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Synthesis and characterization of hexacoordinate cobalt(III) complexes bearing three *C*,*O*-bidentate ligands

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Abstract

Hexacoordinated Co(III) complexes bearing three *C*,*O*-bidentate ligands (**9a** and **9b)** were prepared from 1-bromo-2-(*p*-tolyloxymethyl)benzene (**8a**) and 1-bromo-2,6-bis(*p*-tolyloxymethyl)benzene (**8b**), respectively. Both complexes were stable in air at room temperature. X-ray analyses revealed that the structures of both complexes were essentially the same. According to variable temperature ^{1}H NMR study, it was found that the two oxygen ligands on the same aromatic ring of **9b** interchanged with each other.
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Keywords: Pincer ligand; Cobalt(III) complex; X-ray analysis; Variable temperature NMR

1. Introduction

Cobalt complexes have been playing important roles in organic synthesis as typified by the Pauson–Khand reaction [1] or cyclotrimerization of alkynes [2]. In recent investigations, Oshima et al. reported many useful organocobalt-mediated coupling reactions, including the Mizoroki–Heck type reaction and allylation of tertiary alkyl halides [3]. These reactions show different properties compared with conventional coupling reactions, and are assumed to involve radical intermediates based on the reaction products.

Pincer ligands have been of great interest in the field of recent synthetic chemistry as well as in organometallic chemistry [4]. Over the past decade, a large number of investigations on the catalytic activity of metal–pincer complexes, which involves nickel, palladium, platinum, rhodium, iridium, etc., have clarified that, for example, the Pd(II)–pincer complex **1** acts as a catalyst for the Mizoroki–Heck reaction [4a], and the Ir(III)–pincer complex **2** is capable of aliphatic dehydrogenation [4c]. On the other hand, although the stabilizing effect of the pincer ligand has been extensively investigated, there are only a limited number of known cobalt–pincer complexes until now [5], and compound **3** has not been fully characterized because of its air-sensitivity [5a]. Additionally, some examples of the cyclopentadienylcobalt complexes bearing a 1,3-bis(dimethylaminomethyl)benzene ligand (**4**) have been reported by Pfeffer's group, however, in those cases, one of the two amino groups did not coordinate to the cobalt atom [6] (Fig. 1).

During the course of our studies on rigid tridentate ligands for hypervalent carbon and boron chemistry [7], we reported the first full characterization of novel hypervalent carbon (10-C-5 [8]) species utilizing the 1,8-dimethoxyanthracene ligand (**5**) [7a] as well as the 10-B-5 species (**6**) [7b]. In addition, we also succeeded in the synthesis of 10-C-5 species utilizing the *C*,*O*,*O*-tridentate pincer ligand (**7**), which is more flexible than the anthracene system [7e]. In these studies, the two oxygen atoms of these ligands moderately coordinate to the central cationic carbon atom, that effectively stabilizes the novel 10-C-5 species. On the other hand, utilizing the 1,8-diaminoanthracene [7c] and

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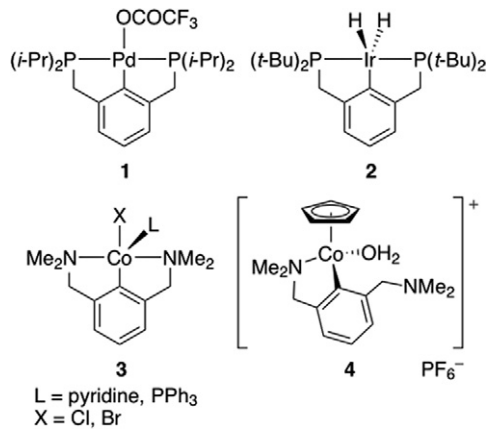


Fig. 1. Examples of organometallic species bearing a pincer ligand.

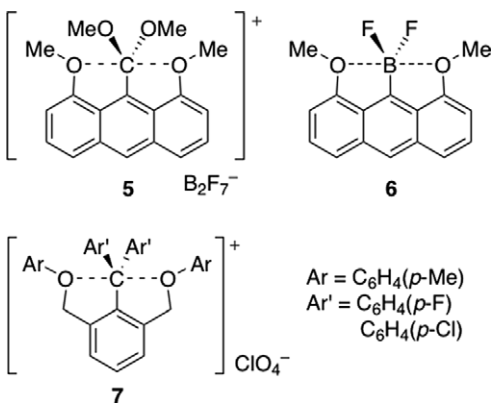


Fig. 2. Isolated hypervalent carbon (10-C-5) and boron (10-B-5) species.

