

**Figure 4.** Enantiomeric analyses of threonine in the rhomb-like crystals of (*R,S*)-serine: (a) tip of the crystal from the  $+b$  direction; (b) tip of the same crystal from the  $-b$  direction; (c) whole crystal. The small amounts of unresolved (*R,S*)-serine are residual from the cation exchange separation of threonine from the serine crystal.

emerges away from these faces (as seen in Figure 2), thus hindering the natural growth perpendicular to them with subsequent increase of their areas (Figure 3b). The same impurity cannot be occluded at the symmetry-related (011) and (01 $\bar{1}$ ) faces; the growth rate perpendicular to these faces is therefore increased with respect to that of the affected faces, thus causing their disappearance. The effect of (*S*)-Thr, which induces the enantiomorphous morphology (Figure 3c) can be explained in an equivalent manner. (*RS*)-Thr induces a morphological change (Figure 3d), which is a simple combination of those induced by each impurity separately, turning the crystals into rhombs.

The morphological changes, and our interpretation thereof, imply that in this last experiment (*RS*)-Thr must segregate along the  $b$  axis during crystal growth; occluded (*R*)-Thr will prevail at the  $+b$  half of the crystal (top half Figure 3d) whereas (*S*)-Thr will prevail at the  $-b$  half of the crystal. Several rhombic crystals ( $1 \times 1 \times 0.4$  mm) whose  $+b$  and  $-b$  directions were characterized by X-rays were either cut in half perpendicular to the  $b$  axis or small pieces were chipped from the  $+b$  and  $-b$  tips of the rhombs. These crystal fragments were examined for an enantiomeric ratio of (*R*)- and (*S*)-Thr by HPLC, on a chiral phase,<sup>8</sup> and the results for a typical sample are illustrated in Figure 4. This analysis shows that (*R*)-Thr is occluded in the  $+b$  half and (*S*)-Thr in the  $-b$  half, with an ee of 84% for both tips of a crystal and 60% for crystals cut in two.

Extension of these preliminary studies to other systems, such as serine/*allo*-threonine, proline/hydroxyproline, and *meso*-dimethylsuccinic acid with its chiral resolved monoesters, are under current investigation.

**Acknowledgment.** We thank the U.S./Israel Binational Foundation, Jerusalem, the donors of the Petroleum Research

Fund, administered by the American Chemical Society, and the Volkswagen Stiftung for financial support.

**Registry No.** (*RS*)-Ser, 302-84-1; (*R*)-Thr, 632-20-2; (*S*)-Thr, 72-19-5; (*RS*)-Thr, 80-68-2.

## Thermal Tetramerization of 1-Phenyl-3,4-dimethylphosphole. An Access to 2,2'-Biphospholes and to 2,2'-Diphosphafulvalene Complexes

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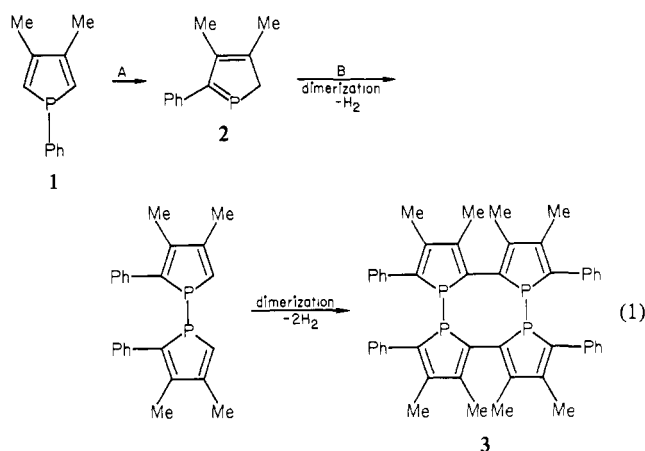
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Received October 16, 1981

In a preceding communication<sup>1</sup> we demonstrated that 1-phenyl-3,4-dimethylphosphole, **1**, isomerized at high temperature



to give 2-phenyl-3,4-dimethyl-5*H*-phosphole, **2**, as an unstable two-coordinate species which was trapped by toluene, methanol, and 2,3-dimethylbutadiene. In view of this unexpected and interesting result,<sup>2</sup> we decided to study the thermolysis of **1** alone. When heated at 170 °C for 60 h, **1** yielded a complex mixture of products. When the mixture stood at room temperature, a pure bright red solid precipitated amidst a colorless liquid. This solid, **3**, contained four phosphole units.<sup>3</sup> Its structure was unambiguously deduced from the X-ray crystal structure of its decacarbonyldimolybdenum complex. The mechanism of the formation of **3** is obviously complicated. We propose eq 1).

