Organometallics **2007,** *26,* 245−246

Synthesis of the First 1,3,4λ^3-Dioxaphospholane Complexes

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Received October 7, 2006

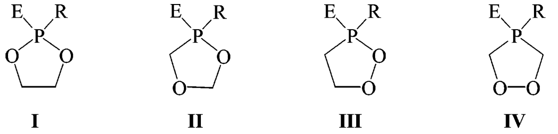
Summary: The first 1,3,4λ^3-dioxaphospholane complexes ***4a,b*** *were obtained by thermolysis of P-Cp*-substituted 2H-azaphosphirene complex* ***1*** *in the presence of aldehydes* ***2a,b****; the intermediate formation of phosphacarbonyl-ylide complexes* ***3a,b*** *is proposed.*

Introduction

1,3,2-Dioxaphospholanes **I** (Scheme 1) have attracted a great deal of interest over the years because of their applicability as precursors for polymeric and/or copolymeric materials,[1] some of which are fire-resistant and some biodegradable[2] Consequently, several valuable synthetic methods have been developed for a wide variety of P^{III} and P^{V} derivatives. In contrast, knowledge about the synthesis and reactivity of 1,3,4-dioxaphospholanes **II** with P^{V} centers is comparatively scarce,[3] and nothing is known about derivatives of **II** with a P^{III} center.[4] Also, derivatives of 1,2,3-dioxaphospholane **III** are very rare[5] and 1,2,4-dioxaphospholanes **IV** are unknown.

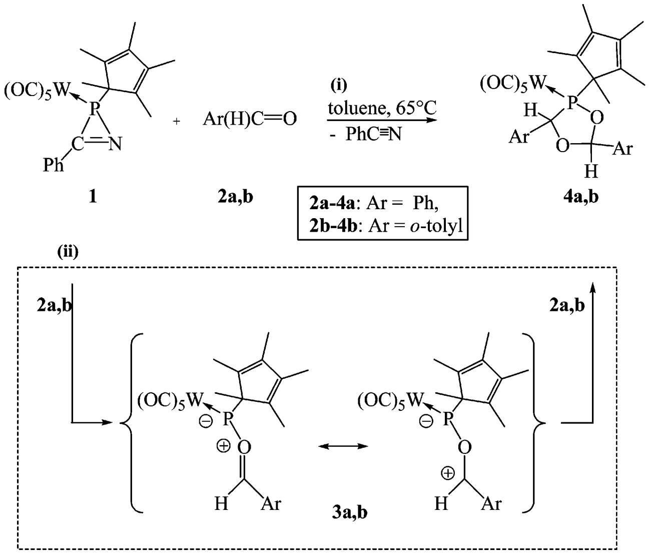
In principle, it might be possible to synthesize 1,3,4λ^3-dioxaphospholanes **II** via consecutive reactions starting from λ^3-oxaphosphiranes; unfortunately, they are unknown. Although, λ^3-oxaphosphirane complexes have been reported by Mathey and co-workers[6] and us,[7] so far no investigations on their chemistry have been reported. On the other hand, transiently formed phosphacarbonyl-ylide complexes, which have a zwitterionic, 1,3-dipolar $CR_2{=}O{-}PR$ moiety, could provide access,[8] although some reactions may yield surprises.[9] Here, we report our first investigations on thermal reactions of a *P*-Cp*-substituted 2*H*-azaphosphirene complex with aldehydes.

Scheme 1. Dioxaphospholanes I−IV[a]



[a] E denotes either two ubiquitous organic substituents, a metal complex, an oxygen, or a lone pair.

Scheme 2. Synthesis of 1,3,4λ^3-Dioxaphospholane Complexes 4a,b (i) and Assumed Formation via Transient Complexes 3a,b (ii)



Experimental Results

A selective reaction was observed when 2*H*-azaphosphirene complex **1**[10] was heated in toluene in the presence of an excess of aldehydes **2a**,**b**. Under these conditions complexes **4a**,**b** were formed regio- and diastereoselectively (Scheme 2, i) and could be easily isolated without using column chromatography. Our assumption on the reaction course (ii) is shown at the bottom of Scheme 2. After transient formation of 1,3-dipole complexes **3a**,**b** (cf. ref 9) an intermolecular [3+2] cycloaddition with aldehydes **2a**,**b** led to the final products **4a**,**b**. Unfortunately, neither **3a**,**b** nor their cyclic isomers, the oxaphosphirane complexes, were detected under these conditions. The observed diastereoselectivity parallels observations made for nitrilium phosphane-ylides (cf. ref 11b) and is, most probably, stereochemically controlled. Further studies to elucidate the mechanism are currently underway.

