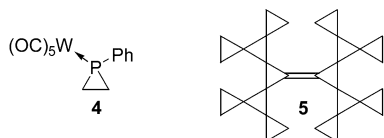# Branched Phospha[7]triangulanes

J. Chris Slootweg,[†] Marius Schakel,[†] Frans J. J. de Kanter,[†] Andreas W. Ehlers,[†]
Sergei I. Kozhushkov,[‡] Armin de Meijere,[‡] Martin Lutz,[§] Anthony L. Spek,[§] and Koop Lammertsma*,[†]

*Department of Chemistry, Faculty of Sciences, Vrije Universiteit, De Boelelaan 1083,
1081 HV Amsterdam, The Netherlands, Institut für Organische und Biomolekulare Chemie der
Georg-August-Universität Göttingen, Tammannstrasse 2, D-37077 Göttingen, Germany, and the Bijvoet Center for
Biomolecular Research, Crystal and Structural Chemistry, Utrecht University, Padualaan 8,
3584 CH Utrecht, The Netherlands*

Received December 11, 2003; E-mail: lammert@chem.vu.nl

Strain gives cyclopropane derivatives their unique electronic and chemical properties.[1] Spirofusion of three-membered rings augments the strain by 8.5 kcal/mol,[2] and yet many stable linear and branched [*n*]triangulanes are known,[3,4] but instead only few hetero[*n*]-triangulanes are known, irrespective of whether it concerns spiro-cyclopropanated aziridines, oxiranes, thiiranes, siliranes, or phosphiranes.[3] The higher reactivity of the heterocyclic ring is believed to be the underlying cause. In contrast, we now report on the exceptional stability of a branched phospha[7]triangulane.

Reaction of carbene-like terminal phosphinidene complex [Ph—P=W(CO)$_5$],[5] generated in situ by cheletropic elimination from **1** at 100 °C in toluene, with second-generation bicyclopropylidene **2**[4] afforded W(CO)$_5$-complexed phospha[7]triangulane **3** (mp 178—179 °C, 88%) as the sole product (Scheme 1). Its ^{31}P NMR resonance at δ −119.6 is deshielded by 9.8 from the first-generation triangulane[6] and by 70.5 ppm from parent **4**.[7] This illustrates little influence of the second spirocyclopropane sphere, but the larger phospha[15]triangulane could not be synthesized from third-generation bicyclopropylidene **5**[4] because of its too congested double bond.[4b]


The stabilizing W(CO)$_5$ group was subsequently removed from **3**. While oxidation with iodine at −30 °C[8] afforded [W(CO)$_4$I]$^+$I$^-$-complexed phospha[7]triangulane [δ(^{31}P) −130.1], quenching with *N*-methylimidazole[8] only led to degradation. Instead direct ligand exchange in refluxing xylene (150 °C!) with (Ph$_2$PCH$_2$)$_2$ (dppe)[9] was more successful, giving free phospha[7]triangulane **6** (mp 168—169 °C, 82%) as the sole product (Scheme 2).[10] Its δ(^{31}P) at −164.0 shows the expected shielding on demetalation, and the increased ^1J(P,C) coupling from 6.2 (**3**) to 37.3 Hz resembles that for the parent 1-phenylphosphirane.[7,11] The molecules of **6** are located on an exact mirror plane in the crystal (Figure 1)[12] and show slightly elongated P—C and P—Ph bonds (by respectively 0.02 and 0.01 Å) due to the absence of the stabilizing W(CO)$_5$ group.

The exceptional thermal stability of **3** and **6** is remarkable as most phosphiranes eliminate or transfer [Ph—P=W(CO)$_5$] at much lower temperatures (≤100−115 °C).[10] That the six spirofused rings indeed stabilize the CCP ring is evident from the mere 6.5 kcal/mol difference in strain energies (SE), determined with homodesmotic reactions at G3(MP2),[13] between parent phospha[7]triangulane

† Vrije Universiteit.
‡ Georg-August-Universität.
§ Utrecht University.