The occurrence of step A was demonstrated in our previous paper.<sup>1</sup> The production of a transient 1,1'-biphosphole through

(8) The HPLC analysis of (*RS*)-threonine was carried out by a method similar to that described elsewhere.<sup>9</sup> Crystal fragments of serine, containing less than 0.5% threonine, were dissolved in 20  $\mu$ L of buffer (0.1 N pyridine with glacial acetic acid added to pH 3.06). Threonine, almost free of serine, was collected from a cation exchange column ( $5 \times 0.46$  cm) self-packed with 5  $\mu$ m resin of the polystyrene-divinylbenzene-sulfonic acid type eluted with the above buffer. The fractions containing the threonine were evaporated to dryness under nitrogen and redissolved in 50  $\mu$ L of the chiral mobile phase, *N,N*-dimethyl-(*S*)-valine (8 mM) and cupric acetate (4 mM) in water. Samples of 20  $\mu$ L were analyzed on a reversed phase column ( $24 \times 0.46$  cm) self-packed with 5  $\mu$ m Nucleosil C<sub>18</sub> (Machery, Nagel and Co., Duren, G. F.R.) eluted with the above chiral mobile phase, using fluorescence detection.<sup>9</sup>

(9) S. Weinstein, M. H. Engel, and P. E. Hare, *Anal. Biochem.*, in press.

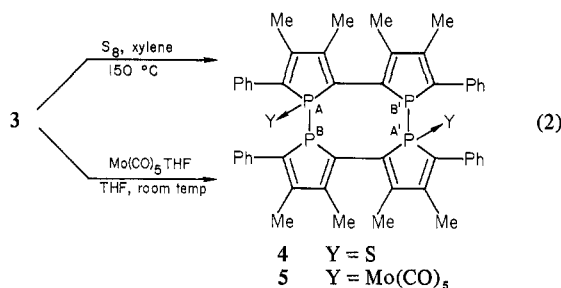
(1) Mathey, F.; Mercier, F.; Charrier, C.; Fischer, J.; Mitschler, A. *J. Am. Chem. Soc.* **1981**, *103*, 4595.

(2) In this case, the behavior of phospholes parallels the behavior of siloles; see: Barton, T. J.; Wulff, W. D.; Arnold, E. V.; Clardy, J. *J. Am. Chem. Soc.* **1979**, *101*, 2733. A similarity between siloles and phospholes has already been noted during UV photodimerization experiments: Barton, T. J.; Nelson, A. *J. Tetrahedron Lett.* **1969**, 5037.

(3) The thermolysis is performed in a sealed glass tube on 1.9 g of **1**. After 60 h at 170 °C, the cooled mixture is recovered with CH<sub>2</sub>Cl<sub>2</sub>. The insoluble red crystals of **3** are removed by filtration: mp > 260 °C; yield 0.38 g (20%); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  2.03 (br s, 12 H, Me), 2.19 (m, 12 H, Me), 7.40 (br s, 20 H, Ph); <sup>31</sup>P NMR (H<sub>3</sub>PO<sub>4</sub>, CDCl<sub>3</sub>,  $\delta$  positive for downfield shifts):  $\delta$  -11.6; mass spectrum (70 eV, 240 °C) *m/e* 744 (M, 100%), 558 (M-C<sub>12</sub>H<sub>11</sub>P, 41%), 372 (M/2, 50%).

