

## Synthesis and structure of 2,2'-biphosphirenes

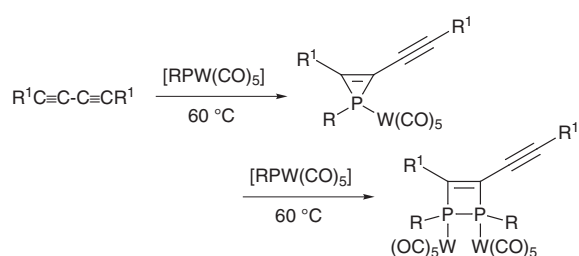
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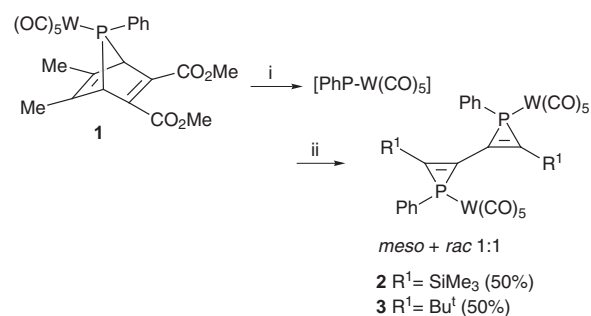
The reaction of an excess of the transient terminal phosphinidene complex  $[\text{PhP}\rightarrow\text{W}(\text{CO})_5]$  with selected 1,3-diyne at 110 °C in toluene affords the corresponding 2,2'-biphosphirene- $\text{W}_2(\text{CO})_{10}$  complexes as a 1:1 *meso* + *rac* mixture; according to the X-ray crystal structure analysis of one of the *rac*-complexes, some delocalisation takes place within the diene sub-unit of these bi-phosphirenes.

The phosphirene ring is now well established as one of the most interesting carbon-phosphorus heterocycles.<sup>1</sup> Numerous syntheses of this ring are available and its rich chemistry, including its coordination chemistry with transition metals, combined with its very peculiar stereoelectronic properties<sup>2</sup> make it an attractive candidate for applications in homogeneous catalysis.<sup>3</sup> In order to develop this potential, we have decided to launch a programme aiming at the incorporation of the phosphirene ring into oligomers or macrocycles. The first step in that direction consists in the preparation of the still unknown 2,2'-biphosphirenes.<sup>4</sup> The most versatile approach to phosphirenes is undoubtedly the [2+1] cyclocondensation between alkynes and electrophilic terminal phosphinidene complexes.<sup>5</sup> Thus it was tempting to study the condensation of these phosphinidene complexes with 1,3-diyne. Unfortunately, both in our group<sup>6</sup> and in the group of Lammertsma,<sup>7</sup> this reaction yielded first a 2-alkynyl-phosphirene, and then a 1,2-dihydro-1,2-diphosphete resulting from the insertion of a second phosphinidene into the conjugatively destabilized P-C(2) bond of the initial three-membered ring (Scheme 1).



Scheme 1

However, the reaction appeared to depend sharply on the nature of the diyne substituent  $\text{R}^1$ . In some cases [ $\text{R}^1 = \text{Bu}$ ,<sup>7</sup>  $\text{Bu}^t$ ,<sup>7</sup>  $\text{SiMe}_3$  (our work)], the insertion does not take place and the reaction apparently stops at the stage of the 2-alkynyl-phosphirene. This surprising observation led us to reinvestigate the condensation of  $[\text{PhP}\rightarrow\text{W}(\text{CO})_5]$  with these diynes at higher temperature. Our and Lammertsma's preliminary experiments were carried out using the  $\text{CuCl}$ -catalyzed decomposition of the appropriate 7-phosphanorbornadiene complex **1** as the generating system of  $[\text{PhP}\rightarrow\text{W}(\text{CO})_5]$  at 60 °C. In our new experiments, the phosphinidene was generated from **1** at 110 °C in boiling toluene *without CuCl as the catalyst*. Under these more severe conditions, the reaction goes one step further (Scheme 2).



Scheme 2 Reagents and conditions: (i), (ii); toluene, 110 °C, 10–12 h, 3.2 eq. of **1** and 1 eq. of  $\text{R}^1\text{C}\equiv\text{C}-\text{C}\equiv\text{CR}^1$ .

