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1,2-Oxaphosphetane Complexes

Synthesis and Reaction of the First 1,2-Oxaphosphetane Complexes**

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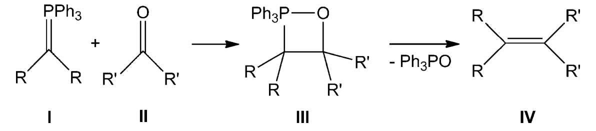
Dedicated to Professor Reinhard Schmutzler

Abstract: *While P^V 1,2-oxaphosphetanes are well known from the Wittig reaction, their P^{III} analogues are still unexplored. Herein, the synthesis and reactions of the first 1,2-oxaphosphetane complexes are presented, which were achieved by reaction of the phosphinidenoid complex [Li(12-crown-4)(solv)][$(OC)_5W\{(Me_3Si)_2HCPCl\}$] with different epoxides. The title compounds appeared to be stable in toluene up to 100 °C, before unselective decomposition started. Acid-induced ring expansion with benzonitrile resulted in selective formation of the first complex bearing a 1,3,4-oxazaphosphacyclohex-2-ene ligand.*

A fundamental breakthrough in the use of strained phosphorus heterocycles in organic synthesis was achieved by Wittig et al., who described the reaction between phosphonium ylides **I** and aldehydes (or ketones) **II** to achieve alkene formation **IV**; the transient P^V 1,2-oxaphosphetanes **III** play a key role here (Scheme 1).[1] Due to the fundamental importance of this C=C bond-forming reaction, great efforts were undertaken to elucidate the mechanism;[1e] several stable derivatives of such P^V 1,2-oxaphosphetanes[2] were not only established by NMR spectroscopy, but also structurally characterized.[3]

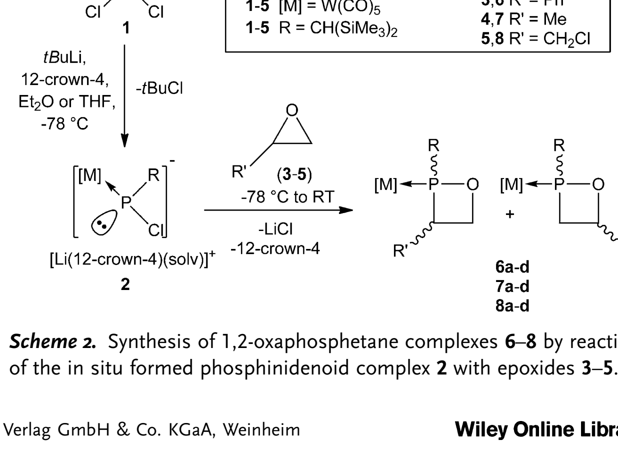
Surprisingly, P^{III} 1,2-oxaphosphetanes and/or their metal complexes are still unknown. In 1987, Mathey and Marinetti reported on the reaction of a transient electrophilic terminal phosphinidene complex[4] with styrene oxide at 110 °C, which led to a mixture of a dioxaphospholane and a phosphirane complex.[5] The proposed reaction mechanism assumed the primary formation and subsequent decomposition of a 1,2-oxaphosphetane complex as the key intermediate. Another approach by Stephan et al. using nucleophilic phosphinidene complexes and epoxides was also not successful in yielding 1,2-oxaphosphetane complexes; instead a formal O/PR group exchange resulted in phosphirane formation.[6]



Scheme 1. The Wittig reaction based on the cleavage of a P^V 1,2-oxaphosphetane ring.

Early studies on the reactions of alkali metal phosphanides with epoxides revealed ring-opening to yield 1,2-phosphanyl alcohols as final products[7] and a preference for nucleophilic attack at the least hindered side of the epoxide ring was observed. In this context, we contemplated what the outcome would be if Li/Cl phosphinidenoid complexes[8] would be employed. Further encouraged by the observation that the latter can be efficiently used as synthetic equivalents of electrophilic terminal phosphinidene complexes under mild conditions, for example, to synthesize small-ring heterocyclic[9] and acyclic[10] P ligands, we were stimulated to renew the quest for 1,2-oxaphosphetane complexes.