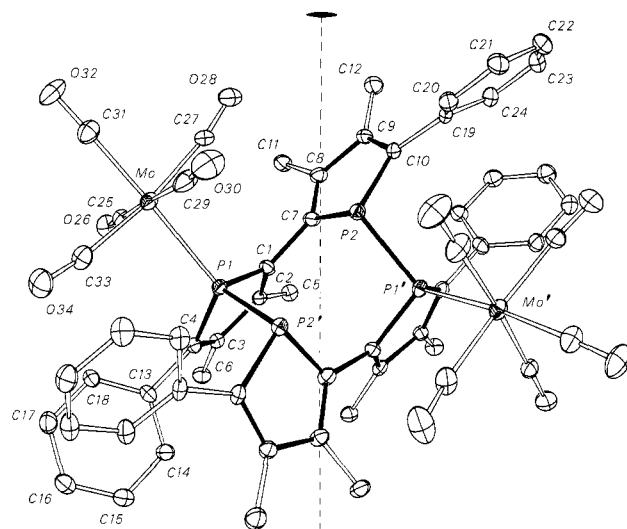
step B is very likely for the following reasons: (1) The thermolysis of 1,2,5-triphenylphosphole produces an analogous 1,1'-biphosphole, which was isolated and fully characterized.<sup>4</sup> (2) The colorless liquid resulting from the thermolysis of **1**, when reacted first with naphthalene-sodium in THF followed by benzyl bromide, produces *inter alia* 1-benzyl-2-phenyl-3,4-dimethylphosphole.<sup>5</sup>

Though the yield of **3** is modest (~20%), nevertheless it is an interesting starting point for building a new chemistry since it is very easily recovered from the crude thermolysis mixture and since **1** is now available on a large scale. We thus began to study the chemistry of **3**. The reactions of sulfur in boiling xylene and of Mo(CO)<sub>5</sub>THF in THF at room temperature afforded respectively the corresponding sulfide **4**<sup>6</sup> and complex **5**<sup>7</sup> (eq 2).



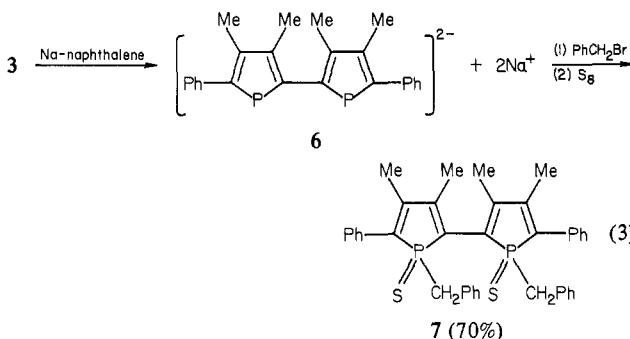
The structure of **5** was confirmed by X-ray crystal structure analysis and is fully described hereafter. The AA'BB' <sup>31</sup>P spectra of these two compounds were computer simulated.<sup>8</sup> The most striking result was the very large coupling constant between P<sub>B</sub> and P<sub>B'</sub> (140.1 Hz for **4** and **5**) whereas the other coupling constants were quite normal (for example J<sub>AA'</sub> = 3.8 Hz for **4** and ≈ 0 Hz for **5**). The crystal structure clearly shows that P<sub>B</sub> (P<sub>2</sub>) is much closer to P<sub>B'</sub> (P<sub>2'</sub>) (3.30 Å) than P<sub>A</sub> (P<sub>1</sub>) is to P<sub>A'</sub> (P<sub>1'</sub>) (4.56 Å) in **5**. Nevertheless, we have here one of the few authenticated cases where a very large through-space <sup>31</sup>P...<sup>31</sup>P coupling has been noted.

Compound **3** is also an ideal starting material for preparing 2,2'-biphospholes, which were previously unknown. Thus, from it, we have prepared a 1,1'-dibenzyl-2,2'-biphosphole that was



**Figure 1.** Structure of **5** showing 50% probability ellipsoids. Selected bond distances (Å): Mo-P1, 2.543 (2); P1-P2', 2.224 (2); P1-P2, 3.565 (2); P1-P1', 4.560 (3); P2-P2', 3.303 (3); mean P-C, 1.784 (3); mean C-C (Phospholyl rings), 1.349 (4) (C $\alpha$ -C $\beta$ ) and 1.471 (7) (C $\beta$ -C $\beta'$ ); C1-C7, 1.510 (8); mean C-C (phenyl rings), 1.376 (3). Selected bond angles (deg): C1P1C4, 89.4 (3); C7P2C10, 91.2 (3).

isolated as a mixture of two diastereoisomeric 1,1'-disulfides, **7**<sup>9</sup> (eq 3).



