Synthesis and Structure of [η^4-Tetrakis(arylethoxyphosphoryl)cyclobutadiene]-(η^5-cyclopentadienyl)cobalt(I) Complexes

Shigeru Sasaki,* Kiyotoshi Kato, Yoshihiro Tanabe, and Masaaki Yoshifuji*
Department of Chemistry, Graduate School of Science, Tohoku University, Aoba, Sendai 980-8578

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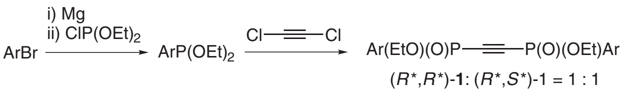
[η^4-Tetrakis(arylethoxyphosphoryl)cyclobutadiene](η^5-cyclopentadienyl)cobalt(I) complexes were synthesized by reaction of bis(arylethoxyphosphoryl)acetylenes with $CpCo(CO)_2$ and several diastereomers were isolated. Whole molecular structure of the tetraphosphorylcyclobutadiene complex was significantly affected by relative configuration of the phosphoryl groups.

Cyclic π-conjugated systems carrying adjacent phosphorus functional groups have received considerable interest. There have been several reports of five[1] and six[2] membered π-conjugated systems carrying phosphorus functional groups in array. Recently, we reported synthesis, structure, and coordination properties of [η^4-tetrakis(diethoxyphosphoryl)cyclobutadiene]-(η^5-cyclopentadienyl)cobalt(I),[3] which acted as a bisbidentate ligand for one dimensional coordination polymer. Tetraphosphorylcyclobutadiene ligands carrying chiral phosphorus centers are expected to have unique structure and properties due to intramolecular interaction among adjacent phosphorus substituents as well as asymmetric coordination or hydrogen bonding of the phosphoryl groups. Herein, we report synthesis and structure of the [η^4-tetrakis(arylethoxyphosphoryl)cyclobutadiene](η^5-cyclopentadienyl)cobalt(I). Several diastereomers of different relative configuration of the four phosphoryl groups were isolated.



(R^*,R^*)-**1**: (R^*,S^*)-1 = 1 : 1
1a: Ar = Ph
1b: Ar = 4-(−)-menthoxymethylphenyl

Bis(arylethoxyphosphoryl)acetylene **1a**[4] was synthesized by the reaction[4] of aryldiethoxyphosphine with dichloroacetylene[5] and was obtained as a 1:1 diastereomeric mixture. Acetylene **1b** was similarly synthesized from 1-bromo-4-[(−)-menthoxymethyl]benzene.[6] Purification of the mixture by silica gel column chromatography followed by GPC (**1a**) or recrystallization (**1b**) gave diastereomeric pure forms.[7]

Relative configuration of phosphoryl groups of (R^*,S^*)-**1b** was determined by X-ray crystallography from the comparison with an internal standard, the (−)-menthoxy groups (Figure 1).[8]

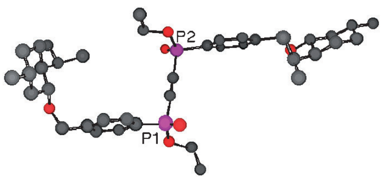
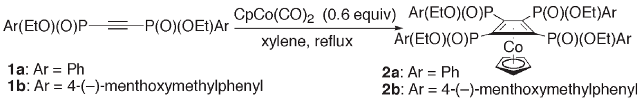


Figure 1. Molecular structure of (R^*,S^*)-**1b**. Hydrogen atoms were omitted for clarity.

^{31}P NMR (δ 8.6 (s)) and ^{13}C NMR of acetylenic carbons (δ 93.6 (dd, $^1J_{PC} = 182.8$ Hz, $^2J_{PC} = 26.3$ Hz)) appeared as single signals in spite of introduction of the (−)-menthoxy groups. Relative configuration of the phosphoryl groups of **1a** was estimated by comparison with the physical data of **1b**.

