/c$  (no. 15);  $a = 37.996(3)$ ,  $b = 8.9553(4)$ ,  $c = 26.4314(15)$  Å,  $\beta = 110.813(5)^{\circ}$ ,  $V = 8406.9(9)$  Å $^3$ ;  $Z = 16$ ;  $R$  [ $I > 2\sigma(I)$ ]:  $R1 = 0.0213$ ,  $wR2 = 0.0462$ . *cis*-**5b** ( $\text{C}_{32}\text{H}_{21}\text{O}_5\text{PW}$ ):  $P2_1/c$  (no. 14);  $a = 10.9428(1)$ ,  $b = 22.9359(2)$ ,  $c = 15.0824(1)$  Å,  $\beta = 133.2674(4)^{\circ}$ ,  $V = 2756.40(4)$  Å $^3$ ;  $Z = 4$ ;  $R$  [ $I > 2\sigma(I)$ ]:  $R1 = 0.0192$ ,  $wR2 = 0.0474$ . *exo*-**3b** (polymorph I,  $\text{C}_{32}\text{H}_{21}\text{O}_5\text{PW}$ ):  $P1$  (no. 2);  $a = 10.4005(8)$ ,  $b = 10.7789(8)$ ,  $c = 14.4436(12)$  Å,  $\alpha = 83.618(6)$ ,  $\beta = 78.886(6)$ ,  $\gamma = 61.670(5)^{\circ}$ ,  $V = 1398.2(2)$  Å $^3$ ;  $Z = 2$ ;  $R$  [ $I > 2\sigma(I)$ ]:  $R1 = 0.0163$ ,  $wR2 = 0.0332$ . *exo*-**3b** (polymorph II,  $\text{C}_{32}\text{H}_{21}\text{O}_5\text{PW}$ ):  $P1$  (no. 2);  $a = 10.4176(8)$ ,  $b = 17.1058(17)$ ,  $c = 23.9196(19)$  Å,  $\alpha = 96.436(6)$ ,  $\beta = 92.693(7)$ ,  $\gamma = 97.143(8)^{\circ}$ ,  $V = 4194.7(6)$  Å $^3$ ;  $Z = 6$ ;  $R$  [ $I > 2\sigma(I)$ ]:  $R1 = 0.0246$ ,  $wR2 = 0.0444$ . CCDC 275002–275007 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

Received: June 27, 2005

Published online: September 13, 2005

**Keywords:** bicyclic compounds · heterocycles · phosphorus · substituent effects · valence isomerization

- [1] *The Chemistry of the Cyclopropyl Group, Part 2* (Ed.: Z. Rappoport), Wiley, Chichester, **1987**, chap. 19.
- [2]  $\text{P}_2\text{C}_2$ : a) E. Niecke, A. Fuchs, M. Nieger, *Angew. Chem.* **1999**, *111*, 3213–3216; *Angew. Chem. Int. Ed.* **1999**, *38*, 3028–3031;  $\text{P}_2\text{B}_2$ : b) D. Scheschkewitz, H. Amii, H. Gornitzka, W. W. Schoeller, D. Bourissou, G. Bertrand, *Angew. Chem.* **2004**, *116*, 595–597; *Angew. Chem. Int. Ed.* **2004**, *43*, 585–587; c) A. Rodriguez, R. A. Olsen, N. Ghaderi, D. Scheschkewitz, F. S. Tham, L. J. Mueller, G. Bertrand, *Angew. Chem.* **2004**, *116*, 4988–4991; *Angew. Chem. Int. Ed.* **2004**, *43*, 4880–4883.
- [3] Phosphorus: a) K. Blatter, W. Rösch, U.-J. Vogelbacher, J. Fink, M. Regitz, *Angew. Chem.* **1987**, *99*, 67–68; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 85–86; b) M. Regitz, S. Haber, U. Hees, *Phosphorus Sulfur Silicon Relat. Elem.* **1990**, *51/52*, 324; silicon: K. Wakita, N. Tokitoh, R. Okazaki, N. Takagi, S. Nagase, *J. Am. Chem. Soc.* **2000**, *122*, 5648–5649.
- [4] R. Bartnik, A. P. Marchand, *Synlett* **1997**, 1029–1039.
- [5] a) K. Lammertsma, M. J. M. Vlaar, *Eur. J. Org. Chem.* **2002**, 1127–1138; b) F. Mathey, N. H. Tran Huy, A. Marinetti, *Helv. Chim. Acta* **2001**, *84*, 2938–2957.
- [6] I. N. Domnin, J. Kopf, S. Keyaniyan, A. de Meijere, *Tetrahedron* **1985**, *41*, 5377–5382.
- [7] *exo*- and *endo*-phosphabicyclo[1.1.0]butanes differ significantly in terms of the  $^{31}\text{P}$  NMR chemical shift; see: a) C. Jones, J. A. Platts, A. F. Richards, *Chem. Commun.* **2001**, 663–664; b) M. White, L. Ricard, F. Mathey, *Organometallics* **2003**, *22*, 4825–4828; c) Ref. [2a].

