## A New Type of Chelating Biphospholene

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Summary: The P-P bond of the [4 + 2] dimer of 2,5diphenyl-5H-phosphole, 1, reacts with IMe and then *EtOTI to give the*  $\alpha,\beta'$ *-connected P-Me, P-OEt biphosp*holene 3, whose chelates with  $[Mo(CO)_4]$  and  $[Rh(cod)]^+$ have been characterized by X-ray crystal structure analysis.

Recent work suggests that enantiopure  $\alpha$ -connected biphospholanes<sup>1</sup> and biphospholenes<sup>2</sup> display high potential as chelating ligands for asymmetric catalysis. In this communication, we wish to present a simple synthesis of original 2,3'-connected biphospholenes where the relative configurations of the various chiral centers are fixed, suggesting a possible use in enantioselective catalysis after resolution. The starting point is the [4 + 2] dimer **1** of 2,5-diphenyl-5*H*-phosphole, which is easily obtained by protonation of the 2,5-diphenylphospholide ion (eq 1).<sup>3</sup>



The [4 + 2] dimerization yields exclusively the P–P dimer, the junction is endo, and the Ph at the bridge is probably syn to the C=C double bond, because the P=C double bond tends to reacts with the diene on its less hindered face opposite to the phenyl substituent at C<sub>5</sub>. This point will be demonstrated later. The monoquaternization of 1 by IMe proceeds easily and exclusively at P<sub>2</sub> (eq 2).

The <sup>31</sup>P resonances of the starting compound ( $\delta$ (<sup>31</sup>P) (CH<sub>2</sub>Cl<sub>2</sub>) 18.4 ppm (P<sub>2</sub>), -23.1 ppm (P<sub>1</sub>),  ${}^{1}J_{P-P} = 200.5$ Hz) are replaced by the resonances of **2** ( $\delta$ (<sup>31</sup>P) +79.5 ppm (P<sub>2</sub>), -31.1 ppm (P<sub>1</sub>),  ${}^{1}J_{P-P} = 272.2$  Hz). These data clearly show that the quaternization has exclusively taken place at  $P_2$ . The crude quaternary salt 2 is treated in situ by thallous ethoxide. The nucleophilic attack by  $EtO^-$  exclusively takes place at  $P_1$  and induces the

cleavage of the P-P bond with formation of the phosphine-phosphinite  $3^4$  (eq 2).



**6** ( $M = [Rh(cod)] + PF_6 ca 30\%$  overall)

The <sup>31</sup>P spectrum of **3** shows the *P*-Me resonance at 7.9 and the P-OEt resonance at 151.0 with no P-P coupling. The compound is further characterized as its P,P-disulfide 4.<sup>5</sup> The X-ray crystal structure of 4 (Figure 1) confirms the relative configurations of all the chiral centers and shows a rather long  $C_4-C_5$  ( $C_{\alpha}-C_{\beta}$ ) bridge at 1.573(3) Å. The phosphine-phosphinite 3 easily chelates Mo and Rh centers (eq 2). Complexes 5 and 6<sup>6</sup>

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<sup>(4)</sup> This chemistry is absolutely similar to that of phosphinestabilized arsenium salts; see: Porter, K. A.; Willis, A. C.; Zank, J.; Wild, S. B. *Inorg. Chem.* **2002**, *41*, 6380.

<sup>(5)</sup> The P,P-disulfide 4 was chromatographed on silica gel with ethyl (b) The 1, Austin the 4 was chromatographic to its find generative with energy accetate and recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O. <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  68.7, 105.2. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.70 (t, Me), 1.40 (d, <sup>2</sup>J<sub>H-P</sub> = 12.1 Hz, Me–P), 4.44 (m, CH bridge), 6.55 (dm, <sup>3</sup>J<sub>H-P</sub> = 37.4 Hz, =CHCH<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  16.00 (d, <sup>3</sup>J<sub>C-P</sub> = 7 Hz, Me), 20.45 (d, <sup>1</sup>J<sub>C-P</sub> = 52.3 Hz, Me–P), 38.56 (d, <sup>2</sup>J<sub>C-P</sub> = 11.4 Hz, CH<sub>2</sub>), 53.76 (dd, <sup>2</sup>J<sub>C-P</sub> = 14.1 Hz), 54.72 (dd) Hz, CH<sub>2</sub> = 52.3 Hz, Me = 52.8 Hz, Me and 3.1 Hz, CH), 54.97 (dd,  ${}^{1}J_{C-P} = 66.9$  Hz,  ${}^{3}J_{C-P} = 6.5$  Hz, CH–P), 56.59 (dd,  ${}^{1}J_{C-P} = 51.8$  Hz,  ${}^{3}J_{C-P} = 10.3$  Hz, C–P), 62.14 (d,  ${}^{2}J_{C-P} = 20.2$ 7.4 Hz, OCH<sub>2</sub>), 139.44 (d,  ${}^{2}J_{C-P}$  = 22.4 Hz, =CH), 145.21 (dd,  ${}^{2}J_{C-P}$  = 29.1 Hz,  ${}^{3}J_{C-P}$  = 5.3 Hz, =CH). MS: m/z 597 (M<sup>+</sup> + H, 50%), 313 (61%), 283 (100%). HRMS for C35H35OP2S2: calcd, 597.1605; found, 597.1604.

