

The reaction of electrophilic terminal phosphinidene complexes with benzophenone and fluorenone: the unexpected formation of six- and eight-membered heterocycles

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Abstract

The phenylphosphinidene–pentacarbonyltungsten complex **2**, as generated from the appropriate 7-phosphanorbornadiene complex **1**, reacts at 60°C with benzophenone to give a benzo-annellated 1-oxa-2-phosphacyclohex-4-ene 2-oxide as a 1:1 mixture of two isomers **3a,b**. The same phosphinidene complex **2** reacts at 120°C with fluorenone. A deoxygenation of fluorenone takes place leading to the bifluorenylidene **4** and to an eight-membered 1,2,8-oxadiphosphocane 2,8-dioxide **5**. Both compounds **3b** and **8** have been fully characterized by X-ray crystal structure analysis. The two reactions are interpreted as resulting from the initial formation of a $P \cdots O$ Lewis adduct between the phosphinidene and the ketone.

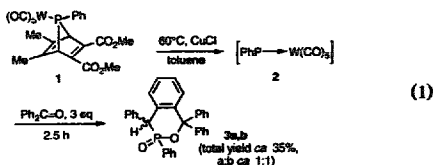
Keywords: Phosphinidene; Benzophenone; Fluorenone; Oxadiphosphocane; 1,2-Oxaphosphacyclohexene

1. Introduction

Whereas nucleophilic terminal phosphinidene complexes display a clear-cut Wittig-type reactivity towards carbonyl derivatives [1,2], i.e. they convert $C=O$ into $C=P$ double bonds, the reactivity of electrophilic terminal phosphinidene complexes towards the same type of compound appears to be almost unpredictable. At least three pathways have been uncovered until now: the [1 + 2] cycloaddition leading to oxaphosphirane complexes [3], the insertion into an $\alpha-C-H$ bond when available [4], and the insertion into the $O-H$ bond of the enol tautomers [4]. Since the acidic α -hydrogens play a central role in the reaction of enolizable ketones with terminal phosphinidene complexes, we decided to also investigate the course of the reaction in the absence of such hydrogens. More precisely, we report hereafter on the results of the reactions of the representative terminal phosphinidene complex $[PhP \rightarrow W(CO)_5]$, as generated from the corresponding 7-phosphanorbornadiene complex [5,6] with benzophenone and fluorenone.

2. The reaction with benzophenone

The catalytic decomposition of the 7-phosphanorbornadiene complex **1** was carried out at 60°C in the presence of an excess of benzophenone:



The monitoring of the crude reaction mixture by ^{31}P NMR spectroscopy showed the formation of several products. Among these, the two major ones **3a,b** were successfully purified by chromatography. The ^{13}C and ^{31}P NMR spectra immediately showed that both **3a** and **3b** were tungsten-free. Besides, the quasi-identity of the ^{31}P and mass spectra of both compounds strongly suggested that **3a,b** was a diastereomeric mixture. Finally, the 1H and ^{13}C spectra also showed that both **3a** and **3b**

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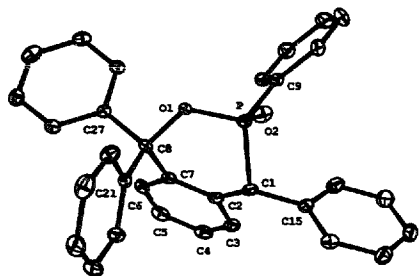


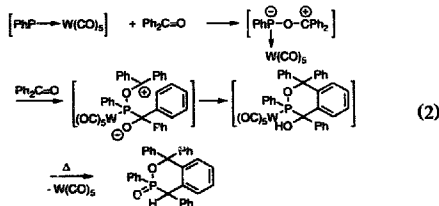
Fig. 1. ORTEP drawing of one molecule of **3b**, as determined by a single crystal X-ray diffraction study. Ellipsoids are scaled to enclose 50% of the electron density. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): P–O(1) 1.586(2), P–O(2) 1.467(2), P–C(1) 1.829(3), P–C(9) 1.786(3), O(1)–C(8) 1.463(3), C(1)–C(2) 1.530(4), C(2)–C(7) 1.400(4), C(7)–C(8) 1.526(4), O(1)–P–O(2) 115.0(1), O(1)–P–C(1) 103.0(1), O(1)–P–C(9) 102.5(1), O(2)–P–C(9) 112.7(1), C(1)–P–C(9) 110.9(1), P–O(1)–C(8) 126.6(2), P–C(1)–C(2) 111.8(2), C(1)–C(2)–C(7) 120.1(2), C(2)–C(7)–C(8) 120.6(2), O(1)–C(8)–C(7) 109.0(2).

