# **ORGANOMETALLICS**

# The Original Reactivity of a Phosphole-Substituted Fischer Carbene Complex

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# **Supporting Information**

**ABSTRACT:** In an unprecedented transformation, a phosphole-substituted Fischer carbene complex reacts with styrene to give an annelated phosphole derivative.

**F** ischer carbene complexes are at the core of transitionmetal organometallic chemistry and display numerous uses in organic synthesis.<sup>1</sup> While a number of furan, thiophene, and pyrrole derivatives of Fischer carbene complexes are known,<sup>2</sup> to the best of our knowledge, nothing is known about the corresponding phosphole derivatives. In view of the rich organic chemistry of Fischer carbene complexes,<sup>1</sup> it seemed quite attractive to prepare similar complexes derived from phospholes, whose functional chemistry is still relatively limited.<sup>3</sup> The much lower aromaticity of the phosphole ring in comparison with that of the other five-membered heteroarenes<sup>4</sup> could induce a greater conjugation between the carbene and the diene unit of the heteroarene in the case of the phosphorus ring. Hence, a significant perturbation of the normal chemistry of Fischer carbene complexes could be observed. This is indeed the case, as shown in this report.

In order to have an idea of what could be expected, we first decided to compute the structure of the phosphole-substituted free carbene 1 by DFT at the B3PW91/6-31G(d)-Lanl2dz(W) level.<sup>5</sup>



The structure is shown in Figure 1. As can be seen, the carbene is not coplanar with the diene (O–C–C=C dihedral angle  $-68.5^{\circ}$ ), so that the overlap between the p orbital of the carbene and the  $\pi$  orbitals of the diene is not maximal. Nevertheless, a substantial conjugation between the two units still exists, as shown by the relatively short C4–C22 bond length of 1.442 Å. This is confirmed by the structure of the LUMO (Figure 2), which is essentially a combination of the p orbital of the carbene with the LUMO of the diene. The structure of the carbene complex 1-W was also computed at the same level. The repulsion between the two W(CO)<sub>5</sub> groups





**Figure 1.** Computed structure of phospholylcarbene (1). Main distances (Å) and angles (deg): P–W = 2.520, P–Me = 1.849, P–C1 = 1.802, P–C4 = 1.840, C4–C22 = 1.442, C22–O23 = 1.301, C1–C2 = 1.354, C2–C3 = 1.475, C3–C4 = 1.377; C1–P–C4 = 91.0, C4–C22–O23 = 120.1, O23–C22–C4–C3 = 68.5.

leads to a drastic change of the O–C–C=C dihedral angle from -68.5 to  $68.8^{\circ}$ . At 1.466 Å, the bond between the carbene and the diene is longer than in 1 (1.442 Å). The back-bonding of W to the p orbital of the carbene probably switches off the conjugation with the diene. This means that the carbene–tungsten bond will probably be rather easily cleaved to reinstall

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Figure 2. Computed HOMO and LUMO of 1 (Kohn-Sham).

the conjugation between the carbene and the diene. Indeed, the dissociation energy of 1-W into 1 and singlet  $W(CO)_5$  is computed to be 61.5 kcal mol<sup>-1</sup>, much lower than the  $D_{a}$  value for  $(OC)_{S}W$ =CHOH at 81.9 kcal mol<sup>-1.6</sup>

Our starting point was the 2-lithiophosphole 4, prepared as previously described.7 It was allowed to react with 2 equiv of tungsten hexacarbonyl at -90 °C. The first equivalent reacts with the carbanion, while the phosphole lone pair coordinates to the second equivalent with elimination of CO. Subsequently, in situ alkylation with MeOTf was carried out. The desired 2phospholylcarbene complex  $2^8$  was obtained in 30% yield after purification by chromatography at -10 °C (eq 1).



The most significant spectroscopic datum of 2 is the carbenic <sup>13</sup>C resonance at 316.87 ppm (CDCl<sub>3</sub>). The structure was established by X-ray crystal structure analysis (Figure.3). The plane of the carbene (O6-C6-C8) makes an angle of 48.2° with the plane of the diene. The bond between the carbene and the diene (C6-C8) is longer than the corresponding computed bond in 1 at 1.475(6) Å and very similar to those of thiophene analogues.<sup>2</sup> Overall, the structure is very close to that computed for 1-W.

