



Preliminary communication / Communication

## Cycloaddition reaction of parent ketene with 1,3-dipolar adducts of [RP-W(CO)<sub>5</sub>] and electron-rich nitriles

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### Abstract

The reaction of parent ketene with the 1,3-dipolar adducts of electrophilic terminal phosphinidene complexes [RP-W(CO)<sub>5</sub>] and activated nitriles yields the previously unknown 4,5-dihydro-1,3,4-oxazaphosphole ring. **To cite this article:** N. Hoffman *et al.*, *C. R. Chimie* 7 (2004).

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### Résumé

Les complexes de phosphinidène [RP-W(CO)<sub>5</sub>] donnent un adduit dipolaire 1,3 avec les nitriles activés. Cet adduit réagit avec le cétène parent pour donner le cycle dihydro-4,5-oxazaphosphole-1,3,4, décrit ici pour la première fois. **Pour citer cet article :** N. Hoffman *et al.*, *C. R. Chimie* 7 (2004).

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**Keywords:** Phosphinidene complexes; Ketene; Cycloaddition

**Mots clés :** Complexes de phosphinidène ; Cétène ; Cycloaddition

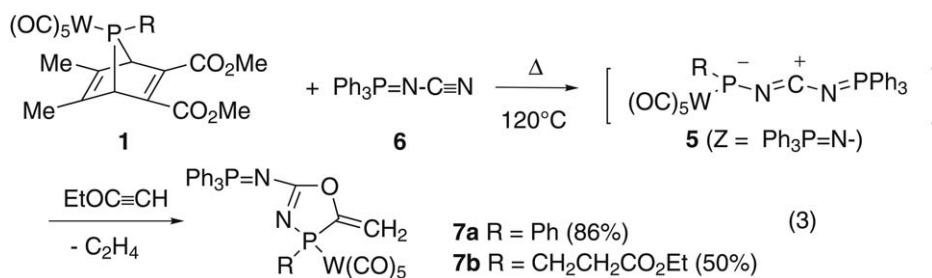
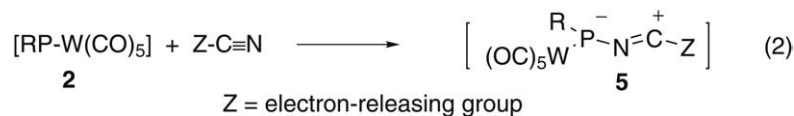
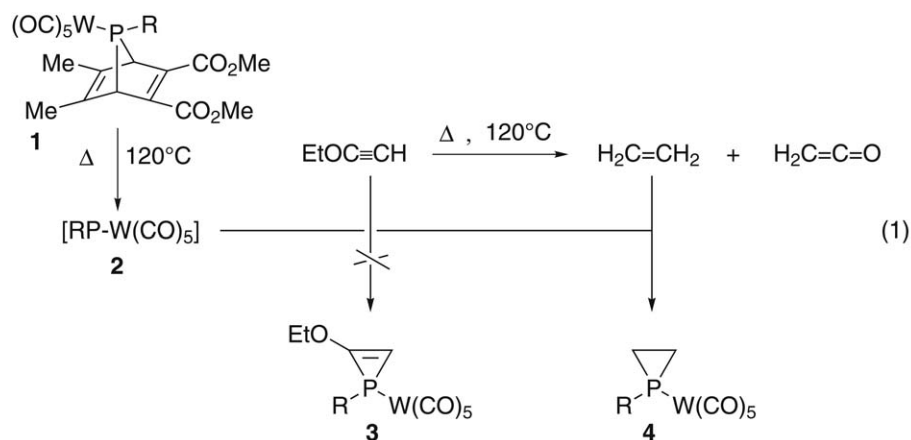
### 1. Introduction

It has been known for some time that ethoxyacetylene and its derivatives decompose to ketenes and ethylene upon heating [1–3]. Some time ago, we studied

the reaction of ethoxyacetylene with electrophilic terminal phosphinidene complexes **2** as generated from the appropriate 7-phosphanorbornadiene complexes **1** [4]. To our surprise, we did not get the expected 3-membered phosphirene complexes **3**, but instead the C-unsubstituted phosphirane complexes **4** resulting from the trapping of ethylene as produced by the thermal decomposition of ethoxyacetylene (Eq. (1)).