incorporated an sp^3 -CH group directly bonded to phosphorus.

3a. CH: $\delta(H) + 4.17$ [$^2J(H-P) = 15.3$ Hz]; $\delta(C) + 48.43$ [$^1J(C-P) = 80.9$ Hz].

3b. CH: $\delta(H) + 4.40$ [$^2J(H-P) = 30.5$ Hz]; $\delta(C) + 50.74$ [$^1J(C-P) = 77.1$ Hz].

The final identification of **3a,b** came from an X-ray crystal structure analysis of **3b** (Fig. 1). The structure of **3b** incorporates a benzo-annellated 1-oxa-2-phosphacyclohex-4-ene ring. With a Ph–P–C₃–Ph torsion angle of 58.41(0.24)°, **3b** displays a *cis* disposition of the phenyl groups on P and C₃, and hence **3a** corresponds to the *trans* isomer. This is in line with the higher $^2J(H-P)$ coupling in **3b** corresponding to a *cis* disposition of C₃–H and P=O [7]. We propose the following mechanism for the formation of **3**:

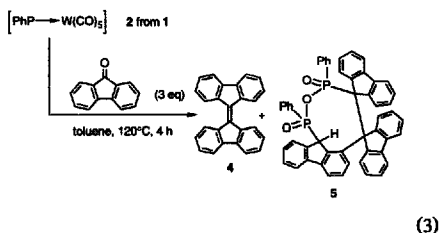


The first step involves the formation of an acid-base Lewis adduct between the benzophenone and the phosphinidene. Such an adduct is similar to the ylids obtained in the reaction of phosphinidene complexes with

amines or phosphines [8]. With a bulky substituent at phosphorus, such an adduct can cyclize to give the oxaphosphirane complex observed by Streubel et al. [3]. The formation of this adduct transforms phosphorus into a nucleophilic centre which can attack a second molecule of benzophenone. Then, a cyclization occurs via an electrophilic substitution reaction at the *ortho* position of one of the phenyl rings of the second molecule of benzophenone. The final decomplexation with isomerisation of the 1-hydroxyalkylphosphine into the corresponding phosphine oxide is more classical [9].

3. The reaction with fluorenone

The reaction of **2** with fluorenone needs more drastic conditions than the reaction with benzophenone. The condensation was performed in boiling toluene without a catalyst, using a 3 molar excess of fluorenone:



The two main products of the reaction are the bifluorenylidene **4** (representing a 24% conversion of the fluorenone used) and the 1,2,8-oxadiphosphocane **5** (27% yield on the basis of **1**). The identification of **4** was based on its characteristic mass [m/z 328 (M^+ , 100%)], 1H NMR and ^{13}C NMR spectra. The structure of the oxadiphosphocane **5** was established by X-ray crystal structure analysis (Fig. 2). The relative orientation of the two P=O double bonds is *trans*. Even in the crude reaction mixture, the *cis*-isomer was not detected.

