A New Type of Chelating Biphospholene

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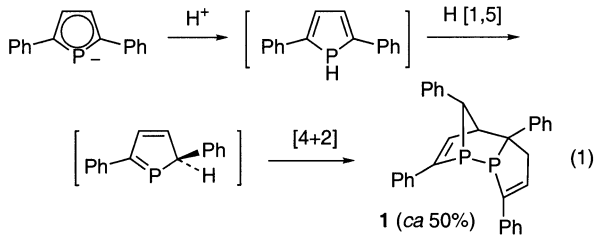
Summary: The P−P bond of the [4 + 2] dimer of 2,5-diphenyl-5H-phosphole, ***1****, reacts with IMe and then EtOTl to give the α,β′-connected P-Me, P-OEt biphospholene* ***3****, whose chelates with [Mo(CO)$_4$] and [Rh(cod)]$^+$ have been characterized by X-ray crystal structure analysis.*

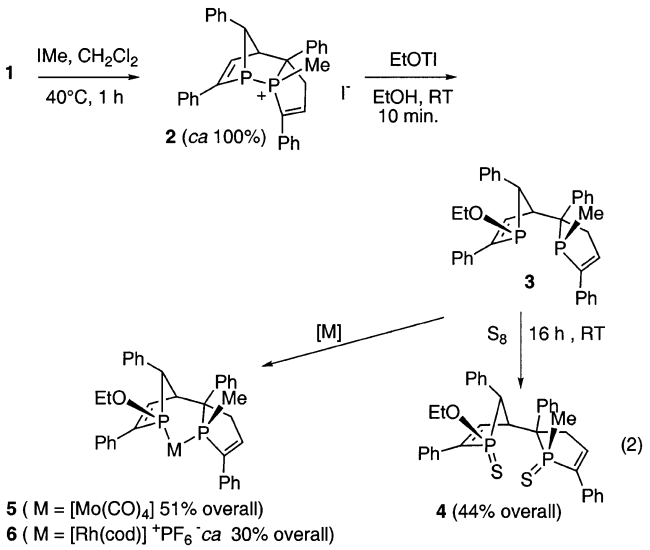
Recent work suggests that enantiopure α-connected biphospholanes[1] and biphospholenes[2] display high potential as chelating ligands for asymmetric catalysis. In this communication, we wish to present a simple synthesis of original 2,3′-connected biphospholenes where the relative configurations of the 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).[3]



(1)

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_5. This point will be demonstrated later. The monoquaternization of **1** by IMe proceeds easily and exclusively at P_2 (eq 2).

The ^{31}P resonances of the starting compound ($\delta(^{31}P)$ (CH_2Cl_2) 18.4 ppm (P_2), −23.1 ppm (P_1), $^1J_{P-P}$ = 200.5 Hz) are replaced by the resonances of **2** ($\delta(^{31}P)$ +79.5 ppm (P_2), −31.1 ppm (P_1), $^1J_{P-P}$ = 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).



(2)

The ^{31}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**.[5] 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**[6]

(1) Tang, W.; Zhang, X. *Angew. Chem. Int. Ed.* **2002**, *41*, 1612.
(2) Bienewald, F.; Ricard, L.; Mercier, F.; Mathey, F. *Tetrahedron: Asymmetry* **1999**, *10*, 4701.
(3) Charrier, C.; Bonnard, H.; de Lauzon, G.; Mathey, F. *J. Am. Chem. Soc.* **1983**, *105*, 6871.

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

(5) The *P*,*P*-disulfide **4** was chromatographed on silica gel with ethyl acetate and recrystallized from CH_2Cl_2/Et_2O. ^{31}P NMR ($CDCl_3$): δ 68.7, 105.2. ^{1}H NMR ($CDCl_3$): δ 0.70 (t, Me), 1.40 (d, $^2J_{H-P}$ = 12.1 Hz, Me−P), 4.44 (m, CH bridge), 6.55 (dm, $^3J_{H-P}$ = 37.4 Hz, ═C*H*CH$_2$). ^{13}C NMR ($CDCl_3$): δ 16.00 (d, $^3J_{C-P}$ = 7 Hz, Me), 20.45 (d, $^1J_{C-P}$ = 52.3 Hz, Me−P), 38.56 (d, $^2J_{C-P}$ = 11.4 Hz, CH_2), 53.76 (dd, $^2J_{C-P}$ = 14.1 and 3.1 Hz, CH), 54.97 (dd, $^1J_{C-P}$ = 66.9 Hz, $^3J_{C-P}$ = 6.5 Hz, CH−P), 56.59 (dd, $^1J_{C-P}$ = 51.8 Hz, $^3J_{C-P}$ = 10.3 Hz, C−P), 62.14 (d, $^2J_{C-P}$ = 7.4 Hz, OCH_2), 139.44 (d, $^2J_{C-P}$ = 22.4 Hz, ═CH), 145.21 (dd, $^2J_{C-P}$ = 29.1 Hz, $^3J_{C-P}$ = 5.3 Hz, ═CH). MS: *m*/*z* 597 (M^+ + H, 50%), 313 (61%), 283 (100%). HRMS for $C_{35}H_{35}OP_2S_2$: calcd, 597.1605; found, 597.1604.