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It was clear that parent ketene was a by-product of this reaction, but could not be trapped by the electrophilic terminal phosphinidene complexes.

It is also known for some time that electrophilic terminal phosphinidene complexes react with electron-rich nitriles to give 1,3-dipolar species **5**, in which the phosphorus centre is nucleophilic (Eq. (2)) [5].

Thus it was tempting to add an electron-rich nitrile to the reaction depicted in Eq. (1). We expected that **5** would not react any more with ethylene but, instead, would selectively trap parent ketene. The experiments were carried out with  $N$ -cyano- $P,P'$ -triphenylphosphazene **6** [6]. The results are shown in Eq. (3) and confirm our expectations.

The formula of **7a** was established by X-ray crystal structure analysis (Fig. 1). The compound incorporates a 1,3,4-oxazaphosphole ring that, to our knowledge, has never been described in the literature until now [7]. The structural parameters deserve no special comments. The  $^{13}C$  NMR spectrum suggests that the very contracted exocyclic  $C=C$  double bond ( $C=C$  1.303(4) Å) is highly polarized ( $\delta$  ( $\underline{C}=\underline{CH}_2$ ) 161.5,  $\delta$  ( $C=\underline{CH}_2$ ) 96.5).

## 2. Experimental section

NMR spectra were recorded on a multinuclear Bruker AVANCE 300 MHz spectrometer operating at

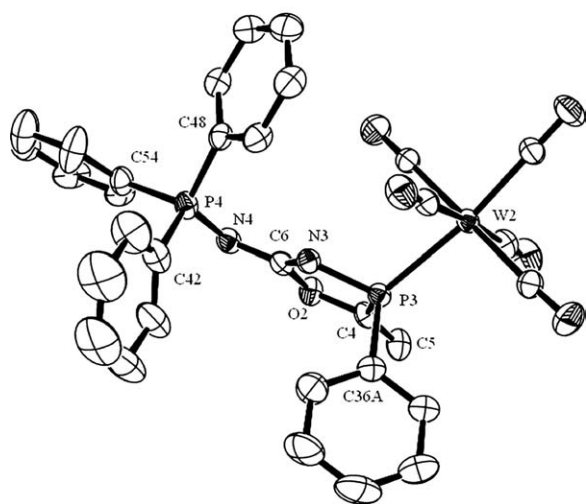


Fig. 1. ORTEP drawing of one molecule of **7a**. Selected bond lengths (Å) and angles (deg): W(2)–P(3) 2.4890(8), P(3)–C(4) 1.833(3), C(4)–C(5) 1.303(4), C(4)–O(2) 1.394(4), O(2)–C(6) 1.391(4), C(6)–W(4) 1.340(4), W(4)–P(4) 1.603(3), C(6)–W(3) 1.298(4), W(3)–P(3) 1.683(3); W(3)–P(3)–C(4) 91.9(1), P(3)–C(4)–O(2) 106.8(2), C(4)–O(2)–C(6) 111.1(2), O(2)–C(6)–W(3) 119.1(3), C(6)–W(3)–P(3) 111.0(2).

300.13 MHz for  $^1\text{H}$ , 75.47 for  $^{13}\text{C}$  and 121.50 MHz for  $^{31}\text{P}$ . Chemical shifts are expressed in parts per million (ppm) downfield from internal tetramethylsilane ( $^1\text{H}$  and  $^{13}\text{C}$ ) and external 85% aqueous  $\text{H}_3\text{PO}_4$  ( $^{31}\text{P}$ ).