Reaction of an isomeric mixture of **1a** ((R^*,S^*)-**1a**: (R^*,R^*)-**1a** = 1:1) with $CpCo(CO)_2$ in refluxing xylenes resulted in formation of an inseparable isomeric mixture of the cyclobutadiene complex **2a**. The ratio of the isomers was estimated to be (R^*,R^*,R^*,R^*)-**2a**:(R^*,S^*,R^*,S^*)-**2a**:(R^*,R^*,S^*,S^*)-**2a**:(R^*,R^*,R^*,S^*)-**2a** = 1:1:2:4 from ^{31}P NMR and ^{1}H NMR signals of cyclopentadienyl protons. On the other hand, the reaction of the single diastereomer, (R^*,R^*)-**1** and (R^*,S^*)-**1**, afforded a mixture composed of two diastereomers, (R^*,R^*,S^*,S^*)-**2** and (R^*,R^*,R^*,R^*)-**2** (1:1), and (R^*,R^*,S^*,S^*)-**2** and (R^*,S^*,R^*,S^*)-**2** (1:1), respectively, and (R^*,R^*,R^*,R^*)-**2a**, (R^*,S^*,R^*,S^*)-**2a**, and (R^*,S^*,R^*,S^*)-**2b** were isolated in a diastereomerically pure form in 12, 21, and 9%, respectively.



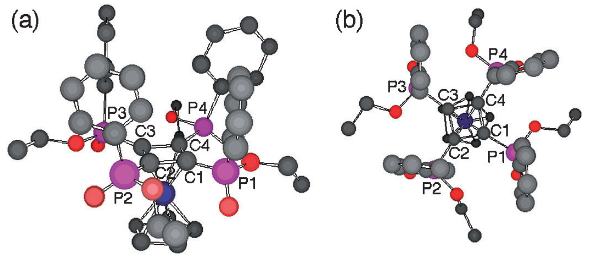


Figure 2. Molecular structures of (R^*,R^*,R^*,R^*)-**2a**. Hydrogen atoms and solvents were omitted for clarity. (a) Side view, (b) Top view.

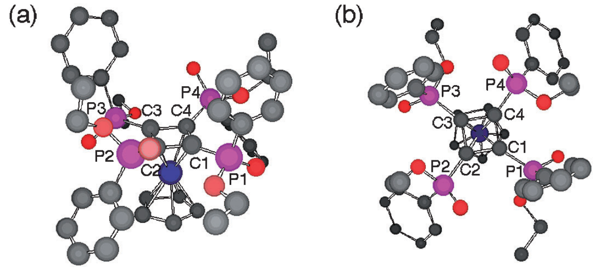


Figure 3. Molecular structures of (R^*,S^*,R^*,S^*)-**2a**. Hydrogen atoms and solvents were omitted for clarity. (a) Side view, (b) top view.

Tetrakis(arylethoxyphosphoryl)cyclobutadiene complexes **2** were characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectra[7] and the structures of complexes (R*,R*,R*,R*)-**2a** and (R*,S*,R*,S*)-**2a** were further investigated by X-ray crystallography (Figures 2 and 3),[8] where difference of the relative configuration of the phosphoryl groups resulted in clear contrast of the whole molecular structure. The cyclobutadiene complex (R*,R*,R*,R*)-**2a** crystallized as racemic crystals with one water molecule. According to (R*,R*,R*,R*) configuration of the phosphoryl groups, four phenyl groups situated opposite to the CoCp moiety, and the phosphoryl oxygens (P(O)) located below the cyclobutadiene plane pointing in the same direction along the cyclobutadiene square. Molecular structure of (R*,S*,R*,S*)-**2a** obtained from X-ray crystallography of a single crystal, which included two water molecules being hydrogen bonded to the phosphoryl oxygens, showed marked difference from the (R*,R*,R*,R*)-**2a**. Four phenyl groups aligned alternately above and below the cyclobutadiene plane and four phosphoryl oxygens also alternately located below and above the cyclobutadiene plane, pointing in the same direction. Two phosphorus atoms of (R*,S*,R*,S*)-**2a** possessing phenyl groups in the CoCp side considerably deviated from the cyclobutadiene plane (0.47(2) (P2) and 0.48(2) (P4) Å above the plane), on the other hand, deviation more than 0.2 Å was not observed for the remaining phpsphorus atoms of (R*,S*,R*,S*)-**2a** as well as the four phosphorus atoms of (R*,R*,R*,R*)-**2a**.