Even if it is difficult to speculate on the mechanism of formation of **5**, it clearly appears that **2** has deoxygenated the fluorenone. Such a reaction has some precedent. Tributylphosphine has been shown to reduce fluorenone to give bifluorenylidene [10]. The transient formation of a carbene was postulated. In toluene, this carbene is able to abstract hydrogen to give a fluorenyl radical which oligomerizes to give trimeric units. The formation of **5** seems to follow a similar pathway. The ability of **2** to use its lone pair to reduce a carbonyl derivative demonstrates the ambident reactivity of such phosphinidene complexes. This finding corroborates earlier results of the group of Streubel on the reactivity

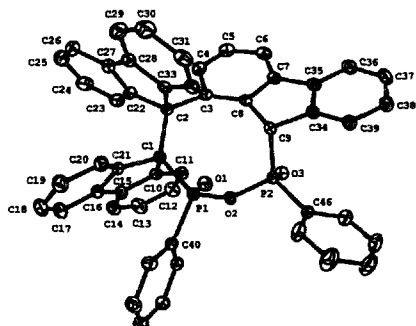


Fig. 2. ORTEP drawing of one molecule of **3b**, as determined by a single crystal X-ray diffraction study. Ellipsoids are scaled to enclose 50% of the electron density. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): P(1)–O(2) 1.604(2), P(1)–C(1) 1.840(2), O(2)–P(2) 1.604(2), P(2)–C(9) 1.820(2), C(9)–C(8) 1.545(3), C(8)–C(3) 1.423(3), C(2)–C(3) 1.569(3), C(1)–C(2) 1.604(3); P(1)–O(2)–P(2) 135.5(1), O(2)–P(2)–C(9) 103.52(9), P(2)–C(9)–C(8) 109.3(1), C(3)–C(8)–C(9) 134.4(2), C(2)–C(3)–C(8) 128.8(2), C(1)–C(2)–C(3) 118.0(2), P(1)–C(1)–C(2) 121.4(1).

of similar species towards both electron-rich and electron-poor alkynes [11]. The versatility of these terminal phosphinidene complexes as synthetic reagents in organophosphorus chemistry is thus highlighted again.

4. Experimental

All reactions were performed under nitrogen; the solvents were purified, dried and degassed by standard techniques. ^1H , ^{13}C and ^{31}P NMR spectra were recorded on a Bruker AC 200 SY spectrometer operating at 200.13, 50.32 and 81.01 MHz respectively. All chemical shifts are reported in parts per million downfield from internal TMS (^1H and ^{13}C) and external 85% H_3PO_4 (^{31}P). Mass spectra (EI) were obtained at 70 eV by the direct inlet method.

4.1. Reaction of **2** with benzophenone

A solution of the 7-phosphanorbomadiene complex **1** (1 g, 1.5×10^{-3} mol) and benzophenone (0.83 g, 4.5×10^{-3} mol) in toluene (10 ml) was heated at 60°C for 2.5 h with copper(I) chloride (20 mg) as a catalyst. After filtration and evaporation of the solution, the residue was chromatographed on silica gel (70–230 mesh Merck) with ether as the eluent: **3a** Rf ~ 0.38, **3b** Rf ~ 0.59.

3a. 0.13 g (18%). ^{31}P NMR (CDCl_3): δ 29.7. ^1H NMR (CDCl_3): δ 4.17 (d, $^2J(\text{H}-\text{P}) = 15.3$ Hz, 1H, CHPh). ^{13}C NMR (CDCl_3): δ 48.43 (d, $^1J(\text{C}-\text{P}) =$

80.9 Hz, CHPh), 92.04 (d, $^2J(\text{C}-\text{P}) = 9.3$ Hz, CPh_2). Mass: m/z 332 ($\text{M}^+ - \text{PhPO}_2$, 78%), 254 (100%).

3b. 0.12 g (17%). ^{31}P NMR (CDCl_3): δ 31.3. ^1H NMR (CDCl_3): δ 4.40 (d, $^2J(\text{H}-\text{P}) = 30.5$ Hz, 1H, CHPh). ^{13}C NMR (CDCl_3): δ 50.74 (d, $^1J(\text{C}-\text{P}) = 77.1$ Hz, CHPh), 92.28 (d, $^2J(\text{C}-\text{P}) = 8.7$ Hz, CPh_2). Mass: m/z 332 ($\text{M}^+ - \text{PhPO}_2$, 56%), 254 (100%).