- [8] a) N. H. Tran Huy, L. Ricard, F. Mathey, *Organometallics* **1988**, *7*, 1791–1795; b) A. Marinetti, L. Ricard, F. Mathey, *Organometallics* **1990**, *9*, 788–793.
- [9] Intrinsic reaction coordinate (IRC) calculations were performed on the transition structures to ascertain the connection between reactant and product: Gaussian 98 (Revision A.11.4): M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, N. Rega, P. Salvador, J. J. Dannenberg, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, **2002**; see also Supporting Information.
- [10] a) J. C. Slootweg, A. W. Ehlers, K. Lammertsma, *J. Mol. Model.* **2005**, *11*, in press; b) J. C. Slootweg, F. J. J. de Kanter, M. Schakel, A. W. Ehlers, B. Gehrhus, M. Lutz, A. M. Mills, A. L. Spek, K. Lammertsma, *Angew. Chem.* **2004**, *116*, 3556–3559; *Angew. Chem. Int. Ed.* **2004**, *43*, 3474–3477.
- [11] a) N. H. Tran Huy, F. Mathey, *Tetrahedron Lett.* **1988**, *29*, 3077–3078.
- [12] a) S. Ito, H. Jin, S. Kimura, M. Yoshifuji, *J. Org. Chem.* **2005**, *70*, 3537–3541; Stable 1-phosphabutadienes are also reported: b) B. A. Boyd, R. J. Thoma, W. H. Watson, R. H. Nellson, *Organometallics* **1988**, *7*, 572–574; c) R. Appel, F. Knoch, H. Kunze, *Chem. Ber./Recueil* **1984**, *117*, 3151–3159.
- [13] a) K. A. Nguyen, M. S. Gordon, *J. Am. Chem. Soc.* **1995**, *117*, 3835–3847; b) L. Deng, T. Ziegler, *J. Phys. Chem.* **1995**, *99*, 612–618; c) O. Wiest, K. N. Houk, K. A. Black, B. E. Thomas IV, *J. Am. Chem. Soc.* **1995**, *117*, 8594–8599.
- [14] K. Lammertsma, A. W. Ehlers, M. L. McKee, *J. Am. Chem. Soc.* **2003**, *125*, 14750–14759;
- [15] R. E. Bulo, A. W. Ehlers, S. Grimme, K. Lammertsma, *J. Am. Chem. Soc.* **2002**, *124*, 13903–13910; and references therein.
- [16] a) J. C. Slootweg, M. Schakel, F. J. J. de Kanter, A. W. Ehlers, S. I. Kozhushkov, A. de Meijere, M. Lutz, A. L. Spek, K. Lammertsma, *J. Am. Chem. Soc.* **2004**, *126*, 3050–3051; b) R. E. Bulo, A. W. Ehlers, F. J. J. de Kanter, M. Schakel, M. Lutz, A. L. Spek, K. Lammertsma, B. Wang, *Chem. Eur. J.* **2004**, *10*, 2732–2738.
- [17] J. Weber, U. H. Brinker, *Angew. Chem.* **1997**, *109*, 1689–1692; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1623–1626.
- [18] a) F. Mercier, C. Hugel-Le Goff, F. Mathey, *Tetrahedron Lett.* **1989**, *30*, 2397–2398; b) S. Haber, P. Le Floch, F. Mathey, *J. Chem. Soc. Chem. Commun.* **1992**, 1799–1800; c) S. Ito, S. Kimura, M. Yoshifuji, *Org. Lett.* **2003**, *5*, 1111–1114.
- [19] Phenyl: A. Padwa, T. Kumagai, M. Tohidi, *J. Org. Chem.* **1983**, *48*, 1834–1840; Methyl: W. R. Moore, K. G. Taylor, P. Müller, S. S. Hall, Z. L. F. Gaibel, *Tetrahedron Lett.* **1970**, 2365–2368.