Structural difference of the isomers was clearly reflected on ^{1}H, ^{13}C, and ^{31}P NMR spectra. ^{31}P NMR of (R*,R*,R*,R*)-**2a** (δ 26.9) and (R*,S*,R*,S*)-**2a** (δ 29.7) appeared as a singlet peak, whereas that of (R*,R*,S*,S*)-**2a** was observed as an AB pattern with a significant magnitude of coupling (δ 29.5, 29.1, $J = 17.8$ Hz) which suggested strongly interacting inequivalent phosphorus atoms, and (R*,R*,R*,S*)-**2a** showed several signals in δ 27–31. ^{1}H NMR spectra of (R*,R*,R*,R*)-**2a** showed the most deshielded Cp (δ 5.81) and the most shielded phenyl protons. On the other hand, opposite tendency was observed for (R*,S*,R*,S*)-**2a** (δ 4.41). (R*,R*,S*,S*)-**2a** showed two inequivalent aryl and ethoxy groups consistent with ^{31}P NMR, and the Cp and Ph groups were observed in the intermediate region between (R*,R*,R*,S*)-**2a** and (R*,S*,R*,S*)-**2a**. ^{13}C NMR of cyclobutadiene carbons of (R*,R*,R*,R*)-**2a** (δ 71.9, ddt, $^{1}J_{CP} = 146.0$, $^{2}J_{CP} = 7.6$, $^{3}J_{CP} = 14.9$ Hz) and (R*,S*,R*,S*)-**2a** (δ 72.1, ddt, $^{1}J_{CP} = 150.0$, $^{2}J_{CP} = 6.8$, $^{3}J_{CP} = 15.1$ Hz) were observed as ddt patterns characteristic of tetraphosphorylcyclobutadiene complexes.[3] Contrary to (R*,S*)-**1b**, influence of (−)-menthoxy groups was observed in the ^{1}H, ^{13}C, and ^{31}P NMR spectra of (R*,S*,R*,S*)-**2b**. The phosphorus signals (δ 29.8, 29.5) as well as cyclobutadiene carbons (δ 72.2 (brd, $^{1}J_{CP} = 145.0$ Hz) 71.6 (brd, $^{1}J_{CP} = 152.0$ Hz)), which were observed as single resonances for (R*,S*,R*,S*)-**2a**, were no longer equivalent, probably due to more congested alignment of the phosphoryl groups than (R*,S*)-**1b**.

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7 Selected ^{1}H (400 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) data: (R*,R*)-**1a**: ^{1}H NMR δ 7.82 (m, 4H), 7.60 (m, 2H), 7.48 (m, 4H), 4.30 (m, 4H), 1.42 (t, $J_{HH} = 7.06$ Hz, 6H); ^{31}P NMR δ 8.7 (s). (R*,S*)-**1a**: ^{1}H NMR δ 7.86 (m, 4H), 7.62 (m, 2H), 7.51 (m, 4H), 4.23 (m, 4H), 1.36 (t, $J_{HH} = 7.06$ Hz, 6H); ^{31}P NMR δ 8.6 (s). (R*,R*)-**1b**: ^{1}H NMR δ 7.77 (m, 4H), 7.44 (m, 4H), 4.29–4.21 (m, 4H), 1.39 (t, $J_{HH} = 7.06$ Hz, 6H); ^{31}P NMR δ 8.7 (s). (R*,S*)-**1b**: ^{1}H NMR δ 7.82 (m, 4H), 7.48 (m, 4H), 4.23–4.18 (m, 4H), 1.35 (t, $J_{HH} = 7.08$ Hz, 6H); ^{31}P NMR δ 8.6 (s). (R*,R*,R*,R*)-**2a**: ^{1}H NMR δ 7.40 (brt, 4H), 7.07 (brt, 8H), 6.73 (brs, 8H), 5.81 (s, 5H), 4.23 (m, 4H), 4.02 (m, 4H), 1.32 (t, $J_{HH} = 7.00$ Hz, 12H); ^{31}P NMR δ 26.9 (s). (R*,R*,S*,S*)-**2a**: ^{1}H NMR δ 7.77 (m, 4H), 7.52 (m, 3H), 7.37 (brm, 9H), 7.19 (m, 4H), 5.11 (s, 5H), 4.16–3.80 (m, 8H), 1.34 (t, $J_{HH} = 7.04$ Hz, 6H), 1.16 (t, $J_{HH} = 7.03$ Hz, 6H); ^{31}P NMR δ 29.5 (d, $J_{PP} = 17.8$ Hz), 29.1(d, $J_{PP} = 17.8$ Hz). (R*,S*,R*,S*)-**2a**: ^{1}H NMR δ 8.22 (brq, 8H), 7.52 (brm, 12H), 4.49 (s, 5H), 3.84 (brm, 8H), 1.20 (t, $J_{HH} = 7.02$ Hz, 12H); ^{31}P NMR δ 29.7 (s). (R*,R*,R*,S*)-**2a**: ^{1}H NMR δ 5.32 (s, 5H, Cp); ^{31}P NMR δ 30.3–27.1. (R*,S*,R*,S*)-**2b**: ^{1}H NMR δ 8.29 (m, 8H), 7.49 (m, 8H), 4.71 (d, $J_{HH} = 12.18$ Hz, 2H), 4.70 (d, $J_{HH} = 11.95$ Hz, 2H), 4.47 (d, $J_{HH} = 12.18$ Hz, 2H), 4.45 (d, $J_{HH} = 11.95$ Hz, 2H), 4.37 (s, 5H), 3.85–3.74 (brm, 8H), 3.22–3.13 (m, 4H), 2.33–2.25 (m, 4H), 2.21–2.15 (brm, 4H), 1.69–1.64 (brm, 4H), 1.65–1.59 (brm, 4H), 1.40–1.33 (brm, 4H), 1.29–1.25 (m, 4H), 1.19–1.15 (m, 12H), 0.97–0.92 (brm, 4H), 0.92 (d, $J_{HH} = 6.55$ Hz, 12H), 0.91–0.88 (brm, 4H), 0.89 (d, $J_{HH} = 7.21$ Hz, 12H), 0.83–0.80 (brm, 4H), 0.71 (d, $J_{HH} = 6.92$ Hz, 12H); ^{31}P NMR δ 29.7 (s), 29.5 (s). (R*,R*,S*,S*)-**2b**: ^{31}P NMR δ 29.7 (d, $J_{PP} = 18.9$ Hz), 29.1(d, $J_{PP} = 18.9$ Hz). (R*,R*,R*,R*)-**2b**: ^{31}P NMR δ 27.9 (s), 26.9 (s).