Scheme 1. Synthesis of Phospha[7]triangulane Complex **3**
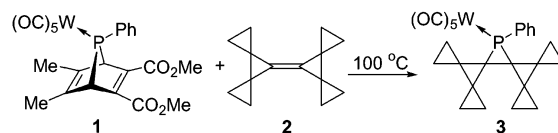
Scheme 2. Decomplexation of **3**
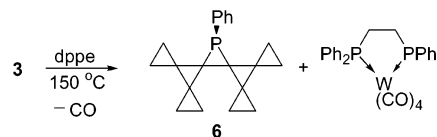
6′ (H for Ph; 224.2 kcal/mol) and alkene **2** (217.7 kcal/mol); phosphirane C$_2$PH$_5$ has an SE of 20.8 kcal/mol. A contributing factor is the release of olefin strain (OS) in **2** that amounts to 23.1 kcal/mol (see Supporting Information). The higher stability of **6** is also related to a higher olefinic π-donor and π*-acceptor ability in **2**[4] caused by spirocyclopropanation, which is reflected in the 9.3 kcal/mol larger exothermicity for reaction of ^{1}PH (A$_1$) with **2** (82.9 kcal/mol) than for ^{1}PH with ethylene (73.5 kcal/mol; G3(MP2)). This behavior is in line with a higher HOMO (−8.45 vs −10.08 eV) and a lower LUMO (4.12 vs 4.88 eV) for **2** when compared to ethylene.[14]

The higher reactivity of alkene **2** is also reflected in the CuCl-catalyzed reaction with **1**,[15] but with surprises. Not only does the reaction already take place at room temperature, instead of the usual 55−60 °C,[15] but it also gives only a modest yield of **3** (42%) besides
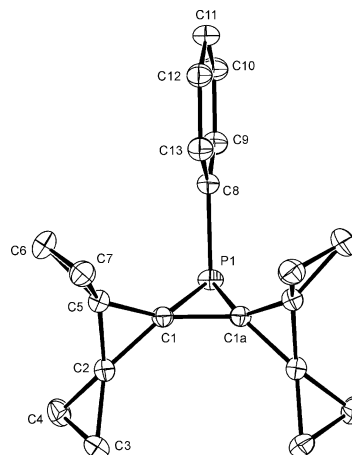

Figure 1. Displacement ellipsoid plot (50%) of **6**. Selected bond lengths [Å] and angles [deg]: P1−C1 1.8430(11), C1−C1a 1.470(2), C1−C2 1.4889(14), C1−C5 1.4879(14), C2−C3 1.4862(15), C2−C4 1.4825(15), C2−C5 1.4712(15), C3−C4 1.5305(17), C5−C6 1.4841(15), C5−C7 1.4869(16), C6−C7 1.5262(18); C1−P1−C1a 47.02(6), P1−C1−C1a 66.49(3). A: *x*, 0.5 − *y*, *z*.
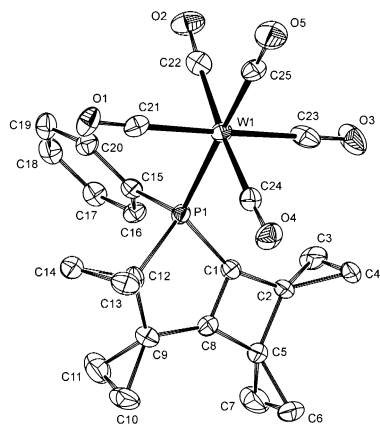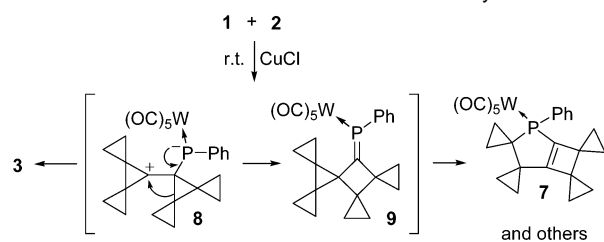
Figure 2. Displacement ellipsoid plot (50%) of **7** (molecule one of two). Selected bond lengths [Å] and angles [deg]: P1−C1 1.805(6), P1−C12 1.877(5), C1−C8 1.339(7), C2−C5 1.524(7), C9−C12 1.539(7); C1−P1−C12 89.2(3).