(4) Charrier, C.; Bonnard, H.; Mathey, F., to be submitted for publication.  
 (5) The colorless liquid resulting from the pyrolysis of **1** (6.5 g) is reacted with sodium-naphthalene (Na, 1 g; C<sub>10</sub>H<sub>8</sub>, 5.5 g) in THF (50 mL). After 1 h at room temperature, the mixture is reacted with benzyl bromide (7 g). A discoloration takes place and sulfur (1 g) is added after 1 h. After 1 night at room temperature, the solvent is evaporated, and the residue is chromatographed on a silica gel column (toluene, then toluene-ethyl acetate: 90:10). A mixture (1.8 g) of 1-benzyl-2-phenyl-3,4-dimethylphosphole *P*-sulfide and 1,1'-dibenzyl-5,5'-diphenyl-3,3',4,4'-tetramethyl-2,2'-biphosphole *P,P*-disulfide, **7**, is thus obtained. The separation of these products is achieved by a second chromatography. Yield of monosulfide, 0.9 g; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.92 (d, <sup>4</sup>J<sub>H-P</sub> = 2.6 Hz, 3 H, Me-C=CPh), 2.0 (dd, 3 H, Me-C=CH), 3.32 (d, <sup>2</sup>J<sub>H-P</sub> = 14.6 Hz, 2 H, CH<sub>2</sub>Ph), 5.95 (d, <sup>2</sup>J<sub>H-P</sub> = 31 Hz, 1H, =CH-P), 7.0-7.7 (m, 10 H, Ph); <sup>31</sup>P NMR (CDCl<sub>3</sub>)  $\delta$  +51.7; mass spectrum (70 eV, 90 °C) *m/e* 310 (M, 30%), 278 (M - S, 18%), 213 (M - CH<sub>2</sub>Ph, 100%), very strong peaks at *m/e* 92 (Ph - CH<sub>3</sub>) and 91 (Ph - CH<sub>2</sub>).

(6) Compound **3** (0.4 g) was heated with sulfur (0.05 g) in boiling xylene. After evaporation, the residue was chromatographed (toluene-ethyl acetate 90:10); yield of **4**, 0.13 g (30%); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.83-2.0 (m, 24 H, Me), 6.6 (m, 4 H, Ph), 7.2-7.4 (m, 16 H, Ph); <sup>31</sup>P NMR (CDCl<sub>3</sub>)  $\delta$  +46.4 (P<sub>A</sub>P<sub>A'</sub>)  $\delta$  -10.3 (P<sub>B</sub>P<sub>B'</sub>); J<sub>AA'</sub> = 3.8 Hz, J<sub>BB'</sub> = 140.1 Hz, J<sub>AB</sub> = J<sub>A'B'</sub> = 314.6 Hz, J<sub>AB'</sub> = J<sub>A'B</sub> = 6.4 Hz; mass spectrum (70 eV, 240 °C) *m/e* 808 (M, 11%), 776 (M - S, 19%), 744 (M - 2 S, 100%).

(7) Molybdenum hexacarbonyl (0.844 g) in THF (250 mL) was irradiated by a 125-W medium-pressure mercury lamp for 1.5 h. The lamp was switched off, and **3** (0.47 g) was added. After 1.5 h, **3** disappeared, the solution was evaporated, and the residue was chromatographed (hexane-toluene, 90:10); yield of **5**, 0.54 g (70%); recrystallized from benzene-hexane, 20:80. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  2.0 (m, 24 H, Me), 6.6 (m, 4 H, Ph), 6.9 (m, 4 H, Ph), 7.1-7.4 (m, 12 H, Ph). According to the X-ray crystal structure analysis of **5**, the phenyl groups of the two 2,2'-biphosphole subunits are interacting, and this explains the appearance of shielded phenyl protons as in **4**. <sup>31</sup>P NMR (CDCl<sub>3</sub>)  $\delta$  +25.8 (P<sub>A</sub>P<sub>A'</sub>)  $\delta$  -7.3 (P<sub>B</sub>P<sub>B'</sub>); J<sub>AA'</sub> = 0 Hz, J<sub>BB'</sub> = 140.1 Hz, J<sub>AB</sub> = J<sub>A'B'</sub> = 363.1 Hz, J<sub>AB'</sub> = J<sub>A'B</sub> = 8.5 Hz; IR (Nujol)  $\nu$ (CO) 2065 m, 1990 m, 1950 vs, 1938 vs, 1920 sh, 1908 s cm<sup>-1</sup>.