We tested three reactions of 2 in order to compare its chemistry with the chemistry of standard Fischer carbene complexes. The first reaction was the oxidation by DMSO (eq 2).



The reaction follows the normal course and gives the ester 5,<sup>8</sup> which was fully characterized by an X-ray crystal structure





Figure 3. X-ray crystal structure of the phosphole-substituted Fischer carbene complex 2. Main distances (Å) and angles (deg): P-W =2.5263(12), P-C14 = 1.821(5), P-C8 = 1.836(4), P-C13 = 1.789(5), C8-C9 = 1.359(7), C9-C11 = 1.486(7), C11-C13 =1.340(7), C8-C6 = 1.475(6), C6-O6 = 1.332(5), C6-W1 = 2.173(4); C8-P-C13 = 90.7(2), O6-C6-C8 = 104.7(4), O6-C6-W1 = 129.5(3), C8-C6-W1 = 124.1(3).

analysis (Figure 4). The ester and phosphole planes are practically coplanar (angle 7.7°), and the C-C bond between the diene and the ester remains at 1.475 Å. The ester group appears at 163.24 ppm in the <sup>13</sup>C NMR spectrum. The reaction with water gave the aldehyde  $6^8$  (eq 3), which was characterized by X-ray analysis (Figure 5). The aldehyde group appears at 10.13 ppm (<sup>1</sup>H NMR) and 185.17 ppm (<sup>13</sup>C NMR). Once again, a similar reactivity has previously been described.9 A completely different picture emerged from the reaction with neat styrene (eq 4).



Various reaction temperatures were tested from 50 to 90 °C. Complete reaction was only achieved at 90 °C. The two isomeric products 7a,b<sup>10</sup> were obtained in a 1:1 ratio according to the  ${}^{31}P$  NMR spectrum of the crude reaction mixture. 7a was fully identified by an X-ray crystal structure analysis (Figure 6). The <sup>13</sup>C NMR spectra show that the cycloadditions leading to 7a,b have the same regiochemistry. In both cases, the styrenic  $CH_2$  is not coupled to P, whereas the CHPh displays a  ${}^{3}J_{C-P}$ 



Figure 4. X-ray crystal structure of ester 5. Main distances (Å) and angles (deg): P-W = 2.5196(7), P-C14 = 1.832(3), P-C6 = 1.794(3), P-C11 = 1.813(3), C6-C7 = 1.346(4), C7-C9 = 1.489(4), C9-C11 = 1.351(4), C11-C12 = 1.475(4), C12-O6 = 1.211(3), C12-O7 = 1.353(3); C6-P-C11 = 90.48(13), C11-C12-O6 = 127.3(3), C12-C11-P = 121.9(2), O6-C12-O7 = 123.23(3).



Figure 5. X-ray crystal structure of aldehyde 6. Main distances (Å) and angles (deg): P-W = 2.4966(16), P-C13 = 1.837(6), P-C7 = 1.807(6), P-C12 = 1.802(6), C7-C8 = 1.352(9), C8-C11 = 1.488(9), C11-C12 = 1.335(9), C6-C7 = 1.456(9), C6-C6 = 1.221(8); C7-P-C12 = 89.9(3), C7-C6-O6 = 123.6(6), C6-C7-P = 121.8(5).

coupling. Since the dissociation of **2** to the corresponding carbene at 90 °C appears unlikely in view of the computed  $D_{e}$ , we are obliged to admit the well-established formation of a transient cyclopropane **8** (eq 5). The isomerization of





**Figure 6.** X-ray crystal structure of bicyclic product 7. Main distances (Å) and angles (deg): P-W = 2.5131(5), P-C22 = 1.8272(19), P-C6 = 1.7972(19), P-C14 = 1.8134(19), C6-C7 = 1.341(3), C7-C9 = 1.478(3), C9-C14 = 1.349(2), C9-C10 = 1.499(3), C10-C11 = 1.521(3), C11-C12 = 1.535(3), C12-C13 = 1.545(2), C13-C14 = 1.502(3), C13-C6 = 1.421(2); C6-P-C14 = 90.99(9), C14-C13-O6 = 109.17(15), C13-C14-P = 126.79(13).

tetracoordinate 3,4-dimethylphospholes to the corresponding 3-methylene-4-methylphosphol-4-enes is also well-known.<sup>11</sup> In 9, the 1,2-migration of H from  $C_2$  to the vicinal cyclopropyl carbon would initiate the rearrangement into 7.