Li/Cl phosphinidenoid complex **2**, formed from dichloro(organo)phosphane complex **1**[11] by chlorine/lithium exchange with *t*BuLi in the presence of 12-crown-4, reacted readily with different epoxide derivatives **3**–**5** to yield selectively 1,2-oxaphosphetane complexes **6**–**8**. Each of these products were obtained as a mixture of four regio- and stereoisomers (Scheme 2), of which two isomers were predominant (Table 1). Workup by column chromatography at low temperatures led to the isolation of stable solids, and some isomers could be enriched (up to 98 %) using fractional crystallization and spectroscopically characterized (for details see the Supporting Information). The ^{1}H NMR spectra of **6**–**8** revealed signals of protons bound to the α-P ring carbon



Scheme 2. Synthesis of 1,2-oxaphosphetane complexes **6**–**8** by reaction of the in situ formed phosphinidenoid complex **2** with epoxides **3**–**5**.

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Table 1: $^{31}P\{^1H\}$ NMR data ($CDCl_3$) for 1,2-oxaphosphetane complexes **6**–**8**.

	$\delta(^{31}P)$ [ppm] ($^1J_{W,P}$ [Hz])				[**a**/**b**/**c**/**d**]
	a	**b**	**c**	**d**	
6	220.2 (275.4)	210.7 –[a]	195.1 (273.1)	179.7 (281.1)	40:4:53:3
7	176.4 (273.4)	169.2 –[a]	164.5 (267.8)	164.4) (268.7)	30:4:19:47
8	182.4 (278.6)	174.8 (281.0)	171.0 (274.4)	170.1 (271.3)	44:7:19:30

atoms at about 5 ppm, which are apparently significantly deshielded. In the same regard it is noteworthy that all 1,2-oxaphosphetane complexes display $^{31}P\{^1H\}$ NMR resonances in a surprising low-field range of $\delta = 160$ to 220 ppm.

Single crystals suitable for X-ray diffraction were obtained from each mixture having one enriched isomer and, therefore, molecular structures of complexes **6**–**8** could be established (Figure 1–3). For example, the complex assigned as **6a** was obtained in almost pure form (ca. 98 % with a small amount of of **6c**) by removing other isomers with *n*-pentane and recrystallizing from diethyl ether. Surprisingly, the regioisomeric 1,2-oxaphosphetane rings having the C-substituent in 3- (**6**, Figure 1) and 4-position (**7** and **8**, Figures 2 and 3) can adopt a *cis* (Figure 1) and *trans* arrangement, (Figures 2 and 3), respectively, relative to the $M(CO)_5$ unit.

Comparison of the molecular parameters of complexes **6**–**8** with those of known P^V 1,2-oxaphosphetanes like **9**[3a] and **10**[3b] (Figure 4) reveals comparable bond lengths but some differences in the endocyclic angles; that is, on going from the P^V to the P^{III} heterocycles an increase of the O-P-C angles by about 2–5° was found.

A preliminary study on the thermal stability and ring-expansion reactivity of the 1,2-oxaphosphetane complexes was performed using a mixture of **7a**/**b**/**c**/**d** (30:4:19:47). Under these conditions, decomposition was observed to occur in toluene at about 100 °C (5 h) leading to a product mixture, yet to be identified. When a methylene chloride solution of complexes **7a**–**d** (same ratio) was treated with CF_3SO_3H (TfOH) at ambient temperature in the presence of benzonitrile followed by addition of triethylamine, a P–O bond-selective ring expansion took place, giving the 1,3,4-oxazaphosphacyclohex-2-ene complex **12** as a mixture of isomers (ratio 93:7; Scheme 3). While the major product (**12a**) was

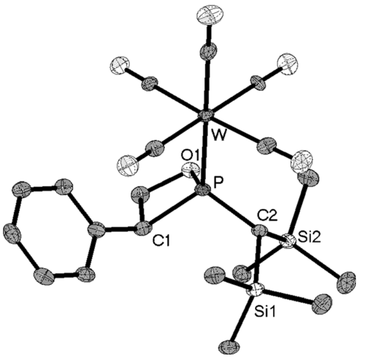


Figure 1. Structure of complex **6a** (ellipsoids set at 50 % probability level; hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: W–P 2.4749(11), P–O1 1.677(3), P–C1 1.894(5), P–C2 1.820(4); C1-P-O1 79.20(18), C2-P-O1 107.28(18), C2-P-C1 109.76(19), O1-P-W 111.47(11), C1-P-W 124.78(14), C2-P-W 116.91(15).