8 (R*,S*)-**1b**: colorless block from ethanol, 0.50 × 0.15 × 0.10 mm^3, $C_{40}H_{60}O_6P_2$, $M = 698.86$, monoclinic, $P2_1$ (#4), $a = 5.5511(4)$, $b = 34.136(4)$, $c = 10.501(1)$ Å, $\beta = 95.192(7)°$, $V = 1982.2(3)$ Å^3, $Z = 2$, $D_{calcd.} = 1.171$ gcm^{-1}, $F(000) = 756.00$, $\mu(\text{Mo K}\alpha) = 0.152$ mm^{-1}, $T = 115$ K, Reflection collected/unique = 5029/3028 ($2\theta_{max} = 52.0°$, $R_{int} = 0.049$), $R_1/R/R_w = 0.060/0.067/0.089$, GOF = 1.07, max/min residual electron density 0.30/−0.66 eÅ^{-3}. (R*,R*,R*,R*)-**2a**·H_2O: yellow block from ethyl acetate, 0.25 × 0.15 × 0.15 mm^3, $C_{41}H_{47}O_9P_4Co$, $M = 866.65$, monoclinic, $P2_1/n$ (#14), $a = 12.037(2)$, $b = 16.087(3)$, $c = 21.797(5)$ Å, $\beta = 104.41(2)°$, $V = 4087(1)$ Å^3, $Z = 4$, $D_{calcd.} = 1.408$ gcm^{-1}, $F(000) = 1808.00$, $\mu(\text{Mo K}\alpha) = 0.630$ mm^{-1}, $T = 120$ K, Reflection collected/unique = 29162/7491 ($2\theta_{max} = 51.1°$, $R_{int} = 0.039$), $R_1/R/R_w = 0.049/0.060/0.069$, GOF = 1.47, max/min residual electron density 0.55/−0.88 eÅ^{-3}. (R*,S*,R*,S*)-**2a**·2H_2O: yellow plate from ethyl acetate, 0.40 × 0.25 × 0.05 mm^3, $C_{41}H_{49}O_{10}P_4Co$, $M = 884.66$, orthorhombic, $Pna2_1/n$ (#33), $a = 14.691(2)$, $b = 19.303(4)$, $c = 15.365(2)$ Å, $V = 4357(1)$ Å^3, $Z = 4$, $D_{calcd.} = 1.348$ gcm^{-1}, $F(000) = 1848.00$, $\mu(\text{Mo K}\alpha) = 0.595$ mm^{-1}, $T = 120$ K, Reflection collected/unique = 4408/4151 ($2\theta_{max} = 51.1°$, $R_{int} = 0.051$), $R_1/R/R_w = 0.030/0.035/0.039$, GOF = 0.93, max/min residual electron density 0.39/−0.38 eÅ^{-3}. All data were collected on a Rigaku RAXIS-IV Imaging Plate. CCDC-236745 ((R*,S*)-**1b**), -236746 ((R*,R*,R*,R*)-**2a**·H_2O), -236747 ((R*,S*,R*,S*)-**2a**·2H_2O).

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