Finally, complex 2 was heated alone in toluene between 50 and 90 °C. No reaction was observed at temperatures lower than 90 °C. However, at 90 °C, a messy <sup>31</sup>P NMR spectrum was obtained with complex 6 as the main product (due to the trace amount of water present in toluene). Other dienophiles such as alkynes (diphenylacetylene) were also tested under the same reaction conditions. Promising results were obtained, but the characterization of the products is still in progress.

## ASSOCIATED CONTENT

#### **S** Supporting Information

Text, figures, and CIF files giving experimental details and characterization data, X-ray crystal structure analyses of compounds 2 and 5-7, and the complete ref 5. This material is available free of charge via the Internet at http://pubs.acs.org.

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## Notes

The authors declare no competing financial interest.

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(7) Deschamps, E.; Mathey, F. Bull. Soc. Chim. Fr. 1992, 129, 486. (8) 2: purified by chromatography on silica gel at -10 °C with hexane/dichloromethane (7/3); deep red solid (30%). <sup>31</sup>P NMR (CH<sub>2</sub>Cl<sub>2</sub>):  $\delta$  23.4 ( $J_{P-W}$  = 221 Hz). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ 2.31 (d,  ${}^{4}J_{H-P} = 1.4$  Hz, 3H, Me), 2.36 (s, 3H, Me), 4.53 (s, 3H, OMe), 6.72 (d,  ${}^{2}J_{H-P}$  = 36.6 Hz, 1H, =CHP), 7.39–7.53 (m, 5H, Ph).  ${}^{13}C$  NMR (CDCl<sub>3</sub>):  $\delta$  17.79 (d,  ${}^{3}J_{C-P}$  = 9.7 Hz, Me), 17.99 (d, 17.99 (d, 19.10 Hz))  ${}^{3}J_{C-P}$  = 8.0 Hz, Me), 69.63 (s, OMe), 128.04 (d,  $J_{C-P}$  = 38.4 Hz, PC(Ph)), 129.43 (d,  $J_{C-P}$  = 10.3 Hz, Ph), 132.03 (s, Ph), 133.06 (d,  $J_{C-P}$  = 13.1 Hz, Ph), 133.15 (d,  $J_{C-P}$  = 41.1 Hz, PCH=), 148.47 (d,  $J_{C-P}$  = 15.3 Hz, CMe), 151.08 (d,  $J_{C-P}$  = 8.5 Hz, CMe), 162.99 (d,  $J_{C-P}$  = 23.1 Hz, PC=), 196.73 (d,  $J_{C-P}$  = 6.3 Hz, PW(CO)<sub>5</sub> cis C= O), 197.00 (s, CW(CO)<sub>5</sub> cis C=O), 198.42 (d,  $J_{C-P}$  = 21.6 Hz, PW(CO)<sub>5</sub> trans C=O), 203.32 (s, CW(CO)<sub>5</sub> trans C=O), 316.87 (s, C=W). Exact mass: calcd C24H15O11PW2Na, 900.9268; found, 900.9276. 