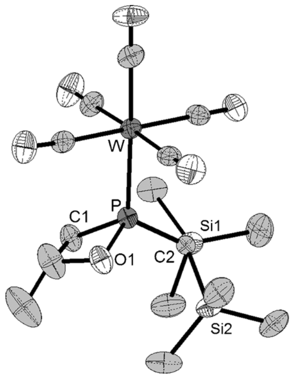


Figure 2. Structure of complex **7** (ellipsoids set at 50 % probability level; hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: W–P 2.4846(14), P–O1 1.672(4), P–C1 1.827(5), P–C2 1.800(5); C1-P-O1 79.7(2), C2-P-O1 108.4(2), C2-P-C1 111.5(3), O1-P-W 113.73(16), C1-P-W 118.9(2), C2-P-W 118.00(17).

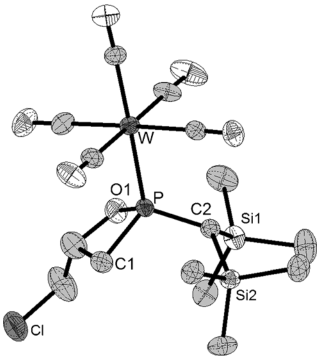
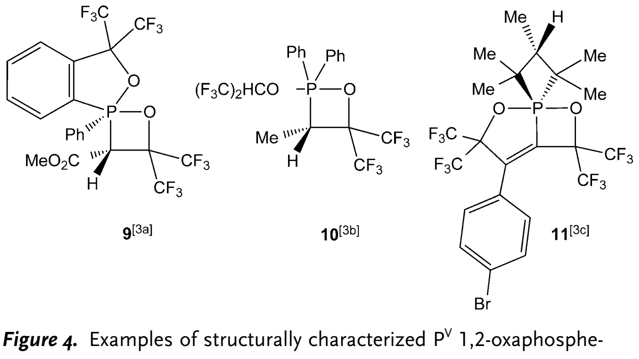
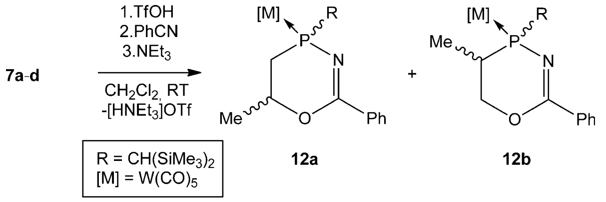


Figure 3. Structure of complex **8** (ellipsoids set at 50 % probability level; hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: W–P 2.4726(10), P–O1 1.693(3), P–C1 1.835(4), P–C2 1.813(4); C1-P-O1 80.35(18), C2-P-O1 108.25(17), C2-P-C1 111.42(19), O1-P-W 112.31(11), C1-P-W 120.31(16), C2-P-W 117.65(13).



9[3a] **10**[3b] **11**[3c]

Figure 4. Examples of structurally characterized P^V 1,2-oxaphosphetanes.



Scheme 3. Acid-induced ring-expansion reaction of 1,2-oxaphosphetane complexes **7a–d**.

isolated in pure form by column chromatography, the minor product could not be obtained. Complex **12a** displays a $^{31}P\{^1H\}$ NMR resonance at $\delta = 40.0$ ($^1J_{W,P} = 258.8$ Hz); the minor product was observed at $\delta = 31.0$ ppm; here, we assume that the latter is the regioisomer **12b**. Subsequent recrystallization afforded yellow single crystals of **12a** and, hence, it was possible to establish the regiochemistry of the ring-expansion product (Figure 5) by X-ray diffraction studies.

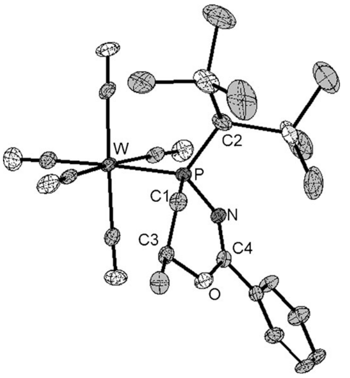


Figure 5. Structure of complex **12a** (ellipsoids set at 50% probability level; hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: W–P 2.4989(10), P–N 1.703(3), P–C1 1.828(4), P–C2 1.821(4); C1-P-N 99.80(16), C2-P-N 104.83(17), C2-P-C1 105.63(18), N-P-W 107.06(11), C1-P-W 118.70(13), C2-P-W 118.40(15).