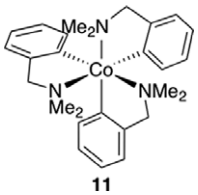
C,*S*,*S*-pincer ligand systems [7e], such hypervalent carbon species, has not been observed probably due to the stronger coordinating ability of nitrogen and sulfur atoms compared to oxygen that made the tetracoordinated carbon (8-C-4) much more preferable than the pentacoordinated state (10-C-5) (Fig. 2).

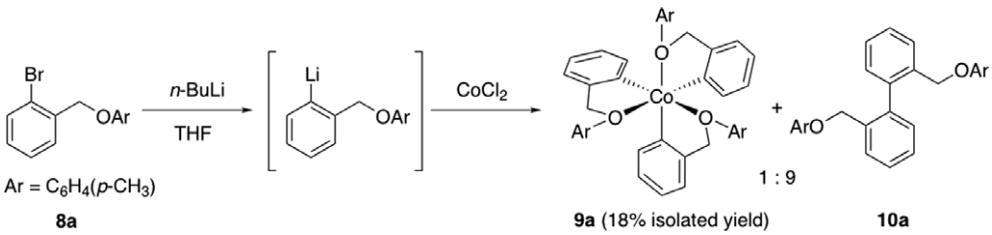
Such an oxygen-ligating multidentate ligand could be a promising solution for organocobalt catalysts because moderate coordination might make it easy to generate active species without reducing its stability during the reaction. In this study, we report the application of the *C*,*O*,*O*-pincer ligand for the synthesis of hexacoordinated organocobalt(III) complexes [9]. Structural characterization and the dynamic process of the intramolecular ligand exchange are also described.

2. Results and discussion

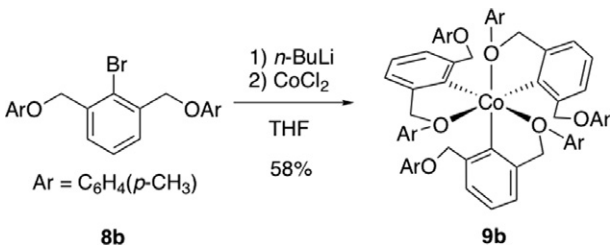
2.1. Synthesis

1-Lithio-2-(*p*-tolyloxymethyl)benzene, which was generated from 1-bromo-2-(*p*-tolyloxymethyl)benzene (**8a**) [10] with *n*-BuLi in THF, was treated with anhydrous cobalt(II) chloride to afford a novel Co(III) complex **9a** along with a considerable amount of the dimer of the ligand **10a** (**9a**:**10a** = ca. 1:9 in the crude mixture) (Scheme 1). The complex **9a** was isolated in 19% yield (based on **8a**). In the case of the pincer ligand **8b** [7e], on the other hand, compound **9b** was isolated in 58% yield, and a trace amount of the corresponding dimer of the ligand was detected in the crude mixture (Scheme 2). Neither the 1:1 nor the 1:2 adduct was obtained. In each case, the cobalt(III) complex was exclusively obtained as a *fac*-isomer, which was identified by X-ray analysis (vide infra). The reaction process is the same as the reported *N*,*C*-bidentate system consisting of the *o*-dimethylaminomethylbenzene ligand (**11**) [9a]. For the synthesis of **9**, we could not observe any meridional isomers in both cases, which might mean that the *mer*-isomer, if it exists, decomposes during the reaction or purification process. Though the reaction mechanism is not clear, the *ortho*-disubstituted ligand **8b** is obviously effective to suppress the dimerization, which would reduce the yield of **9**, during the synthesis. Both compounds were found to be stable in air at room temperature, however, they decomposed upon heating at the melting point (159–161 °C for **9a**, and 144–146 °C for **9b**) in the solid state. These complexes are quite soluble in dichloromethane, chloroform, 1,2-dichloroethane, toluene, benzene and THF, slightly soluble in ether and acetone, and almost insoluble in hexane.





Scheme 1. Synthesis of **9a**.



Scheme 2. Synthesis of **9b**.

2.2. Crystal structure

Single crystals of **9a** (red) and **9b** (dark red) were obtained by recrystallization from a hexane/CH_2Cl_2 solution. X-ray analyses revealed that both complexes have a hexacoordinate structure, and the substituents are facially located (*fac*-isomer) in the slightly distorted octahedral geometry (Fig. 3). Both crystals consisted of a 1:1 mixture of the Δ and Λ enantiomers. The molecular structures of both compounds are essentially the same, however, the degree of distortion is somewhat different. According to the bond parameters listed in Table 1, the O–Co–O angles for **9b** (average = 86.0°) are smaller than those for **9a** (average = 90.2°), whereas the opposite was observed for the C–Co–C angles (average for **9a** = 93.5°, for **9b** = 100.2°). This means that the steric repulsion between the spectator tolyloxy ligands of **9b** slightly affect the core structure in the solid state.