(8) We have used the PANIC program included in the Bruker WP 80 software.

From another standpoint, **3** has a tremendous potential in coordination chemistry. For example its reaction (eq 4) with [CpFe(CO)<sub>2</sub>]<sub>2</sub> at 150 °C affords the phosphorus analogue of a biferrocene **8**,<sup>10</sup> again as a mixture of two diastereoisomers.

Similarly, the reaction of the dianion **6**, first with MgBr<sub>2</sub> and then with FeCl<sub>2</sub> according to a procedure that was developed for

(9) Sodium (0.05 g, 2.2  $\times$  10<sup>-3</sup> mol) was stirred with naphthalene (0.3 g, 2.3  $\times$  10<sup>-3</sup> mol) in THF (25 mL) under argon until complete dissolution. **3** (0.4 g, 5  $\times$  10<sup>-4</sup> mol) was then added to the resulting blue solution, which rapidly turned red. After 1 h of stirring at room temperature, an excess of benzyl bromide (1 mL) was added. An immediate discoloration took place, and the solution turned orange-yellow. After 1 h, sulfur (0.2 g) was added. Then, after 1 night, the solution was evaporated and the residue was chromatographed on silica gel (toluene-ethyl acetate, 95:5); yield of **7**, 0.43 g (70%). First isomer (relative abundance ~60%): <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  2.0 (d, <sup>4</sup>J<sub>H-P</sub> = 2.4 Hz, 12 H, Me), 3.56 (d, <sup>2</sup>J<sub>H-P</sub> = 15.6 Hz, 4 H, CH<sub>2</sub>Ph), 7.02 (s, 10 H, CH<sub>2</sub>Ph), 7.35-7.85 (m, 10 H, Ph); <sup>31</sup>P NMR (CDCl<sub>3</sub>)  $\delta$  +55.5. Second isomer (relative abundance ~40%): <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  2.0 (d, <sup>4</sup>J<sub>H-P</sub> = 2.4 Hz, 12 H, Me), 3.40 (d, <sup>2</sup>J<sub>H-P</sub> = 15.2 Hz, 4 H, CH<sub>2</sub>Ph), 7.02 (s, 10 H, CH<sub>2</sub>Ph), 7.35-7.85 (m, 10 H, Ph); <sup>31</sup>P NMR (CDCl<sub>3</sub>)  $\delta$  +53.7; mass spectrum (70 eV, 150 °C) *m/e* 618 (M, 44%), 495 (M - PhCH<sub>2</sub>-S, 100%); correct C, H, P, S elemental analyses.

(10) A mixture of **3** (0.37 g, 5  $\times$  10<sup>-4</sup> mol) and dicyclopentadienyltetra-carbonyldiiron (0.7 g, 2  $\times$  10<sup>-3</sup> mol) was refluxed for 5 h in xylene under argon. After filtration and evaporation, the residue was chromatographed on silica gel (hexane-toluene, 50:50); yield of **8**, 0.3 g (48%). According to <sup>1</sup>H and <sup>31</sup>P NMR data, **8** is a mixture of two diastereoisomers (80:20). Main isomer: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  2.13 (s, 6 H, Me), 2.57 (s, 6 H, Me), 3.96 (s, 10 H, Cp), 7.08-7.40 (m, 10 H, Ph); <sup>31</sup>P NMR (CDCl<sub>3</sub>)  $\delta$  -59.58. Minor isomer: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  2.01 (s, 6 H, Me), 2.08 (s, 6 H, Me), 4.33 (s, 10 H, Cp), 7.08-7.40 (m, 10 H, Ph); <sup>31</sup>P NMR (CDCl<sub>3</sub>)  $\delta$  -61.01; mass spectrum (70 eV, 200 °C) *m/e* 614 (M, 100%); correct C, H, Fe, P elemental analyses.