In conclusion, facile access to the first 1,2-oxaphosphetane complexes was achieved using low-temperature ring expansion of epoxides with a Li/Cl phosphinidenoid complex. Two aspects of this (formal) insertion of a P_1 building block deserve particular attention: 1) The formation of regioisomeric four-membered rings is very rare in epoxide ring-expansion chemistry as the least hindered side of epoxides is usually preferred. 2) The high functional group tolerance of the Li/Cl phosphinidenoid complex **2** (in the case of epoxide **5**) provides interesting perspectives for the follow-up chemistry of 1,2-oxaphosphetane complexes. The reactivity of the title compounds was illustrated by an acid-induced ring-expansion reaction using **7a–d**, thus yielding a novel six-membered heterocyclic ligand (in **12**).

Experimental Section

6–8: A solution of 292.5 mg (0.5 mmol) of complex **1** and 80 µL (0.5 mmol, 1.0 equiv) of 12-crown-4 in 10 mL of diethyl ether was cooled to −78 °C and 0.3 mL (0.51 mmol, 1.7 M in *n*-pentane, 1.02 equiv) of *t*BuLi was added dropwise. Subsequently, 0.06 mL of styrene oxide (0.52 mmol, 1.04 equiv), 0.04 mL of propylene oxide (0.57 mmol, 1.14 equiv), or 0.04 mL of epichlorohydrin (0.51 mmol, 1.02 equiv) was added with a syringe and the solution allowed to warm to ambient temperature. All volatiles were removed in vacuo (ca. 2×10^{-2} mbar) and the products were extracted with *n*-pentane (3×15 mL). Products **6–8** were purified by low-temperature column chromatography (SiO$_2$, −20 °C, eluent: petroleum ether, petroleum ether/diethyl ether 10:0.1).The products were obtained as solids after all volatiles had been removed in vacuo (ca. 2×10^{-2} mbar) from the second fractions. The products were recrystallized by slow evaporation of saturated *n*-pentane solutions at 4 °C to yield colorless solid compounds as mixtures of isomers (Table 1) Yield: **6**: 40 %, **7**: 58 %, **8**: 61 %. For analytical data see the Supporting Information.[12]

12a,b: First 572 mg (1.0 mmol) **7a–d** was dissolved in 20 mL of CH$_2$Cl$_2$. Then 0.11 mL (1.1 mmol) of PhCN and, subsequently, 0.13 mL (1.5 mmol) of triflic acid was added. The mixture was stirred for 30 min at ambient temperature and cooled to 0 °C and 0.21 mL (1.5 mmol) of Et$_3$N was added. After 20 min the solvent was removed under reduced pressure (ca. 2×10^{-2} mbar). The residue was purified by column chromatography (SiO$_2$, −20 °C, eluent: petroleum ether, petroleum ether/diethyl ether 10:0.1). After evaporation of the second fraction and recrystallized by slow evaporation of a saturated diethyl ether solution, the product **12a** was obtained as a yellow solid in 56 % yield. For analytical data see the Supporting Information.[12]

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Keywords: oxaphosphetane complexes · phosphinidenoid complexes · ring expansion · ring insertion · Wittig reaction

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[1] a) G. Wittig, G. Geissler, *Justus Liebigs Ann. Chem.* **1953**, *580*, 44–57; b) G. Wittig, U. Schöllkopf, *Chem. Ber.* **1954**, *87*, 1318–1330; c) B. E. Maryanoff, A. B. Reitz, *Chem. Rev.* **1989**, *89*, 863–927; d) O. I. Kolodiazhnyi, *Phosphorus Ylides*, Wiley, Weinheim, **1999**; e) P. A. Byrne, D. G. Gilheany, *Chem. Soc. Rev.* **2013**, *42*, 6670–6696.

[2] F. López-Ortiz, J. Garciá López, R. Álvarez Manzaneda, I. J. Pérez Álvarez, *Mini-Rev. Org. Chem.* **2004**, *1*, 65–76.

[3] a) T. Kawashima, K. Kato, R. Okazaki, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 869–870; *Angew. Chem.* **1993**, *105*, 941–942; b) M. Mazhar-ul-Haque, C. N. Caughlan, F. Ramirez, J. F. Pilot, C. P. Smith, *J. Am. Chem. Soc.* **1971**, *93*, 5229–5235; c) H. A. E Aly, J. H. Barlow, D. R. Russell, D. J. H. Smith, M. Swindles, S. Trippett, *J. Chem. Soc. Chem. Commun.* **1976**, *12*, 449–450; d) S. Kojima, M. Sugino, S. Matsukawa, M. Nakamoto, K. Akiba, *J. Am. Chem. Soc.* **2002**, *124*, 7674–7675; e) M. Hamaguchi, Y. Iyama, E. Mochizuki, T. Oshima, *Tetrahedron Lett.* **2005**, *46*, 8949–8952.

