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Synthesis and structure of 2,2′-biphosphirenes

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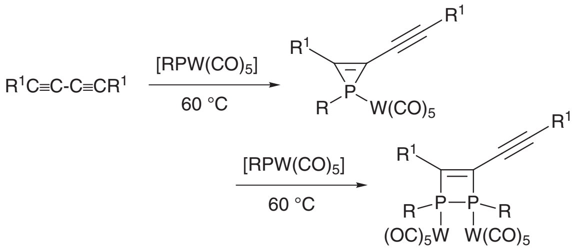
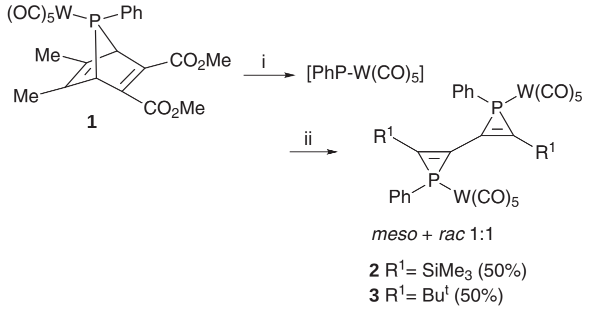
The reaction of an excess of the transient terminal phosphinidene complex [PhP→W(CO)$_5$] with selected 1,3-diynes at 110 °C in toluene affords the corresponding 2,2′-biphosphirene–W$_2$(CO)$_{10}$ complexes as a 1:1 *meso* + *rac* mixture; according to the X-ray crystal structure analysis of one of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

The phosphirene ring is now well established as one of the most interesting carbon–phosphorus heterocycles.[1] 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[2] make it an attractive candidate for applications in homogeneous catalysis.[3] 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.[4] The most versatile approach to phosphirenes is undoubtedly the [2+1] cyclocondensation between alkynes and electrophilic terminal phosphinidene complexes.[5] Thus it was tempting to study the condensation of these phosphinidene complexes with 1,3-diynes. Unfortunately, both in our group[6] and in the group of Lammertsma,[7] 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 R^1. In some cases [R^1= Bu,[7] Bu^t,[7] 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 [PhP→W(CO)$_5$] with these diynes at higher temperature. Our and Lammertsma's preliminary experiments were carried out using the CuCl-catalyzed decomposition of the appropriate 7-phosphanorbornadiene complex **1** as the generating system of [PhP→W(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 R^1 C≡C–C≡CR^1.