The structures of complexes **4a**,**b** in solution and solid state were unambiguously established by multinuclear NMR studies,

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(1) As most results are described in patents, just some selected references: (a) Huang, X.-J.; Xu, Z.-K.; Wan, L.-S.; Wang, Z.-G.; Wang, J.-L. *Macromol. Biosci.* **2005**, *5*, 322. (b) Fontaine, L.; Derouet, D.; Brosse, J. C. *Eur. Polym. J.* **1990**, *26*, 865. (c) Biela, T.; Klosinski, P.; Penczek, S. *J. Polym. Sci. Part A: Polym. Chem.* **1989**, *27*, 763. (d) Yasuda, H.; Sumitani, M.; Nakamura, A. *Macromolecules* **1981**, *14*, 458.

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(3) (a) Novikova, Z. S.; Odinets, I. L.; Lutsenko, I. F. *Zh. Obshch. Khim.* **1987**, *57*, 706. (b) Boisdon, M.; Barrans, T. J. *J. Chem. Soc., Chem. Commun.* **1988**, 615.

(4) A current literature search revealed no example of the free ligand system **II** having a P^{III} center.

(5) For a bicyclic derivative, see: Edmundson, R. S. R. S.; Mitchell, E. W. *J. Chem. Soc. C* **1971**, *19*, 3179.

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10.1021/om0609214 CCC: \$37.00

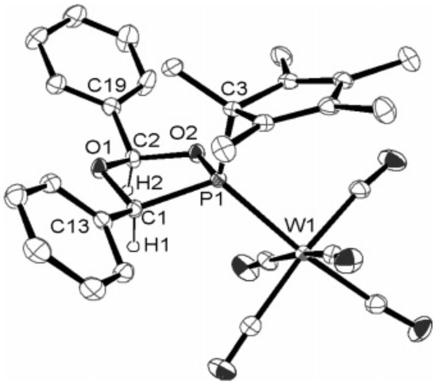

Figure 1. Molecular structure of **4a** in the crystal (thermal ellipsoids at 50% probability level). H atoms (except H1 and H2) are omitted for clarity. Selected bond lengths [Å] and angles [deg]: P1−W1 2.497(1), P1−C1 1.899(2), P1−O2 1.645(2), P1−C3 1.877(2), C1−O1 1.423(3), O1−C2 1.416(3), C2−O2 1.447(3); C1−P1−O2 88.9(1), P1−C1−O1 102.7(1), C1−O1−C2 107.5(2), O2−C2−O1 108.2(2), P1−O2−C2 114.4(1), C1−P1−O2−C2 6.3(2).[14]

mass spectrometry, and elemental analyses and, in addition, complex **4a** by single-crystal X-ray diffraction analysis.

The $^{31}P\{^1H\}$ NMR parameters of the new compounds are of special interest, as they show resonances around 138 ppm (**4a**: 138.6 (^1J(W,P) = 284.8 Hz) and **4b**: 137.4 (^1J(W,P) = 282.3 Hz)), which is significantly highfield-shifted in comparison to known 1,3,2-oxaphospholane complexes, which resonate between 170 and 195 ppm and also have significantly higher phosphorus−tungsten coupling constant magnitudes.[9] The two heterocyclic ring carbon atoms of **4a**,**b** display resonances at 94.5 (s, PCO) and 102.7 ($^{(2+3)}J$(P,C) = 9.4 Hz, OCO) (**4a**) and 92.1 (d, J(P,C) = 6.1 Hz, PCO) and 99.5 ($^{(2+3)}J$(P,C) = 8.7 Hz, OCO) (**4b**), thus confirming the different carbon environments; this assignment was made tentatively. It should be noted that small coupling constants have been observed previously for endocyclic phosphorus−carbon bonds in heterocyclic P^{III} complexes.[12]

The structure of **4a** (Figure 1) shows the nonplanar 1,3,4-dioxaphospholane ring as a central unit having the two phenyl groups and the Cp* in a *cis* position; O1 is 0.57 Å out of the best plane (C1−P1−O2−C2 torsion angle 6.3° and folding angle with C2−O1−C1 138°). Noteworthy is also that the two P−C distances (P1−C1 1.899(2) Å, P1−C3 1.877(2) Å) are at the upper boundary for $P-C_{sp3}$ single bonds.[13]