### 2.1. General procedure for the synthesis of 1,3,4-oxazaphospholes **7a,b**

To a solution of 7-phosphanorbornadiene complexes (1.2 mmol each), dissolved in 1,2-dichlorobenzene (4 ml), *N*-cyano-*P,P,P*-triphenyl-phospha- $\lambda^5$ -azene (2.4 mmol) and ethoxyacetylene (40% in *n*-hexane, 4 ml) was added and the solutions heated at 120 °C for 45 min with slow stirring. All volatile components were removed in vacuo (ca. 0.01 mbar) and the products separated by low-temperature column chromatography ( $\text{SiO}_2$ , –10 °C, 10 × 2 cm, *n*-pentane/diethyl ether 2:1). Evaporation of the third fractions yielded complexes **7a,b** as brown oils.

#### 2.1.1. Complex **7a**

Yield: 800 mg, (85.9%);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  4.68 (dd,  $^2J_{\text{HH}} = 2.4$  Hz,  $^3J_{\text{PH}} = 6.1$  Hz, 1H, =CH<sub>2</sub>), 5.02 (dd,  $^2J_{\text{HH}} = 2.7$  Hz,  $^3J_{\text{PH}} = 22.8$  Hz, 1H, =CH<sub>2</sub>), 7.00 (m<sub>c</sub>, 5H, Ph), 7.25 (m<sub>c</sub>, 10H, Ph), 7.58 (m<sub>c</sub>, 5H,

Ph);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  96.5 (d,  $^2J_{\text{PC}} = 18.5$  Hz, =CH<sub>2</sub>), 126.3 (d,  $^1J_{\text{PC}} = 102.6$  Hz, ipso-Ph<sub>3</sub>P), 127.8 (d,  $^4J_{\text{PC}} = 3.2$  Hz, para-Ph), 128.1 (d,  $^3J_{\text{PC}} = 12.1$  Hz, meta-Ph), 128.2 (d,  $^2J_{\text{PC}} = 9.8$  Hz, ortho-Ph), 128.8 (d,  $^1J_{\text{PC}} = 61.4$  Hz, ipso-Ph), 128.7 (d,  $^3J_{\text{PC}} = 12.6$  Hz, meta-Ph<sub>3</sub>P), 132.7 (d,  $^4J_{\text{PC}} = 2.7$  Hz, para-Ph<sub>3</sub>P), 133.2 (d,  $^2J_{\text{PC}} = 10.1$  Hz, ortho-Ph<sub>3</sub>P), 161.5 (dd,  $^1J_{\text{PC}} = 20.1$  Hz,  $^4J_{\text{PC}} = 3.0$  Hz, PCO), 164.6 (dd,  $^2J_{\text{PC}} = 12.4$  Hz,  $^2J_{\text{PC}} = 6.0$  Hz, PNC), 196.2 (d,  $^2J_{\text{PC}} = 8.0$  Hz,  $^1J_{\text{WC}} = 126.0$  Hz, cis-CO), 200.0 (d,  $^2J_{\text{PC}} = 23.7$  Hz, trans-CO);  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  24.6 (s, PPh<sub>3</sub>), 69.0 (s,  $^1J_{\text{WP}} = 266.6$  Hz); UV/vis ( $\text{CH}_3\text{CN}$ )  $\lambda$  (log  $\epsilon$ ) = 228 (4.85), 250 (4.51), 262 (4.33), 270 (4.18), 282 (3.88); IR (KBr)  $\bar{\nu}$  2047 (s, CO), 2011 (s, CO), 1947 (vs, CO), 1921 (vs, CO)  $\text{cm}^{-1}$ ; MS (pos.-DCI( $\text{NH}_3$ );  $^{35}\text{Cl}$ ,  $^{184}\text{W}$ ):  $m/z$  (%) = 776 (60)  $[\text{M}]^+$ ; MS (neg.-DCI( $\text{NH}_3$ );  $^{35}\text{Cl}$ ,  $^{184}\text{W}$ ):  $m/z$  (%) = 776 (18)  $[\text{M}]^-$ , 748 (32)  $[\text{M}-\text{CO}]^-$ , 324 (100)  $[\text{W}(\text{CO})_5]^-$ .