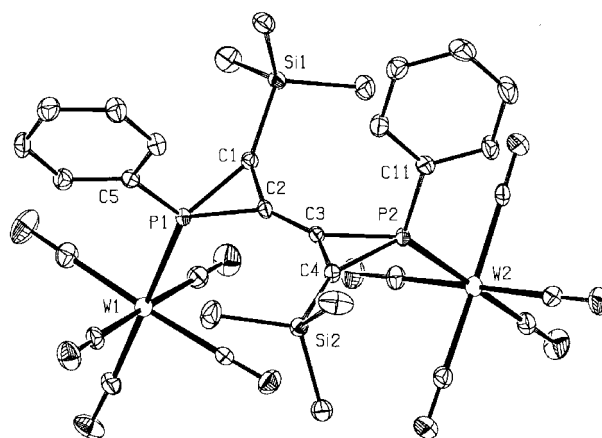


Fig. 1 Crystal structure of *rac*-**2**. Significant bond distances (Å) and angles (°): W(1)–P(1) 2.484(1), W(2)–P(2) 2.501(1), P(1)–C(1) 1.826(4), P(1)–C(2) 1.791(3), P(1)–C(5) 1.822(4), P(2)–C(3) 1.793(3), P(2)–C(4) 1.835(4), P(2)–C(11) 1.821(4), C(1)–C(2) 1.327(5), C(2)–C(3) 1.421(5), C(3)–C(4) 1.318(5); C(2)–P(1)–C(1) 43.0(2), C(3)–P(2)–C(4) 42.6(2), C(1)–C(2)–P(1) 69.9(2), C(2)–C(1)–P(1) 67.1(2), C(3)–C(4)–P(2) 67.0(2), C(4)–C(3)–P(2) 70.4(2), C(3)–C(2)–P(1) 147.8(3), C(2)–C(3)–P(2) 144.7(3).

Only minor quantities of the 2-alkynyl-phosphirenes were obtained and the main products were the 2,2'-biphosphirene complexes **2** and **3** obtained as *meso* + *rac*-1:1 mixtures.† We were able to get good crystals of *rac*-**2** and to perform their X-ray analysis (Fig. 1).‡ The structure of the phosphirene rings of *rac*-**2** are very similar to those already published.<sup>5</sup> The two rings are almost coplanar with a *trans*-disposition: interplane angle 157.8°. The C(2)–C(3) bridge is very short at 1.421(5) Å. This means that some conjugation takes place between the two C=C double bonds. The structure of *meso*-**3** was also obtained (C–C bridge 1.435(5) and C=C 1.315(4) Å) but the data are only marginally different from those of *rac*-**2** and are not detailed here. We are presently investigating the synthesis of higher oligophosphirenes.

## Notes and references

† Selected analytical and spectroscopic data: **2**: purified by chromatography on silica gel (hexane-CH<sub>2</sub>Cl<sub>2</sub>, 10:1) *meso* (eluted first): <sup>31</sup>P NMR (CDCl<sub>3</sub>): δ -154.5, <sup>1</sup>J<sub>P-W</sub> 257 Hz; <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ -0.92 (s, SiMe<sub>3</sub>), 128.76 (pseudo-t, <sup>2</sup>J<sub>C-P</sub> 10.0 Hz, *o*-Ph), 130.91 (s, *p*-Ph), 131.46 (pseudo-t, <sup>3</sup>J<sub>C-P</sub> 16.4 Hz, *m*-Ph), 137.9 (pseudo-s, C<sub>3</sub>C<sub>3</sub>), 196.03 (pseudo-t, *cis*-CO); *m/z* (<sup>184</sup>W) 975 (*M* - 3CO + 1, 25%), 863 (*M* - 7CO + 1, 100), 779 (*M* - 10CO + 1, 90); Anal. Calc. for C<sub>32</sub>H<sub>28</sub>O<sub>10</sub>P<sub>2</sub>Si<sub>2</sub>W<sub>2</sub>: C, 36.32; H, 2.67. Found: C, 36.58; H, 2.72%. *rac*: <sup>31</sup>P NMR (CDCl<sub>3</sub>): δ -156.4, <sup>1</sup>J<sub>P-W</sub> 264.7 Hz; <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ -0.97 (s, SiMe<sub>3</sub>), 128.89 (pseudo-t, <sup>2</sup>J<sub>C-P</sub> 10.4 Hz, *o*-Ph), 131.06 (s, *p*-Ph), 131.56 (pseudo-t, <sup>3</sup>J<sub>C-P</sub> 16.6 Hz, *m*-Ph), 138.09 (pseudo-s, C<sub>3</sub>C<sub>3</sub>), 141.91 (pseudo-t, *ipso*-Ph), 195.91 (pseudo-t, <sup>2</sup>J<sub>C-P</sub> 7.5 Hz, *cis*-CO), 197.54 (d, <sup>2</sup>J<sub>C-P</sub> 33 Hz, *trans*-CO).