Experimental Section

General Procedures. All reactions and manipulations were carried out under an atmosphere of deoxygenated dry argon, using standard Schlenk techniques with conventional glassware, and solvents were dried according to standard procedures. NMR data were collected on a Typ Bruker DMX 300 (303 K), at 121.5 MHz (^{31}P), 75 MHz (^{13}C), and 300.1 MHz (^1H), using TMS and 85% H_3PO_4 as standard references; J/Hz. Mass spectra were recorded on a Kratos MS 50 spectrometer (70 eV); only m/z values are given. Melting points were obtained on a Büchi 535 capillary apparatus. Elemental analyses were performed using a Elementar (Vario EL) analytical gas chromatograph. The κP notation in the nomenclature is intended to differentiate between P- and O-coordination of the appropriate heterocycle to the metal.

Synthesis of Complexes 4a,b. Ninety-six milligrams (0.16 mmol) (**a**) or 147 mg (0.25 mmol) (**b**) of **1** and 10 equiv of the corresponding aldehyde (**a**: benzaldehyde, **b**: *o*-tolylaldehyde) dissolved in 1.2 or 1.7 mL, respectively, of toluene were stirred at 65 °C for 2 h. The solvent was evaporated and the solids were washed with *n*-pentane to deliver the products as colorless solids.

Selected data for **4a**. Mp: 168 °C. Yield: 47 mg (42%). ^1H NMR (C_6D_6): 0.87 (s, 3H, Cp*-CH_3), 1.18 (d, ^3J(P,H) = 10.4 Hz, 3H, Cp*(C1)-CH_3), 1.51 (dd, J(H,H) = 5.5 Hz, J(H,H) = 0.9 Hz, 3H, Cp*-CH_3), 1.57 (dd, J(H,H) = 3.7 Hz, J(H,H) = 0.9 Hz, 3H, Cp*-CH_3), 1.83 (s, 3H, Cp*-CH_3), 5.64 (d, J(P,H) = 13.6 Hz, 1H, PCH), 5.71 (s, 1H, POCH), 7.06−7.24 (m_c, 6H, Ph), 7.67 (dm_c, J(H,H) = 6.5 Hz, 2H, Ph), 7.79 (br d, J(H,H) = 7.5 Hz, 2H, Ph). $^{13}C\{^1H\}$ NMR (C_6D_6): 9.8 (d, J(P,C) = 1.0 Hz, Cp*-CH_3), 10.2 (d, J(P,C) = 1.9 Hz, Cp*-CH_3), 10.4 (d, J(P,C) = 1.3 Hz, Cp*-CH_3), 11.5 (s, Cp*-CH_3), 13.4 (d, J(P,C) = 5.5 Hz, Cp*(C1)-CH_3), 65.0 (d, ^1J(P,C) = 5.5 Hz, Cp*(C1)), 94.5 (s, PCO), 102.7 (d, J(P,C) = 9.4 Hz, OCO), 125.1 (s, Ph), 125.8 (d, J(P,C) = 2.9 Hz, Ph), 127.2 (d, J(P,C) = 2.6 Hz, Ph), 127.3 (s, Ph), 127.6 (d, J(P,C) = 2.3 Hz, Ph), 128.3 (s, Ph), 132.5 (d, J(P,C) = 2.3 Hz, Ph), 134.3 (d, J(P,C) = 10.3 Hz, Cp*), 134.7 (d, J(P,C) = 2.3 Hz, Ph), 137.9 (s, Cp*), 141.2 (d, J(P,C) = 5.2 Hz, Cp*), 141.7 (d, J(P,C) = 9.1 Hz, Cp*), 195.2 (d_{Sat}, ^2J(P,C) = 7.4 Hz, ^1J(W,C) = 125.4 Hz, *cis*-CO), 196.5 (d, ^2J(P,C) = 30.1 Hz, *trans*-CO) ppm. MS (EI, 70 eV): m/z = 702 [M^+, 9]. 197.9 (d, ^2J(P,C) = 33.5 Hz, *trans*-CO) ppm. MS (EI, 70 eV): m/z = 588 [M^+, 28]. Anal. Calc: C 40.84, H 3.60. Found: C 41.39, H 3.80.