#### 2.1.2. Complex **7b**

240 mg, (50.0%);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.16 (t,  $^3J_{\text{HH}} = 7.1$  Hz, 3H,  $\text{CO}_2\text{CH}_2\text{CH}_3$ ), 1.74 (m<sub>c</sub>, 2H,  $\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_3$ ), 2.14 (m<sub>c</sub>, 2H,  $\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_3$ ), 3.99 (q,  $^3J_{\text{HH}} = 7.1$  Hz, 2H,  $\text{CO}_2\text{CH}_2\text{CH}_3$ ), 4.63 (dd,  $^2J_{\text{HH}} = 2.7$  Hz,  $^3J_{\text{PH}} = 6.4$  Hz, 1H, =CH<sub>2</sub>), 5.22 (dd,  $^2J_{\text{HH}} = 2.7$  Hz,  $^3J_{\text{PH}} = 22.3$  Hz, 1H, =CH<sub>2</sub>), 7.40 (m<sub>c</sub>, 5H, Ph), 7.51 (m<sub>c</sub>, 3H, Ph), 7.73 (m<sub>c</sub>, 7H, Ph);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  15.2 (s,  $\text{CH}_2\text{CH}_3$ ), 29.1 (d,  $^2J_{\text{PC}} = 3.7$  Hz,  $\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_3$ ), 37.2 (d,  $^1J_{\text{PC}} = 18.1$  Hz,  $-\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_3$ ), 61.8 (s,  $\text{OCH}_2\text{CH}_3$ ), 97.5 (d,  $^2J_{\text{PC}} = 17.1$  Hz, =CH<sub>2</sub>), 127.3 (d,  $^1J_{\text{PC}} = 102.7$  Hz, ipso-Ph), 129.7 (d,  $^3J_{\text{PC}} = 12.7$  Hz, meta-Ph), 133.8 (d,  $^4J_{\text{PC}} = 2.8$  Hz, para-Ph), 134.2 (d,  $^2J_{\text{PC}} = 10.1$  Hz, ortho-Ph), 160.4 (dd,  $^1J_{\text{PC}} = 19.2$  Hz,  $^4J_{\text{PC}} = 2.9$  Hz, PCO), 165.1 (dd,  $^2J_{\text{PC}} = 12.4$  Hz,  $^2J_{\text{PC}} = 5.8$  Hz, PNC), 173.1 (d,  $^3J_{\text{PC}} = 13.7$  Hz,  $\text{CO}_2\text{CH}_2\text{CH}_3$ ), 197.1 (d,  $^2J_{\text{PC}} = 8.0$  Hz,  $^1J_{\text{WC}} = 125.6$  Hz, cis-CO), 200.9 (d,  $^2J_{\text{PC}} = 23.5$  Hz, trans-CO);  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  23.6 (s, PPh<sub>3</sub>), 72.0 (s,  $^1J_{\text{WP}} = 264.0$  Hz,  $^2J_{\text{PH}} = 20.9$  Hz); MS (EI, 70 eV,  $^{184}\text{W}$ ):  $m/z$  (%) = 774 (5)  $[\text{M}-\text{CO}]^+$ , 746 (17)  $[\text{M}-2\text{CO}]^+$ , 261 (100)  $[\text{PPh}_3-\text{H}]^+$ .

## 3. Supplementary Material

The supplementary material has been sent to the Cambridge Crystallographic Data Centre, 12 Union

Road, Cambridge CB2 1EZ, UK/Fachinformationzentrum Karlsruhe, Abt. PROKA, 76344 Eggenstein-Leopoldshafen, Germany, as supplementary material CCDC 212951 and can be obtained by contacting the CCDC/FIZ (quoting the article details and the corresponding SUP number).

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