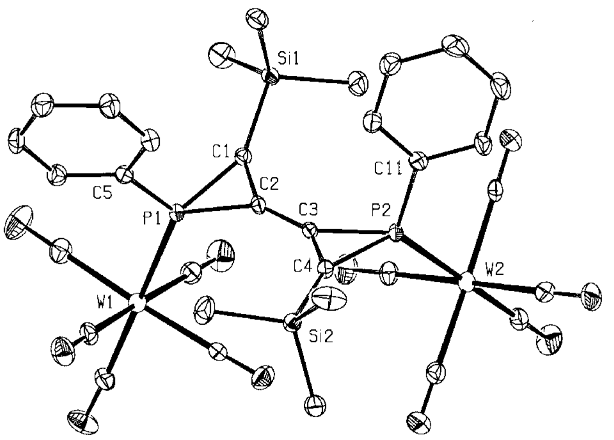


Fig. 1 Crystal structure of *rac*-**2**. Significant bond distances (Å) and angles (°): W(1)–P(1) 2.484(1), W(2)–P(2) 2.501(1), P(1)–C(1) 1.826(4), P(1)–C(2) 1.791(3), P(1)–C(5) 1.822(4), P(2)–C(3) 1.793(3), P(2)–C(4) 1.835(4), P(2)–C(11) 1.821(4), C(1)–C(2) 1.327(5), C(2)–C(3) 1.421(5), C(3)–C(4) 1.318(5); 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.[5] 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_2Cl_2 10:1) *meso* (eluted first): ^{31}P NMR ($CDCl_3$): δ −154.5, $^{1}J_{P-W}$ 257 Hz; ^{13}C NMR ($CDCl_3$): δ −0.92 (s, $SiMe_3$), 128.76 (pseudo-t, $^{2}J_{C-P}$ 10.0 Hz, *o*-Ph), 130.91 (s, *p*-Ph), 131.46 (pseudo-t, $^{3}J_{C-P}$ 16.4 Hz, *m*-Ph), 137.9 (pseudo-s, $C_3C_{3'}$), 196.03 (pseudo-t, *cis*-CO); *m*/*z* (^{184}W) 975 (M − 3CO + 1, 25%), 863 (M − 7CO + 1, 100), 779 (M − 10CO + 1, 90); Anal. Calc. for $C_{32}H_{28}O_{10}P_2Si_2W_2$: C, 36.32; H, 2.67. Found: C, 36.58; H, 2.72%. *rac*: ^{31}P NMR ($CDCl_3$): δ −156.4, $^{1}J_{P-W}$ 264.7 Hz; ^{13}C NMR ($CDCl_3$): δ −0.97 (s, $SiMe_3$), 128.89 (pseudo-t, $^{2}J_{C-P}$ 10.4 Hz, *o*-Ph), 131.06 (s, *p*-Ph), 131.56 (pseudo-t, $^{3}J_{C-P}$ 16.6 Hz, *m*-Ph), 138.09 (pseudo-s, $C_3C_{3'}$), 141.91 (pseudo-t, *ipso*-Ph), 195.91 (pseudo-t, $^{2}J_{C-P}$ 7.5 Hz, *cis*-CO), 197.54 (d, $^{2}J_{C-P}$ 33 Hz, *trans*-CO).

3: *meso* (eluted first): ^{31}P NMR ($CDCl_3$): δ −138.6; ^{13}C NMR ($CDCl_3$): δ 29.51 (s, Me), 35.30 (pseudo-s, *C*Me$_3$), 111.74 (pseudo-s, $C_2C_{2'}$), 128.91 (pseudo-t, $^{2}J_{C-P}$ 10.5 Hz, *o*-Ph), 131.12 (s, *p*-Ph), 131.57 (pseudo-t, $^{3}J_{C-P}$ 15.8 Hz, *m*-Ph), 137.60 (pseudo-s, $C_3C_{3'}$), 196.27 (pseudo-t, *cis*-CO); *m*/*z* (^{184}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 $C_{34}H_{28}O_{10}P_2W_2$: C, 39.79; H, 2.75. Found: C, 40.01; H, 2.81%. *rac*: ^{31}P NMR ($CDCl_3$): δ −140.2, $^{1}J_{P-W}$ 250.7 Hz; ^{13}C NMR ($CDCl_3$): δ 29.71 (s, Me), 35.76 (d, $^{2}J_{C-P}$ 3.6 Hz, *C*Me$_3$), 112.03 (pseudo-t, $C_2C_{2'}$), 129.33 (pseudo-t, $^{2}J_{C-P}$ 10.5 Hz, *o*-Ph), 131.55 (s, *p*-Ph), 132.13 (pseudo-t, $^{3}J_{C-P}$ 15.5 Hz, *m*-Ph), 138.09 (pseudo-s, $C_3C_{3'}$), 148.50 (pseudo-t, $^{1}J_{C-P}$ 18 Hz, *ipso*-Ph), 196.41 (pseudo-t, $^{2}J_{C-P}$ 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.[8] While initial refinement was performed with the latter, final least-squares was conducted with SHELXL 97.[9] Illustrations were made using Platon.[10] Crystal data. $C_{32}H_{28}O_{10}P_2Si_2W_2$, $M = 1058.36$ g mol^{-1}, monoclinic, $a = 12.0110(2)$, $b = 17.3150(2)$, $c = 18.9720(3)$ Å, $\beta = 104.2090(6)°$, $V = 3824.91(10)$ Å^3, $T = 150$ K, space group $P2_1/n$, $Z = 4$, μ(Mo-Kα) = 6.207 cm^{-1}. 8114 reflections measured, 7801 unique ($R_{int} = 0.021$) which were used in all calculations. The final $wR(F^2)$ was 0.0612 (all data).

CCDC reference number 186/1519.

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

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