

# ( $\eta^5$ -Cyclopentadienyl)( $\eta^4$ -di- and tetra-phosphorylcyclobutadiene)cobalt(I): Synthesis, structure, and formation of 1-D coordination polymer<sup>†</sup>

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Received (in Cambridge, UK) 17th May 2002, Accepted 11th July 2002

First published as an Advance Article on the web 25th July 2002

( $\eta^5$ -Cyclopentadienyl)( $\eta^4$ -di- and tetra-phosphorylcyclobutadiene)cobalt(I) complexes were synthesized by the reaction of mono- and diphosphorylacetylenes with  $\text{CpCo}(\text{CO})_2$ , respectively. The tetraphosphoryl derivative has proved to work as a bis-bidentate ligand affording a one-dimensional coordination polymer with  $\text{Ce}(\text{III})$ .

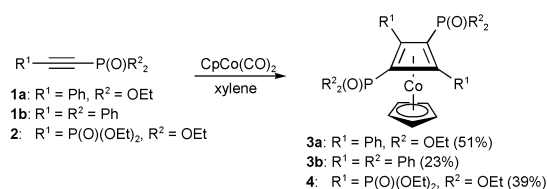
Cyclic  $\pi$ -conjugated systems fully substituted by heteroatoms have attracted considerable attention, since they are expected to have a unique structure due to intramolecular interaction between the adjacent functional groups, unique physical properties due to intermolecular interaction between  $\pi$ -conjugated systems and the functional groups, and ability for coordination or hydrogen bonding to form a novel molecular assembly. However, the number of cyclic  $\pi$ -conjugated systems carrying neighbouring phosphorus functional groups is still limited. Pentaphosphinocyclopentadienyl complex,<sup>1</sup> 1,2,3,4-tetraphosphinobenzene,<sup>2</sup> tetraphosphorylbenzoquinone<sup>3</sup> have been reported so far. Oligomerization of acetylenes by ( $\eta^5$ -cyclopentadienyl)cobalt(I) complexes<sup>4</sup> is a general method to prepare  $\pi$ -conjugated systems such as benzenes, ( $\eta^4$ -cyclobutadiene)( $\eta^5$ -cyclopentadienyl)cobalt(I), and cobaltacyclopentadienes, depending on the substrates and conditions. In fact, hexaborylbenzene was synthesized by the reaction of diborylacetylene with  $\text{CpCo}(\text{CO})_2$ .<sup>5</sup> Herein, we report synthesis of ( $\eta^5$ -cyclopentadienyl)( $\eta^4$ -di- and tetra-phosphorylcyclobutadiene)cobalt(I) complexes by the reaction of phosphorylacetylenes with  $\text{CpCo}(\text{CO})_2$ , and their structures, together with redox properties and unique transition metal complex formation.

Acetylene **1a**<sup>6</sup> was allowed to react with  $\text{CpCo}(\text{CO})_2$  in refluxing xylene and the reaction was monitored by <sup>31</sup>P NMR spectroscopy (Scheme 1). Formation of the cyclobutadiene complex **3a** as a single isomer without significant side reactions was confirmed by disappearance of the signal of alkynylphosphoryl group of **1a** ( $\delta_{\text{P}} = -5.3$ ) and growing signals due to the phosphoryl group of **3a** ( $\delta_{\text{P}} = 20.6$ ) attached to the cyclobutadiene. Acetylene **1b**<sup>7</sup> afforded complex **3b** as a main product similarly to **1a** except for the formation of a significant amount of a side product.<sup>8</sup> Diphosphorylacetylene **2**<sup>9</sup> was also converted to complex **4** in moderate yield. Irradiation<sup>10</sup> with a 500 W Xe-lamp slightly improved the yield in some cases and addition of a catalytic amount of  $\text{CpCo}(\text{CO})_2$  afforded only a trace amount of the cyclobutadiene complex with recovery of the starting material. A compound of the ( $\eta^4$ -cyclopentadieno-