4.2. Reaction of **2** with fluorenone

A solution of complex **1** (1.3 g, 2×10^{-3} mol) and fluorenone (1.1 g, 6×10^{-3} mol) in toluene (10 ml) was heated at 120°C in a sealed tube for 4 h. After evaporation of the solution, the residue was chromatographed on silica gel with hexane/ CH_2Cl_2 /ether in various ratios as the eluent. The bifluorenylidene **4** was recovered with hexane/ CH_2Cl_2 7:3 (0.24 g).

4. ^1H NMR (CDCl_3): δ 7.27 (pseudo t, 4H, $\text{H}_{2,2',7,7'}$ or $\text{H}_{3,3',6,6'}$), 7.38 (pseudo t, 4H, $\text{H}_{3,3',6,6'}$ or $\text{H}_{2,2',7,7'}$), 7.75 (d, $^3J(\text{H}-\text{H}) = 7.1$ Hz, 4H, $\text{H}_{4,4',5,5'}$), 8.46 (d, $^3J(\text{H}-\text{H}) = 7.7$ Hz, 4H, $\text{H}_{1,1',8,8'}$). ^{13}C NMR (CDCl_3): δ 119.93, 126.78, 126.86, 129.18 (4s, CH), 138.37 (s, C), 141.09 (s, $\text{C}_9 = \text{C}_9$), 141.41 (s, C). Mass: m/z 328 (M^+ , 100%).

5 was recovered with ether (0.4 g).

5. ^{31}P NMR (CDCl_3): δ 31.21 and 36.89, $^2J(\text{P}-\text{P}) = 37$ Hz. ^1H NMR (CDCl_3): δ 5.70 (d, $^2J(\text{H}-\text{P}) = 7.8$ Hz, 1H, $\text{P}-\text{C}-\text{H}$). ^{13}C NMR (CDCl_3): δ 54.14 (s, C_9 in fluorenylidene), 57.16 (d, $^1J(\text{C}-\text{P}) = 69.7$ Hz, $\text{P}-\text{CH}$), 65.76 (d, $^1J(\text{C}-\text{P}) = 81.7$ Hz, $\text{P}-\text{C}$ fluorenylidene). Mass: m/z 756 (M^+ , 6%), 326 (100%).

4.3. X-ray structure determination

Crystals of **3b**, $\text{C}_{32}\text{H}_{25}\text{O}_2\text{P}^+\text{CH}_2\text{Cl}_2^-$, and **5**, $\text{C}_{51}\text{H}_{34}\text{O}_3\text{P}_2^+\text{CH}_2\text{Cl}_2^-$, were grown from dichloromethane solutions of the compounds. Data were collected at $-150 \pm 0.5^\circ\text{C}$ on an Enraf–Nonius CAD-4 diffractometer using Mo K α radiation ($\lambda = 0.71073$ Å) and a graphite monochromator. The crystal structures were solved and refined using the Enraf–Nonius MOLEN package. Compound **3b** crystallises in space group $P2_1/n$ (No. 14), $a = 16.685(2)$, $b = 9.153(1)$, $c = 18.905(2)$ Å, $\beta = 110.48(1)^\circ$, $V = 2704.6(1)$ Å 3 , $Z = 4$, $d_{\text{calc}} = 1.369$ g cm $^{-3}$, $\mu = 3.3$ cm $^{-1}$, $F(000) = 1160$. Compound **5** crystallises in space group $P\bar{1}$ (No. 2), $a = 10.647(1)$, $b = 11.960(1)$, $c = 16.835(2)$ Å, $\alpha = 104.21(1)^\circ$, $\beta = 102.31(1)^\circ$, $\gamma = 95.22(1)^\circ$, $V = 2006.81(84)$ Å 3 , $Z = 2$, $d_{\text{calc}} = 1.393$ g cm $^{-3}$, $\mu = 2.8$ cm $^{-1}$, $F(000) = 872$. The crystal structures were solved by direct methods. The hydrogen atoms were included as fixed contributions in the final stages of least-squares refinement while using anisotropic temperature factors for all other atoms. A non-Poisson weighting scheme was applied with a p factor equal to 0.08.

The final agreement factors were $R = 0.048$, $R_w = 0.064$, $GOF = 1.09$ for **3b** and $R = 0.042$, $R_w = 0.058$, $GOF = 1.08$ for **5**.

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