(6) Complex **5** was obtained by reaction of [Mo(CO)$_4$(nbd)] with **3** and recrystallized from hexane/CH_2Cl_2. ^{31}P NMR (CH_2Cl_2): δ 37.9, 165.7 (d, $^2J_{P-P}$ = 13.8 Hz). ^{1}H NMR ($CDCl_3$): δ 0.68 (t, Me), 1.68 (d, $^2J_{H-P}$ = 5.1 Hz, Me−P), 4.20 (d, $^2J_{H-P}$ = 10.7 Hz, PCHPh). ^{13}C NMR ($CDCl_3$): δ 14.94 (d, $^3J_{C-P}$ = 7.2 Hz, Me), 17.25 (dd, $^1J_{C-P}$ = 16.9 Hz, $^3J_{C-P}$ = 5.8 Hz, Me−P), 47.10 (s, CH_2), 51.81 (dd, $^1J_{C-P}$ = 20.1 Hz, $\sum J_{C-P'}$ = 2.2 Hz, C−P), 56.99 (dd, $^1J_{C-P}$ = 14.3 Hz, $\sum J_{C-P'}$ = 5.6 Hz, CH−P), 63.10 (d, $^2J_{C-P}$ = 2.3 Hz, OCH_2), 63.29 (t, $^2J_{C-P}$ $^2J_{C-P'}$ = 10.0 Hz, CH), 135.89 (d, $^2J_{C-P}$ = 5.6 Hz, ═CH), 203.45 (pseudo t, CO), 212.14 (dd, CO), 214.77 (CO), 215.17 (CO). MS: *m*/*z* 630 (M^+ − 4CO, 75%), 282 (44%), 251 (100%). HRMS for $C_{39}H_{35}O_5P_2Mo$: calcd, 743.1014 (^{98}Mo); found, 743.1015. Complex **6** was obtained by reaction of $[Rh(cod)_2]^+PF_6^-$ with **3** in CH_2Cl_2 and recrystallized from methanol/CH_2Cl_2. ^{31}P NMR (CH_2Cl_2): δ 25.5 (dd, $^1J_{Rh-P}$ = 145 Hz, $^2J_{P-P}$ = 47 Hz), 139.7 (dd, $^1J_{Rh-P}$ = 159 Hz, $^2J_{P-P}$ = 47 Hz).

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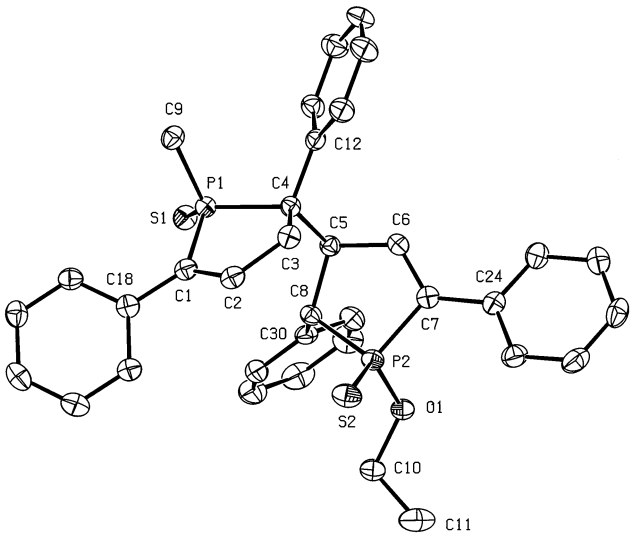

Figure 1. ORTEP drawing of **4** (thermal ellipsoids enclose 50% of the electronic density). Significant bond distances (Å) and angles (deg): P(1)−C(1) = 1.808(2), P(1)−S(1) = 1.951(1), P(1)−C(4) = 1.880(2), P(1)−C(9) = 1.806(2), C(1)−C(2) = 1.329(3), C(2)−C(3) = 1.500(3), C(3)−C(4) = 1.553(3), C(4)−C(5) = 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)−S(1) = 114.42(8), C(9)−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

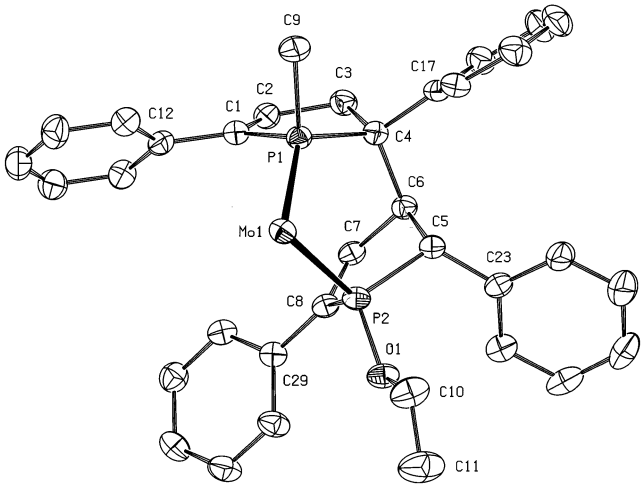

Figure 2. ORTEP drawing of **5** (thermal ellipsoids enclose 50% of the electronic density; carbonyls have been omitted for clarity). Significant bond distances (Å) and angles (deg): Mo(1)−P(1) = 2.5498(8), Mo(1)−P(2) = 2.461(1), P(1)−C(4) = 1.902(3), C(4)−C(6) = 1.587(4), C(6)−C(5) = 1.554(3), C(5)−P(2) = 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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