Scheme 3. Formation of **3** and **7** under CuCl Catalysis

other products, including **7** (6%) (Scheme 3).[16] The structure of **7**, the first 2-phosphabicyclo[3.2.0]hept-1(5)-ene derivative,[17] spiro-cyclopropanated at each carbon, was established by single-crystal X-ray crystallography (Figure 2).[12]

The formation of **7** is attributed to the influence of CuCl on the cycloaddition process as **3** converts with added CuCl only slowly in refluxing toluene to **7** and other products. This CuCl-catalyzed cycloaddition behavior concurs with a recent analysis suggesting that a CuCl−alkene complex facilitates the fragmentation of **1** to give a reactive [PhP(Cl)W(CO)$_5$]−Cu−alkene intermediate that subsequently undergoes an S$_N$2-type addition with alkenes.[18] This bulky Cu-containing reagent likely hampers the concerted [1+2]-cycloaddition, thereby enabling the formation of zwitterion **8**, which can ring-close to **3** but also rearrange to **9** in analogy to the cyclopropanation reaction of **2** with N$_2$CHCO$_2$Et in which both products were obtained.[4b] However, contrasting its stable hydrocarbon analogue, the more reactive P=C bond of **9** enables a subsequent [1,3]-sigmatropic shift[19] to give **7**. This conversion is 19.9 kcal/mol exothermic at B3LYP/6-31G* for the parent system (H for Ph, no W(CO)$_5$).[20]

In conclusion, a highly strained, thermally stable (up to 150 °C) branched phospha[7]triangulane was synthesized from second-generation bicyclopropylidene **2** and phosphinidene [Ph−P=W(CO)$_5$], followed by demetalation in refluxing xylene. Bulkier transient CuCl−alkene-complexed phosphinidene gave also a 2-phosphabicyclo[3.2.0]hept-1(5)-ene. Spirocyclopropane-annelation is stabilizing both of these novel compounds.