5: purified by chromatography with hexane/dichloromethane (4/1); yellow oil (70%). <sup>31</sup>P NMR (CH<sub>2</sub>Cl<sub>2</sub>): δ 17.7 ppm  $(J_{P-W} = 221 \text{ Hz})$ . <sup>1</sup>H NMR  $(CD_2Cl_2)$ :  $\delta$  2.24 (d, <sup>4</sup> $J_{H-P} = 1.4 \text{ Hz}$ , 3H, Me), 2.55 (s, 3H, Me), 3.68 (s, 3H, OMe), 6.71 (d,  ${}^{2}J_{H-P} = 34.4$  Hz, 1H, =CHP), 7.36–7.53 (m, 5H, Ph). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  15.14 (d,  ${}^{3}J_{C-P} = 6.4$  Hz, Me), 16.70 (d,  ${}^{3}J_{C-P} = 9.7$  Hz, Me), 50.98 (s, OMe), 128.17 (d,  $J_{C-P}$  = 36.9 Hz, PC(Ph)), 128.40 (d,  $J_{C-P}$  = 10.5 Hz, Ph), 130.53 (d,  $J_{C-P} = 2.3$  Hz, Ph), 131.63 (d,  $J_{C-P} = 12.9$  Hz, Ph), 133.73 (d,  $J_{C-P}$  = 43.7 Hz, PCCO<sub>2</sub>Me), 135.13 (d,  $J_{C-P}$  = 41.5 Hz, PCH=), 149.80 (d,  $J_{C-P}$  = 6.2 Hz, CMe), 161.63 (d,  $J_{C-P}$  = 12.7 Hz, CMe), 163.24 (d,  $J_{C-P}$  = 16.9 Hz, C=O), 195.89 (d,  $J_{C-P}$  = 6.6 Hz,  $W(CO)_5 \text{ cis } C=O)$ , 198.29 (d,  $J_{C-P} = 20.1 \text{ Hz}$ ,  $W(CO)_5 \text{ trans } C=O)$ . Exact mass: calcd C<sub>19</sub>H<sub>15</sub>O<sub>7</sub>PW, 570.0065; found 570.0068. 6: purified by chromatography with hexane/dichloromethane (4/1); yellow oil (70%). <sup>31</sup>P NMR (CH<sub>2</sub>Cl<sub>2</sub>):  $\delta$  14.9 ppm ( $J_{P-W}$  = 219 Hz). <sup>1</sup>H NMR  $(CD_2Cl_2): \delta 2.29 \text{ (d, } {}^4J_{H-P} = 1.4 \text{ Hz}, 3H, \text{ Me}), 2.51 \text{ (s, 3H, Me)}, 6.94$  $(d, {}^{2}J_{H-P} = 34.8 \text{ Hz}, 1H, =CH-P), 7.39-7.57 (m, 5H, Ph) 10.13 (d, 2)$  ${}^{3}J_{H-P}$  = 16.5 Hz, 1H, CHO).  ${}^{13}$ C NMR (CDCl<sub>3</sub>):  $\delta$  14.29 (d,  ${}^{3}J_{C-P}$  = 6.8 Hz, Me), 17.08 (d,  ${}^{3}J_{C-P}$  = 9.4 Hz, Me), 129.17 (d,  $J_{C-P}$  = 41.8 Hz, PC(Ph) ipso) 129.14 (d,  $J_{C-P} = 10.7$  Hz, Ph), 131.08 (s, Ph), 131.80 (d,  $J_{C-P} = 12.6$  Hz, Ph), 137.85 (d,  $J_{C-P} = 40.6$  Hz, PCH=), 142.92 (d,  $J_{C-P}$  = 35.9 Hz, PCCHO), 150.23 (d,  $J_{C-P}$  = 5.6 Hz, CMe), 162.37 (d,  $J_{C-P}$  = 12.3 Hz, CMe), 185.17 (d,  $J_{C-P}$  = 12.1 Hz, CHO), 196.04 (d,  $J_{C-P} = 6.6$  Hz, W(CO)<sub>5</sub> cis C=O), 198.61 (d,  $J_{C-P} = 20.2$  Hz, W(CO)<sub>5</sub> trans C=O); Exact mass: calcd C<sub>18</sub>H<sub>13</sub>O<sub>6</sub>PW, 539.9959; found 539.9962.