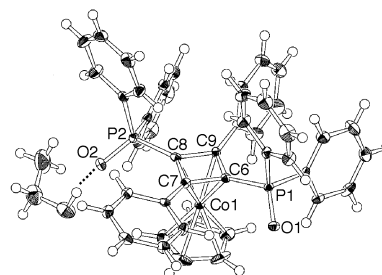
ne)( $\eta^5$ -cyclopentadienyl)cobalt(I) type reported by Baxter *et al.*,<sup>11</sup> obtained by the reaction of dimethyl 1-propynylphosphonate with  $\text{CpCo}(\text{CO})_2$  under very similar conditions to ours, was not obtained. Products of the reaction seemed to depend significantly on the substituent. Complexes **3a**, **3b**, and **4** were purified by column chromatography on  $\text{SiO}_2$ .

The structures of complexes **3a**, **3b**, and **4** were characterized by <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR, MS, IR, and UV-Vis spectra. Formation of the cyclobutadiene ring and the position of the substituents were clearly characterized by <sup>13</sup>C NMR signals. The cyclobutadiene carbons of **3a** and **3b** attached to the phosphoryl substituent appeared as dd (**3a**:  $\delta$  57.0 (dd, <sup>1</sup>J<sub>PC</sub> = 211.0, <sup>3</sup>J<sub>PC</sub> = 19.6 Hz), **3b**:  $\delta$  66.1 (dd, <sup>1</sup>J<sub>PC</sub> = 99.8, <sup>3</sup>J<sub>PC</sub> = 15.8 Hz)), while the other cyclobutadiene carbons were observed at lower field as a triplet (**3a**:  $\delta$  83.6 (t, <sup>2</sup>J<sub>PC</sub> = 7.5 Hz), **3b**:  $\delta$  87.7 (t, <sup>2</sup>J<sub>PC</sub> = 4.9 Hz)). The magnitude and pattern of <sup>13</sup>C–<sup>31</sup>P coupling strongly suggested formation of head-to-tail cyclobutadiene complexes as observed in the previous reports.<sup>12</sup> The cyclobutadiene carbon of **4** was interpreted by assigning the <sup>1</sup>J<sub>PC</sub>, <sup>2</sup>J<sub>PC</sub> and <sup>3</sup>J<sub>PC</sub> values similar to those of **3a** (**4**:  $\delta$  66.0 (ddt, <sup>1</sup>J<sub>PC</sub> = 216.0, <sup>2</sup>J<sub>PC</sub> = 8.2, <sup>3</sup>J<sub>PC</sub> = 16.7 Hz)). Coupling constants between the phosphorus atoms (<sup>3</sup>J<sub>PP</sub> and <sup>4</sup>J<sub>PP</sub>), which are generally small (*ca.* 10 Hz)<sup>13</sup> between the phosphoryl phosphorus nuclei, seemed to have little influence on the spin–spin coupling system. <sup>31</sup>P NMR (81 MHz,  $\text{CDCl}_3$ ) signals of **3a**, **3b**, and **4** were observed in the typical region of the phosphoryl groups (**3a**:  $\delta$  20.6, **3b**:  $\delta$  26.5, **4**:  $\delta$  16.0). Significant intramolecular interaction among neighboring phosphoryl groups in **4** was ruled out from the small difference in chemical shift between **3a** and **4**. The effect of the phosphoryl group was not significant in the UV-Vis spectra, which were similar to those of an unsubstituted derivative.<sup>14</sup> The structure and alignment of substituents in **3b** were finally confirmed by X-ray crystallography of **3b**·EtOH (Fig. 1).<sup>‡</sup>

Structural parameters of **3b** were within the range of the reported ( $\eta^4$ -cyclobutadiene)( $\eta^5$ -cyclopentadienyl)cobalt(I).<sup>15</sup> One of the oxygens of the phosphoryl groups (O2) was weakly hydrogen-bonded to ethanol, and that was in agreement with  $\nu_{\text{OH}} = 3372 \text{ cm}^{-1}$  observed in IR spectrum (KBr). Such hydrogen bond formation by phosphoryl compounds in the crystals is well known.<sup>16</sup>



Scheme 1



**Fig. 1** ORTEP drawing of **3b** with thermal ellipsoid of 50% probability. Selected bond lengths (Å) and angles (°): P1–C6 1.783(4), P1–O1 1.487(3), P2–C8 1.782(4), P2–O2 1.499(3), C6–C7 1.467(6), C7–C8 1.466(6), C8–C9 1.461(5), C6–C9 1.462(6), C6–C7–C8 90.1(3), C7–C8–C9 89.8(3), C6–C9–C8 90.5(3), C7–C6–C9 89.7(3). The hydrogen bond is shown by the dotted line.