Selected data for **4b**. Mp: 198 °C (dec). Yield: 68 mg (37%). ^1H NMR ($CDCl_3$): 0.99 (s, 3H, Cp*-CH_3), 1.32 (d, ^3J(P,H) = 10.6 Hz, 3H, Cp*(C1)-CH_3), 1.71−1.75 (m, 6H, Cp*-CH_3), 1.82 (s, 3H, Cp*-CH_3), 2.52 (s, 3H, Ar-CH_3), 2.75 (s, 3H, Ar-CH_3), 6.02 (d, J(P,H) = 16.4 Hz, 1H, PCH), 6.22 (d, J(P,H) = 1.7 Hz, 1H, POCH), 7.22−7.44 (m_c, 6H, Ar), 7.22−7.44 (m_c, 2H, Ar) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 9.5 (d, J(P,C) = 1.3 Hz, Cp*-CH_3), 10.4 (d, J(P,C) = 1.9 Hz, Cp*-CH_3), 11.0 (d, J(P,C) = 1.3 Hz, Cp*-CH_3), 11.3 (s, Cp*-CH_3), 13.6 (d, J(P,C) = 5.5 Hz, Cp*(C1)-CH_3), 18.0 (s, Ar-CH_3), 21.6 (s, Ar-CH_3), 64.7 (d, ^1J(P,C) = 5.8 Hz, Cp*(C1)), 92.1 (d, J(P,C) = 6.1 Hz, PCO), 99.5 (d, J(P,C) = 8.7 Hz, OCO), 124.4 (s, Ar-CH), 124.7 (d, J(P,C) = 1.6 Hz, Ar-CH), 124.9 (s, Ar-CH), 126.9 (d, J(P,C) = 2.3 Hz, Ar-CH), 127.4 (d, $J_{P,C}$ = 2.3 Hz, Ar-CH), 128.6 (s, Ar-CH), 129.7 (d, $J_{P,C}$ = 1.6 Hz, Ar-CH), 129.8 (s, Ar−CH), 132.4 (d, J(P,C) = 2.9 Hz, Ar), 132.7 (d, J(P,C) = 3.9 Hz, Ar), 134.0 (d, J(P,C) = 11.3 Hz, Cp*), 135.0 (d, J(P,C) = 2.9 Hz, Ar), 136.1 (s, Ar), 138.6 (s, Cp*), 141.4 (d, $J_{P,C}$ = 5.5 Hz, Cp*), 141.5 (d, J(P,C) = 9.1 Hz, Cp*), 195.6 (d, ^2J(P,C) = 7.4 Hz, ^1J(W,C) = 125.8 Hz, *cis*-CO), 196.3 (d, ^2J(P,C) = 29.7 Hz, *trans*-CO) ppm. MS (EI, 70 eV): m/z = 730 [M^+, 19]. Anal. Calc: C 50.98, H 4.28. Found: C 50.46, H 4.31.

Crystallographic data of **4a** have been deposited at the Cambridge Crystallographic Data Centre under the number CCDC 615112. Copies may be requested free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, England (E-mail: deposit@ccdc.cam.ac.uk).

OM0609214

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[12] This phenomenon was observed in heterocycles of various ring sizes and constitutions; for example in three-membered heterocycles: (a) P,C heterocycles: F. P, C: Mathey, F. *Chem. Rev.* **1990**, *90*, 997. (b) P, C heterocycles with one additional N-ring center: Streubel, R.; Jeske, J.; Jones, P. G.; Jones, R.; Herbst-Irmer, G. R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 80.

[13] Allen, F. A.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *Chem. Soc., Perkin Trans. 2* **1987**, 1.

[14] Crystal structure determination of **4a**, $C_{29}H_{27}O_7PW$. Crystal data: triclinic, space group $P\bar{1}$ (no. 2), a = 9.2701(2) Å, b = 11.6638(3) Å, c = 13.5918(3) Å, α = 94.216(1)°, β = 94.884(1)°, γ = 110.355(1)°, U = 1364.44(5) Å^3, Z = 2, T = 123 K. Data collection: a crystal 0.40 × 0.30 × 0.20 mm was used to register 11 368 intensities (Mo Kα radiation, $2\theta_{max}$ 559) on a Nonius KappaCCD diffractometer. A semiempirical absorption correction was applied. Structure solution and refinement: the structure was solved by Patterson methods (SHELXS-97[15a]) and refined anisotropically (full-matrix least-squares on F^2 (program SHELXL-97[15b])) to wR2 = 0.0525 (for all data), R1 = 0.0206 ($I < 2\sigma(I)$) for 347 parameters and 5931 independent reflections. Hydrogen atoms were included using a riding model.

[15] (a) Sheldrick, G. M. *Acta Crystallogr. A* **1990**, *46*, 467. (b) Sheldrick, G. M. *SHELXL-97*; University of Göttingen, 1997.