[4] a) F. Mathey, *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 275–286; *Angew. Chem.* **1987**, *99*, 285–296; b) K. B. Dillon, F. Mathey, J. F. Nixon, *Phosphorus: The Carbon Copy*, Wiley, Chichester, **1998**, 19; c) F. Mathey, N. H. Tran Huy, A. Marinetti, *Helv. Chim. Acta* **2001**, *84*, 2938–2957; d) F. Mathey, *Dalton Trans.* **2007**, 1861–1868; e) J. C. Slootweg, K. Lammertsma, *Sci. Synth.* **2009**, 15–36; f) R. Waterman, *Dalton Trans.* **2009**, 16–26; g) H. Jansen, J. C. Slootweg, A. W. Ehlers, K. Lammertsma, *Organometallics* **2010**, *29*, 6653–6659; h) Y. X. Ng, F. Mathey, *Angew. Chem. Int. Ed.* **2013**, *52*, 14140–14142; *Angew. Chem.* **2013**, *125*, 14390–14392.

[5] A. Marinetti, F. Mathey, *Organometallics* **1987**, *6*, 2189–2191.

[6] T. L. Breen, D. W. Stephan, *J. Am. Chem. Soc.* **1995**, *117*, 11914–11921.

[7] K. Issleib, H.-R. Roloff, *Chem. Ber.* **1965**, *98*, 2091 – 2098.

[8] a) A. Özbolat, G. v. Frantzius, J. M. Perez, M. Nieger, R. Streubel, *Angew. Chem. Int. Ed.* **2007**, *46*, 9327 – 9330; *Angew. Chem.* **2007**, *119*, 9488 – 9491; b) M. Bode, J. Daniels, R. Streubel, *Organometallics* **2009**, *28*, 4636 – 4638; c) V. Nesterov, G. Schnakenburg, A. Espinosa, R. Streubel, *Inorg. Chem.* **2012**, *51*, 12343 – 12349; d) R. Streubel, A. Özbolat-Schön, G. von Frantzius, H. Lee, G. Schnakenburg, D. Gudat, *Inorg. Chem.* **2013**, *52*, 3313 – 3325.

[9] Selected recent examples: a) J. M. Pérez, M. Klein, A. W. Kyri, G. Schnakenburg, R. Streubel, *Organometallics* **2011**, *30*, 5636 – 5640; b) R. Streubel, M. Klein, G. Schnakenburg, *Organometallics* **2012**, *31*, 4711 – 4715; c) R. Streubel, E. Schneider, G. Schnakenburg, *Organometallics* **2012**, *31*, 4707 – 4710; d) C. Albrecht, E. Schneider, M. Engeser, G. Schnakenburg, A. Espinosa, R. Streubel, *Dalton Trans.* **2013**, *42*, 8897 – 8906; e) L. Abdrakhmanova, A. Espinosa, R. Streubel, *Dalton Trans.* **2013**, *42*, 10510 – 10514; f) J. M. Villalba Franco, A. Espinosa, G. Schnakenburg, R. Streubel, *Chem. Commun.* **2013**, *49*, 9648 – 9650; g) V. Nesterov, G. Schnakenburg, A. Espinosa, R. Streubel, *Chem. Eur. J.* **2014**, *20*, 7010 – 7016.

[10] Selected recent examples: a) A. Özbolat-Schön, M. Bode, G. Schnakenburg, A. Anoop, M. van Gastel, F. Neese, R. Streubel, *Angew. Chem. Int. Ed.* **2010**, *49*, 6894 – 6898; *Angew. Chem.* **2010**, *122*, 7047 – 7051; b) V. Nesterov, L. Duan, G. Schnakenburg, R. Streubel, *Eur. J. Inorg. Chem.* **2011**, 567 – 572; c) V. Nesterov, T. Heurich, R. Streubel, *Pure Appl. Chem.* **2013**, *85*, 829 – 834; d) R. Streubel, A. W. Kyri, L. Duan, G. Schnakenburg, *Dalton Trans.* **2014**, *43*, 2088 – 2097.

[11] A. A. Khan, C. Wismach, P. G. Jones, R. Streubel, *Dalton Trans.* **2003**, 2483 – 2487.

[12] See the Supporting Information for NMR, IR, MS, and EA data, melting points, NMR sample spectra for complex **12a**, and details on the X-ray diffraction analysis. CCDC 999679 (**6a**), CCDC 999680 (**7**), CCDC 999681 (**8**), and CCDC 999682 (**12a**) 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.