<sup>†</sup> Electronic supplementary information available: Synthetic procedure, physical data, and crystallographic data. See <http://www.rsc.org/suppdata/cc/b2/b204779a/>

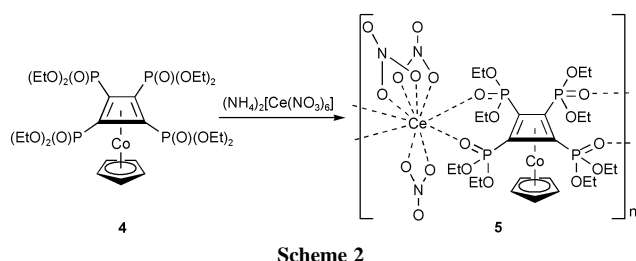
( $\eta^4$ -Cyclobutadiene)( $\eta^5$ -cyclopentadienyl)cobalt(I) complexes are generally oxidized at moderate potential.<sup>17</sup> Redox potentials of **3a**, **3b**, and **4** obtained by cyclic voltammetry are summarized in Table 1. The cyclic voltammograms of **3a**, **3b**, and **4** consisted of irreversible oxidation and reversible reduction waves. Effect of the phosphoryl groups as electron-withdrawing substituents appeared clearly in the redox potentials, where substitution of the phosphoryl group raised and lowered the oxidation and reduction potentials, respectively. Thus, **4** has a higher oxidation potential by 0.61 V and a lower reduction potential by 0.19 V, respectively, than **3a**.

**Table 1** Redox potentials of **3a**, **3b**, and **4**<sup>a</sup>

Complex	Solvent	$E_{ox}/V^b$	$E_{red}/V^c$
<b>3a</b>	Dichloromethane	0.97	
	DMF	0.71	-2.27
<b>3b</b>	Dichloromethane	1.11	
	DMF	0.81	-2.26
<b>4</b>	Dichloromethane	1.58	
	DMF		-2.08

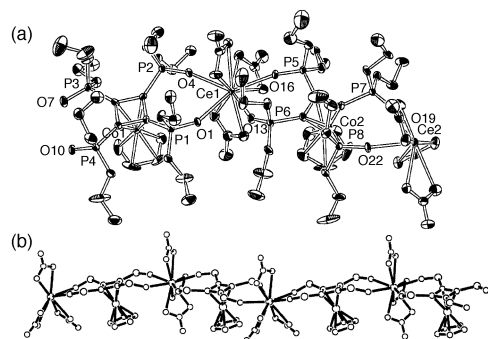
<sup>a</sup> Solvent: dichloromethane or DMF with 0.10 mol L<sup>-1</sup> *n*-Bu<sub>4</sub>NClO<sub>4</sub> as a supporting electrolyte, working electrode: glassy carbon, counter electrode: Pt wire, reference electrode: 0.01 mol L<sup>-1</sup> AgNO<sub>3</sub> in acetonitrile with 0.10 mol L<sup>-1</sup> *n*-Bu<sub>4</sub>NClO<sub>4</sub>/Ag, ferrocene/ferrocenium = 0.18 V for dichloromethane and 0.04 V for DMF, scan rate: 30 mV s<sup>-1</sup>. <sup>b</sup> Irreversible, peak potential. <sup>c</sup> Half wave potential.