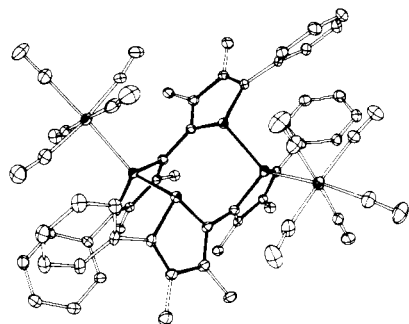
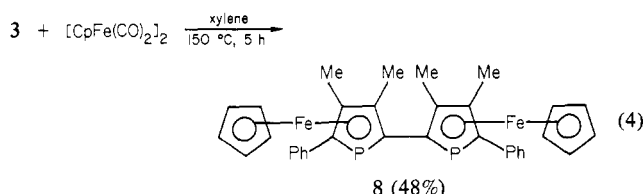
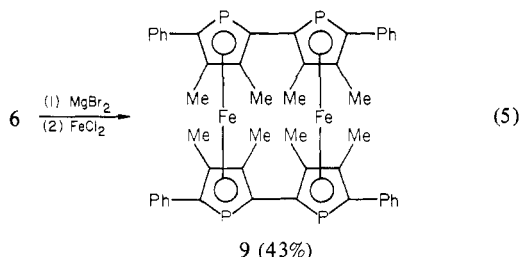


Figure 2. Stereoview of complex 5.



the synthesis of 1,1'-diphosphaferrocene,<sup>11</sup> gives the analogue of a bis(fulvalene)diiron,<sup>9,12</sup> (eq 5).



In this case, only one diastereoisomer is isolated. In view of the deep and recent interest in the chemistry of bis(fulvalene)-dimetal complexes,<sup>13</sup> the coordination chemistry of 3 obviously deserves further investigation.

In order to establish beyond any doubt the tetrameric structure of 3, we performed an X-ray crystal structure analysis of its molybdenum complex 5.

Single crystals of 5 were obtained by slow evaporation of a CH<sub>2</sub>Cl<sub>2</sub> solution at room temperature. They belong to the monoclinic system, space group C2/c with  $a = 13.121$  (4) Å,  $b = 16.390$  (5) Å,  $c = 28.821$  (8) Å,  $\beta = 93.45$  (4)°, [C<sub>29</sub>H<sub>22</sub>MoO<sub>5</sub>P<sub>2</sub>]<sub>2</sub> mol wt 1216,  $Z = 4$ ,  $\rho_c = 1.39$  g cm<sup>-3</sup>.

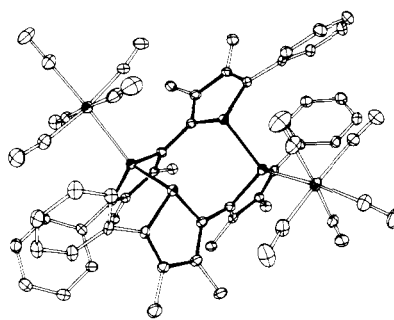
Diffraction data were collected with the  $\theta/2\theta$  flying step-scan technique using a Philips PW1100/16 automatic diffractometer and graphite monochromated Cu K $\alpha$  radiation. Absorption corrections were applied with the method of Busing and Levy.<sup>14</sup> The structure was solved by Patterson techniques and refined by

(11) De Lauzon, G.; Deschamps, B.; Fischer, J.; Mathey, F.; Mitschler, A. *J. Am. Chem. Soc.* **1980**, *102*, 994.