<sup>(6)</sup> Complex 5 was obtained by reaction of [Mo(CO)<sub>4</sub>(nbd)] with 3 and recrystallized from hexane/CH2Cl2. <sup>31</sup>P NMR (CH2Cl2): & 37.9, 165.7 (d,  ${}^{2}J_{P-P} = 13.8$  Hz). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.68 (t, Me), 1.68 (d, 165.7 (d,  ${}^{2}J_{P-P} = 13.8$  Hz). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.68 (t, Me), 1.68 (d,  ${}^{2}J_{H-P} = 5.1$  Hz, Me–P), 4.20 (d,  ${}^{2}J_{H-P} = 10.7$  Hz, PCHPh). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  14.94 (d,  ${}^{3}J_{C-P} = 7.2$  Hz, Me), 17.25 (dd,  ${}^{1}J_{C-P} = 16.9$  Hz,  ${}^{3}J_{C-P} = 5.8$  Hz, Me–P), 47.10 (s, CH<sub>2</sub>), 51.81 (dd,  ${}^{1}J_{C-P} = 20.1$  Hz,  ${}^{2}J_{C-P'} = 2.2$  Hz, C–P), 56.99 (dd,  ${}^{1}J_{C-P} = 14.3$  Hz,  ${}^{2}J_{C-P'} = 5.6$  Hz, CH–P), 63.10 (d,  ${}^{2}J_{C-P} = 2.3$  Hz, OCH<sub>2</sub>), 63.29 (t,  ${}^{2}J_{C-P'} = 2J_{C-P'} = 10.0$  Hz, CH), 135.89 (d,  ${}^{2}J_{C-P} = 5.6$  Hz, =CH), 203.45 (pseudo t, CO), 212.14 (dd, CO), 214.77 (CO), 215.17 (CO). MS: *m*/*z* 630 (M<sup>+</sup> – 4CO, 75%), 282 (44%), 251 (100%). HRMS for C<sub>39</sub>H<sub>35</sub>O<sub>5</sub>P<sub>2</sub>Mo: calcd, 743.1015. (<sup>98</sup>Mo); found, 743.1015. Complex **6** was obtained by reaction of  $[Rh(cod)_2]^+PF_6^-$  with **3** in CH<sub>2</sub>Cl<sub>2</sub> and recrystallized from methanol/CH<sub>2</sub>Cl<sub>2</sub>. <sup>31</sup>P NMR (CH<sub>2</sub>Cl<sub>2</sub>):  $\delta$  25.5 (dd, <sup>1</sup>J<sub>Rh-P</sub> = 145 Hz, <sup>2</sup>J<sub>P-P</sub> = 47 Hz), 139.7 (dd, <sup>1</sup>J<sub>Rh-P</sub> = 159 Hz, <sup>2</sup>J<sub>P-P</sub> = 47 Hz).



**Figure 1.** ORTEP drawing of **4** (thermal ellipsoids enclose 50% of the electronic density). Significant bond distances (Å) and angles (deg): P(1)-C(1) = 1.808(2), P(1)-S(1) = 1.951(1), P(1)-C(4) = 1.880(2), P(1)-C(9) = 1.806(2), C(1)-C(2) = 1.329(3), C(2)-C(3) = 1.500(3), C(3)-C(4) = 1.553(3), C(4)-C(5) = 1.575(3), P(2)-S(2) = 1.941(1), P(2)-O(1) = 1.591(2), P(2)-C(7) = 1.796(2), P(2)-C(8) = 1.845(2), C(8)-C(5) = 1.565(3), C(5)-C(6) = 1.507(3), C(6)-C(7) = 1.336(3); C(1)-P(1)-C(4) = 94.0(1), C(1)-P(1)-S(1) = 117.71(7), C(9)-P(1)-C(4) = 105.3(1), C(4)-P(1)-C(1) = 105.4(1), C(9)-P(1)-C(4) = 105.3(1), C(4)-P(1)-S(1) = 117.43(7), O(1)-P(2)-C(7) = 104.6(1), O(1)-P(2)-C(8) = 109.6(1), C(7)-P(2)-C(8) = 95.1(1), O(1)-P(2)-S(2) = 113.67(6), C(7)-P(2)-S(2) = 117.43(7), C(8)-P(2)-S(2) = 114.67(7).

have both been characterized by X-ray crystal structure analysis. The structure of **5** is given as an example (Figure 2). The P–Mo–P and P–Rh–P angles are 83.45 and 87.65°, respectively. A preliminary testing of the catalytic activity of complex **6** has been performed. At room temperature in methanol under 3 bar of hydrogen



**Figure 2.** ORTEP drawing of **5** (thermal ellipsoids enclose 50% of the electronic density; carbonyls have been omitted for clarity). Significant bond distances (Å) and angles (deg): Mo(1)-P(1) = 2.5498(8), Mo(1)-P(2) = 2.461(1), P(1)-C(4) = 1.902(3), C(4)-C(6) = 1.587(4), C(6)-C(5) = 1.554(3), C(5)-P(2) = 1.850(3); P(2)-Mo(1)-P(1) = 83.45(3), C(1)-P(1)-C(9) = 100.7(1), C(1)-P(1)-C(4) = 92.4(1), C(9)-P(1)-C(4) = 102.5(1), C(1)-P(1)-Mo(1) = 117.8(1), C(9)-P(1)-Mo(1) = 115.0(1), C(4)-P(1)-Mo(1) = 124.11(8), O(1)-P(2)-C(8) = 102.6(1), O(1)-P(2)-C(5) = 108.1(1), C(8)-P(2)-C(5) = 92.0(1), O(1)-P(2)-Mo(1) = 123.51(7), C(8)-P(2)-Mo(1) = 115.8(1), C(5)-P(2)-Mo(1) = 110.1(1).

with 5% of catalyst, complete hydrogenation of (Z)-acetylcinnamic acid is achieved in less than 2 h. Further work will be directed toward the synthesis of enantiopure analogues of **3**.

**Supporting Information Available:** Text giving experimental details and characterization data and tables giving crystallographic data for **4** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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