To remove the CpCo moiety from the cyclobutadiene ligand,<sup>18</sup> complex **4** was allowed to react with (NH<sub>4</sub>)<sub>2</sub>[Ce(NO<sub>3</sub>)<sub>6</sub>] in acetone. Contrary to expectation, no products originated from decomplexation were obtained, but yellow crystals **5** with the composition of **4**·[Ce(NO<sub>3</sub>)<sub>3</sub>] were isolated in 48% yield after recrystallization from DMF-ethanol (Scheme 2). The complex **5** was sparingly soluble in most organic solvents. The <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectra of **5** dissolved in DMSO-*d*<sub>6</sub> as well as the UV-Vis spectrum in DMF suggested dissociation of the free **4** from the complex.



**Scheme 2**

The structure of **5** was finally determined by X-ray crystallography (Fig. 2).<sup>‡</sup> Three nitrates and two pairs of adjacent phosphoryl groups of **4** coordinated as bidentate ligands to the Ce(III) ion of coordination number 10. Interestingly, **4** acted as a bis-bidentate ligand and the whole



**Fig. 2** (a) ORTEP drawing of unit structure of **5** with thermal ellipsoid of 50% probability. (b) One-dimensional polymeric structure of **5** running parallel to the *b* axis, ethoxy groups are omitted for clarity.

structure of **5** became a one-dimensional polymeric chain with the alternate distances of Co(I) and Ce(III) as 5.28 and 5.42 Å. The high oxidation potential and molecular structure of **4** suitable for a bis-bidentate ligand would be responsible for the formation of the one-dimensional coordination polymer. The Ce(IV) ions were presumably reduced to Ce(III) during the work-up procedure.

Financial support by Tokuyama Science Foundation, The Japan Securities Scholarship Foundation, and Grants-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology (Nos. 12740335, 08454193 and 09239101) is gratefully acknowledged. The authors also thank the Instrumental Analysis Center for Chemistry, Graduate School of Science, Tohoku University, for measurement of 600 MHz NMR, mass spectra, and elemental analysis.

## Notes and references

<sup>‡</sup> Crystal data for **3b**·EtOH: C<sub>47</sub>H<sub>41</sub>CoO<sub>3</sub>P<sub>2</sub>, *M* = 774.72, triclinic, *P*1̄ (#2), *a* = 12.41(2), *b* = 16.793(4), *c* = 9.731(2) Å,  $\alpha$  = 105.17(2),  $\beta$  = 97.21(1),  $\gamma$  = 97.70(4)°, *V* = 1912(2) Å<sup>3</sup>, *Z* = 2, *D*<sub>c</sub> = 1.345 g cm<sup>-3</sup>, *F*(000) = 808.00,  $\mu$ (Mo-K $\alpha$ ) = 0.575 mm<sup>-1</sup>, Rigaku RAXIS-IV Imaging Plate, *T* = 120 K, Reflection collected/unique = 10597/6242 ( $2\theta_{max}$  = 50.1°, *R*<sub>int</sub> = 0.032), *R*/*R*<sub>w</sub> = 0.063/0.091(all data), GOF = 1.75, max./min. residual electron density 0.57/-0.57 e Å<sup>-3</sup>.

Crystal data for **5**: C<sub>50</sub>H<sub>50</sub>N<sub>6</sub>O<sub>42</sub>P<sub>8</sub>Co<sub>2</sub>Ce<sub>2</sub>, *M* = 2093.17, monoclinic, *P*2<sub>1</sub>/*c* (#14), *a* = 18.845(3), *b* = 20.469(4), *c* = 21.270(8) Å,  $\beta$  = 106.65(2)°, *V* = 7860(3) Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.769 g cm<sup>-3</sup>, *F*(000) = 4232.00,  $\mu$ (Mo-K $\alpha$ ) = 1.812 mm<sup>-1</sup>, Rigaku RAXIS-IV Imaging Plate, *T* = 120 K, Reflection collected/unique = 14426/14038 ( $2\theta_{max}$  = 51.1°, *R*<sub>int</sub> = 0.034), *R*/*R*<sub>w</sub> = 0.066/0.055(all data), GOF = 1.14, max./min. residual electron density 1.35/-1.14 e Å<sup>-3</sup>.

CCDC reference numbers 183873 and 183874. See <http://www.rsc.org/suppdata/cc/b2/b204779a/> for crystallographic data in .cif or other electronic format.

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