(12) Sodium (0.078 g,  $3.4 \times 10^{-3}$  mol) was stirred with naphthalene (0.46 g,  $3.5 \times 10^{-3}$  mol) in THF (30 mL) under argon until complete dissolution. To the blue solution were added successively at room temperature and under constant stirring (a) 3 (0.6 g,  $8 \times 10^{-4}$  mol), (b) then after 1 h, MgBr<sub>2</sub> (0.62 g,  $3.4 \times 10^{-3}$  mol), (c) then, after 2 h more, FeCl<sub>2</sub> (0.26 g,  $2 \times 10^{-3}$  mol). One hour after the addition of FeCl<sub>2</sub>, the solution was evaporated, and the residue was quickly chromatographed on a short column of silica gel with toluene. The eluted products are rechromatographed on silica gel (hexane-toluene, 80:20); yield of 9 0.3 g (43%); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.55 (s, 12 H, Me), 2.90 (s, 12 H, Me), 7.2-7.6 (m, 20 H, Ph); <sup>31</sup>P NMR (CDCl<sub>3</sub>)  $\delta$  -40.6; mass spectrum (70 eV, 200 °C)  $m/e$  856 (M, 100%); correct C, H, Fe, P elemental analyses.

(13) See, for example: Davison, A.; Smart, J. C. *J. Organomet. Chem.* **1973**, *49*, C43. Le Vanda, C.; Bechgaard, K.; Cowan, O. D.; Mueller-Westerhoff, U. T.; Eilbracht, P.; Candela, A. G.; Collins, R. L. *J. Am. Chem. Soc.* **1976**, *98*, 3181. Smart, J. C.; Curtis, C. J. *Ibid.* **1977**, *99*, 3518. Smart, J. C.; Pinsky, B. L. *J. Am. Chem. Soc.* **1980**, *102*, 1009. Sharp, P. R.; Raymond, K. N.; Smart, J. C.; McKinney, R. J. *J. Am. Chem. Soc.* **1981**, *103*, 753.

(14) Busing, W. R. "Crystallographic Computing"; Ahmed, F. R., Ed.; Munksgaard: Copenhagen, Denmark, 1970; p 319.



full least-squares analysis to convergence. A total of 2478 reflexions having  $F^2 > 3\sigma(F^2)$  with weights as  $\sigma^2(I) = \sigma^2_{\text{counts}} + (pI)^2$  were used. Final results are  $R = 0.060$ ,  $R_w = 0.075$ , standard deviation of a unit-weight observation = 1.97 for  $p = 0.08$ . For all computations the Enraf-Nonius Structure Determination Package<sup>15</sup> on a PDP 11/60 computer was used.

The structure (Figures 1 and 2) consists of (PC<sub>6</sub>H<sub>6</sub>-C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>-Mo(CO)<sub>5</sub> dimers related by a 2-fold crystallographic axis. Selected bond lengths and angles are given in the caption of Figure 1.

As expected, the phosphole rings are not planar: P1 is out of the mean plane C1 to C<sub>4</sub> by 0.140 (2) Å and P2 is out of the C7 to C10 mean plane by 0.207 (2) Å, leading to dihedral angles around C1...C4 and C7...C10 axis of 6.3 and 9.5°, respectively. The dihedral angle between the two phosphole rings is 5.18°.

Further work on these phosphole tetramers will be reported in due course.

**Registry No.** 1, 30540-36-4; 3, 80737-80-0; 4, 80737-81-1; 5, 80753-73-7; 7, isomer I, 80737-82-2; 7, isomer II, 80737-83-3; 8, isomer I, 80738-14-3; 8, isomer II, 80779-86-8; 9, 80738-15-4; 1-benzyl-2-phenyl-3,4-dimethylphosphole *P*-sulfide, 80737-84-4; dicyclopentadienyltetracarbonyldiiron, 12154-95-9; molybdenum hexacarbonyl, 13939-06-5.

**Supplementary Material Available:** Listings of atomic positional and thermal parameters (Table 1), observed and calculated structure factors ( $\times 10$ , Table 2), bond distances and angles (Table 3), and selected mean planes (Table 4) (16 pages). Ordering information is given on any current masthead page.

(15) Frenz, B. A. "Computing in Crystallography"; Schenk, H., Olthoff-Hazenkamp, R., Van Koenigsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978; p 64.

## A New Design for Chiral Induction: A Highly Regioselective Differentiation between Two Identical Groups in an Acyclic Compound Having a Prochiral Center

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Received December 14, 1981

Recently, the utilization of optically active, simple acyclic compounds has been increasing<sup>1</sup> because they can be useful as