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(10) 7a: purified by chromatography with hexane/dichloromethane (1/1); yellow solid (40%). <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  13.1 ppm ( $J_{P-W}$  = 217.8 Hz). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  2.01–2.07 (m, 2H), 2.17 (d, <sup>4</sup> $J_{H-P}$  = 1.4 Hz, 3H, Me), 2.28–2.36 (m, 1H), 2.49–2.59 (m, 1H), 2.85 (s, 3H, OMe), 3.07–3.14 (m, 1H, CHPh), 3.90 (d,  $J_{H-H}$  = 6.3 Hz, CHOMe), 6.54 (d, <sup>2</sup> $J_{H-P}$  = 37.6 Hz, 1H, =CHP), 6.97–6.99 (m, 2H, Ph), 7.13–7.19 (m, 3H, Ph), 7.41–7.43 (m, 3H, Ph), 7.51–7.57 (m, 2H, Ph). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  16.92 (d, <sup>3</sup> $J_{C-P}$  = 10.3 Hz, Me), 24.23 (d,  $J_{C-P}$  = 7.7 Hz, CH<sub>2</sub>), 27.88 (s, CH<sub>2</sub>), 44.70 (d,  $J_{C-P}$  = 4.0 Hz, CHPh), 59.10 (s, OMe), 80.33 (d,  $J_{C-P}$  = 8.3 Hz, CHOMe), 126.67 (s, CH, PhC), 127.76 (s, CH, PhC), 128.47 (s, CH, PhC), 129.12 (d, CH,  $J_{C-P}$  = 10.1 Hz, PhP), 129.93 (d, C,  $J_{C-P}$  = 38.5 Hz, PhP), 130.88 (d, CH,

 $J_{C-P} = 2.2$  Hz, PhP), 130.90 (d,  $J_{C-P} = 43.5$  Hz, PCH=), 132.07 (d, CH,  $J_{C-P}$  = 12.5 Hz, PhP), 142.90 (s, PhC), 145.53 (d,  $J_{C-P}$  = 41.3 Hz, PC=), 147.20 (d,  $J_{C-P}$  = 13.8 Hz, CCH<sub>2</sub>), 149.29 (d,  $J_{C-P}$  = 8.1 Hz, CMe), 196.93 (d,  $J_{C-P}$  = 6.9 Hz, W(CO)<sub>5</sub> cis C=O), 199.49 (d,  $J_{C-P}$ = 19.5 Hz, W(CO)<sub>5</sub> trans C=O). Exact mass: calcd  $C_{27}H_{23}O_6PW$ , 658.0742; found 658.0746. 7b: eluted after 7a (20%). <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  16.1 ppm ( $J_{P-W}$  = 216.7 Hz). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  1.93– 1.99 (m, 2H), 2.19 (d,  ${}^{4}J_{H-P}$  = 1.2 Hz, 3H, Me), 2.55 (br, 2H), 2.60 (s, 3H, OMe), 2.92 (m, 1H, CH-Ph), 4.75 (d,  $J_{H-H}$  = 8.7 Hz, CHOMe),  $6.57 (d, {}^{2}J_{H-P} = 36.2 Hz, 1H, = CHP), 7.19-7.31 (m, 5H, Ph), 7.33-$ 7.40 (m, 3H, Ph), 7.55–7.60 (m, 2H, Ph).  $^{13}\mathrm{C}$  NMR (CDCl<sub>3</sub>):  $\delta$ 17.03 (d,  ${}^{3}J_{C-P}$  = 10.3 Hz, Me), 25.78 (d,  $J_{C-P}$  = 8.5 Hz, CH<sub>2</sub>), 30.76 (s, CH<sub>2</sub>), 47.08 (d,  $J_{C-P}$  = 6.3 Hz, CHPh), 57.06 (s, OMe), 81.90 (d,  $J_{C-P}$  = 9.5 Hz, CHOMe), 127.04 (s, CH, PhC), 127.92 (s, CH, PhC), 128.71 (d, CH,  $J_{C-P}$  = 10.7 Hz, PhP), 128.97 (s, CH, PhC), 130.50 (d, C,  $J_{C-P}$  = 41.2 Hz, PhP), 130.59 (d,  $J_{C-P}$  = 46.7 Hz, PCH=), 130.87 (d, CH,  $J_{C-P} = 2.2$  Hz, PhP), 133.08 (d, CH,  $J_{C-P} = 13.1$  Hz, PhP), 144.30 (s, PhC), 144.84 (d,  $J_{C-P}$  = 37.3 Hz, PC=), 148.92 (d,  $J_{C-P}$  = 12.7 Hz, CCH<sub>2</sub>), 149.69 (d,  $J_{\rm C-P}$  = 8.5 Hz, CMe), 197.05 (d,  $J_{\rm C-P}$  = 6.7 Hz, W(CO)<sub>5</sub> cis C=O), 199.08 (d, J<sub>C-P</sub> = 18.4 Hz, W(CO)<sub>5</sub> trans C=O).

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