**3**: *meso* (eluted first): <sup>31</sup>P NMR (CDCl<sub>3</sub>): δ -138.6; <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 29.51 (s, Me), 35.30 (pseudo-s, CMe<sub>3</sub>), 111.74 (pseudo-s, C<sub>2</sub>C<sub>2</sub>), 128.91 (pseudo-t, <sup>2</sup>J<sub>C-P</sub> 10.5 Hz, *o*-Ph), 131.12 (s, *p*-Ph), 131.57 (pseudo-t, <sup>3</sup>J<sub>C-P</sub> 15.8 Hz, *m*-Ph), 137.60 (pseudo-s, C<sub>3</sub>C<sub>3</sub>), 196.27 (pseudo-t, *cis*-CO); *m/z* (<sup>184</sup>W) 942 (*M* - 3CO, 8%), 830 (*M* - 7CO, 36), 747 (*M* - 10CO + 1, 41), 562 (*M* - 10CO - W, 57), 292 (PhPW, 100); Anal. Calc. for C<sub>34</sub>H<sub>28</sub>O<sub>10</sub>P<sub>2</sub>W<sub>2</sub>: C, 39.79; H, 2.75. Found: C, 40.01; H, 2.81%. *rac*: <sup>31</sup>P NMR (CDCl<sub>3</sub>): δ -140.2, <sup>1</sup>J<sub>P-W</sub> 250.7 Hz; <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 29.71 (s, Me), 35.76 (d, <sup>2</sup>J<sub>C-P</sub> 3.6 Hz, CMe<sub>3</sub>), 112.03 (pseudo-t, C<sub>2</sub>C<sub>2</sub>), 129.33 (pseudo-t, <sup>2</sup>J<sub>C-P</sub> 10.5 Hz, *o*-Ph), 131.55 (s, *p*-Ph), 132.13 (pseudo-t, <sup>3</sup>J<sub>C-P</sub> 15.5 Hz, *m*-Ph), 138.09 (pseudo-s, C<sub>3</sub>C<sub>3</sub>), 148.50 (pseudo-t, <sup>1</sup>J<sub>C-P</sub> 18 Hz, *ipso*-Ph), 196.41 (pseudo-t, <sup>2</sup>J<sub>C-P</sub> 7.4 Hz, *cis*-CO).

‡ X-Ray structure determination for *rac*-**2**: crystals suitable for X-ray diffraction were obtained from a pentane-dichloromethane solution of the compound. Data were collected with a Nonius Kappa CCD diffractometer. The crystal structure was solved using maXus.<sup>8</sup> While initial refinement was performed with the latter, final least-squares was conducted with SHELXL 97.<sup>9</sup> Illustrations were made using Platon.<sup>10</sup> Crystal data. C<sub>32</sub>H<sub>28</sub>O<sub>10</sub>P<sub>2</sub>Si<sub>2</sub>W<sub>2</sub>, *M* = 1058.36 g mol<sup>-1</sup>, monoclinic, *a* = 12.0110(2), *b* = 17.3150(2), *c* = 18.9720(3) Å, β = 104.2090(6)°, *V* = 3824.91(10) Å<sup>3</sup>, *T* = 150 K, space group *P*2<sub>1</sub>/*n*, *Z* = 4, μ(Mo-Kα) = 6.207 cm<sup>-1</sup>. 8114 reflections measured, 7801 unique (*R*<sub>int</sub> = 0.021) which were used in all calculations. The final *wR*(*F*<sup>2</sup>) was 0.0612 (all data).

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See <http://www.rsc.org/suppdata/dt/1999/2409/> for crystallographic files in .cif format.

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