Supporting Information Available: Crystallographic data (CIF) of **6** and **7**, experimental details and spectroscopic and computational data for **3**, **6**, and **7** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References
(1) (a) Cyclopropanes and Related Rings. de Meijere, A., Ed.; *Chem. Rev.* **2003**, *103*, 931−1625. (b) Carbocyclic Three-Membered Ring Compounds. *Methods of Organic Chemistry (Houben-Weyl)*; de Meijere, A., Ed.; Thieme: Stuttgart; 1997; Vol. E17a−c. (c) *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; Wiley: Chichester, 1995; Vol. 2.
(2) Beckhaus, H.-D.; Rüchardt, C.; Kozhushkov, S. I.; Belov, V. N.; Verevkin, S. P.; de Meijere, A. *J. Am. Chem. Soc.* **1995**, *117*, 11854−11860.
(3) de Meijere, A.; Kozhushkov, S. I. *Chem. Rev.* **2000**, *100*, 93−142.
(4) (a) von Seebach, M.; Kozhushkov, S. I.; Boese, R.; Benet-Buchholz, J.; Yufit, D. S.; Howard, J. A. K.; de Meijere, A. *Angew. Chem.* **2000**, *112*, 2617−2620; *Angew. Chem., Int. Ed.* **2000**, *39*, 2495−2498. (b) de Meijere, A.; von Seebach, M.; Zöllner, S.; Kozhushkov, S. I.; Belov, V. N.; Boese, R.; Haumann, T.; Benet-Buchholz, J.; Yufit, D. S.; Howard, J. A. K. *Chem.-Eur. J.* **2001**, *7*, 4021−4034.
(5) (a) Lammertsma, K.; Vlaar, M. J. M. *Eur. J. Org. Chem.* **2002**, 1127−1138. (b) Mathey, F.; Tran Huy, N. H.; Marinetti, A. *Helv. Chim. Acta* **2001**, *84*, 2938−2957.
(6) Lammertsma, K.; Wang, B.; Hung, J.-T.; Ehlers, A. W.; Gray, G. M. *J. Am. Chem. Soc.* **1999**, *121*, 11650−11655.
(7) (a) Huy, N. H. T.; Mathey, F. *Phosphorus, Sulfur Silicon Relat. Elem.* **1990**, *47*, 477−481. (b) Hung, J.-T.; Yang, S.-W.; Gray, G. M.; Lammertsma, K. *J. Org. Chem.* **1993**, *58*, 6786−6790.
(8) Marinetti, A.; Mathey, F.; Fischer, J.; Mitschler, A. *J. Chem. Soc., Chem. Commun.* **1984**, 45−46.
(9) Deschamps, B.; Mathey, F. *Synthesis* **1995**, *8*, 941−943.
(10) Marinetti, A.; Charrier, C.; Mathey, F.; Fischer, J. *Organometallics* **1985**, *4*, 2134−2138.
(11) Li, X.; Robinson, K. D.; Gaspar, P. P. *J. Org. Chem.* **1996**, *61*, 7702−7710.
(12) **6**: C$_{20}$H$_{21}$P, Fw = 292.34, colorless needle, 0.46 × 0.36 × 0.09 mm^3, temperature = 150(2) K, monoclinic, P2$_1$/m (No. 11), a = 7.8462(1), b = 12.9734(2), c = 8.7058(1) Å, β = 115.6968(6)°, V = 798.537(18) Å^3, Z = 2, D$_x$ = 1.216 g/cm^3. No absorption correction (μ = 0.164 mm^{-1}). 15 383 measured reflections, 1913 reflections were unique [(sin θ/λ)$_{max}$ = 0.65 Å^{-1}]. 138 refined parameters. R-values [I > 2σ(I)]: R1 = 0.0307, wR2 = 0.0784. R-values [all refl.]: R1 = 0.0354, wR2 = 0.0812. GOF = 1.047. **7**: C$_{25}$H$_{21}$O$_5$PW, Fw = 616.24, colorless plate, 0.09 × 0.09 × 0.03 mm^3, temperature = 150(2) K, orthorhombic, Pca2$_1$ (no. 29), a = 18.9647(1), b = 11.3278(1), c = 21.7733(2) Å, V = 4677.52(6) Å^3, Z = 8, D$_x$ = 1.750 g/cm^3. Analytical absorption correction (μ = 5.041 mm^{-1}, 0.58−0.89 transmission). 80 568 measured reflections, 10 736 reflections were unique [(sin θ/λ)$_{max}$ = 0.65 Å^{-1}]. 577 refined parameters. Flack parameter x = −0.022(5). R-values [I > 2σ(I)]: R1 = 0.0285, wR2 = 0.0378. R-values [all refl.]: R1 = 0.0450, wR2 = 0.0405. GOF = 0.975. (See Supporting Information for crystal structure determinations.)
(13) (a) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1999**, *110*, 4703−4709. (b) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.11.3; Gaussian, Inc.: Pittsburgh, PA, 2002. (c) See Supporting Information.
(14) Orbital energies at MP2/6-31G*.[13b] The lowest ionization energies (π-IE$_v$) determined by PE spectroscopy are 8.93 eV for bicyclopropylidene (Gleiter, R.; Haider, R.; Conia, J.-M.; Barnier, J.-P.; de Meijere, A.; Weber, W. *J. Chem. Soc., Chem. Commun.* **1979**, 130−132. Hofland, A.; de Boer, Th. J. *Recl. Trav. Chim. Pays-Bas* **1987**, *106*, 558−562. Gleiter, R.; Spanget-Larson, J. In *Advances in Strain in Organic Chemistry*; Halton, B., Ed.; JAI Press: London, 1992; Vol. 2, p 143ff), 8.70 eV for 1-(cyclopropylidene)spiropentane, and 8.50 eV for 7-(cyclopropylidene)-dispiro-[2.0.2.1]heptane) (Gleiter, R.; Kozhushkov, S. I.; de Meijere, A., unpublished results).
(15) Marinetti, A.; Mathey, F. *Organometallics* **1984**, *3*, 456−461.
(16) A byproduct in the crude reaction mixture [ca. 20%; δ(^{31}P) = 119.5, $^1J_{P−W}$ = 254.4 Hz] did not survive workup.
(17) To our knowledge, only a 3-phosphabicyclo[3.2.0]heptene has been reported earlier: Quin, L. D.; Middlemas, E. D. *J. Am. Chem. Soc.* **1977**, *99*, 8370−8371.
(18) Lammertsma, K.; Ehlers, A. W.; McKee, M. L. *J. Am. Chem. Soc.* **2003**, *125*, 14750−14759.
(19) Bulo, R. E.; Ehlers, A. W.; Grimme, S.; Lammertsma, K. *J. Am. Chem. Soc.* **2002**, *124*, 13903−13910. This rearrangement of **9** is a heteroanalogue of the vinylcyclopropane-cyclopentene rearrangement: Baldwin, J. E. In *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; Wiley: Chichester, 1995; Vol. 2, pp 469−494. Baldwin, J. E. *J. Comput. Chem.* **1998**, *19*, 222−231. Baldwin, J. E. *Chem. Rev.* **2003**, *103*, 1197−1212.
(20) The geometries of **9′** and **7′** (PH instead of PhPW(CO)$_5$) were optimized at the B3LYP/6-31G* level (see Supporting Information).[13b]

JA031648P