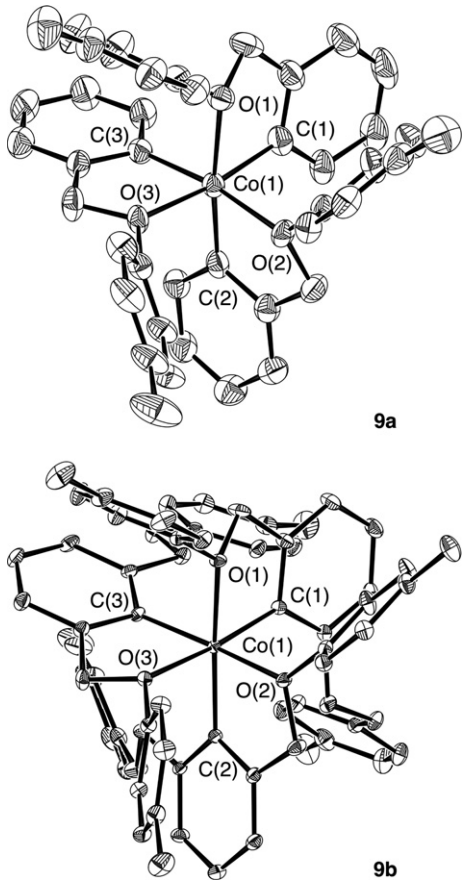


Fig. 3. ORTEP drawings of **9a** and **9b** (30% thermal ellipsoids). Hydrogen atoms are omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) for **9a** and **9b**

	9a	**9b**
Bond lengths (Å)		
Co(1)–O(1)	2.136(5)	2.081(2)
Co(1)–O(2)	2.079(4)	2.121(2)
Co(1)–O(3)	2.090(4)	2.175(2)
Co(1)–C(1)	1.926(7)	1.927(3)
Co(1)–C(2)	1.917(7)	1.969(3)
Co(1)–C(3)	1.923(6)	1.978(3)
Bond angles (°)		
O(1)–Co(1)–O(2)	91.34(19)	85.89(10)
O(1)–Co(1)–O(3)	89.4(2)	87.02(10)
O(1)–Co(1)–C(1)	82.5(3)	84.24(12)
O(1)–Co(1)–C(2)	173.4(2)	167.81(12)
O(1)–Co(1)–C(3)	93.3(2)	88.88(12)
O(2)–Co(1)–O(3)	89.77(18)	84.96(10)
O(2)–Co(1)–C(1)	93.0(2)	92.12(13)
O(2)–Co(1)–C(2)	83.7(2)	83.53(13)
O(2)–Co(1)–C(3)	171.3(2)	168.03(12)
O(3)–Co(1)–C(1)	171.5(3)	170.96(12)
O(3)–Co(1)–C(2)	94.9(2)	86.03(12)
O(3)–Co(1)–C(3)	82.9(2)	84.02(12)
C(1)–Co(1)–C(2)	93.4(3)	102.16(14)
C(1)–Co(1)–C(3)	95.0(3)	98.06(14)
C(2)–Co(1)–C(3)	92.2(3)	100.33(14)

2.3. NMR study

The ^{1}H NMR spectrum of **9a** shows sharp signals, in which all three bidentate ligands are magentically equivalent (Fig. 4a). The diastereotopic methylene protons are separately observed as two doublets at 4.71 and 5.03 ppm, and the spectrum is in good agreement with that expected on the basis of the crystal structure. In contrast, the ^{1}H NMR spectrum of **9b** showed highly broadened signals at room temperature as shown in Fig. 4b. Though the spectrum was still broadened at 60 °C (Fig. 4c) and not fully assigned yet due to the significant decomposition of **9b** at higher temperatures, the result suggests that the coordination exchange of **9b**, e.g., interchange of the two oxygen atoms (O^a and O^b), takes place in the solution state (Scheme 3). Based on the spectrum of **9a** (Fig. 4a), the benzylic protons of **9b** (Fig. 4b) can be assigned as Ha, Hb, and Hc (δ 4–5 ppm, total 12H), and the aromatic protons (probably ortho to the oxygen) in the *p*-tolyl group can be assigned as Hd and He (δ 6–6.5 ppm, 6H each). At 60 °C (Fig. 4c), Hd and He coalesced to a broad peak (12H), which should be coupled with Hg (12H, doublet at 60 °C). The fact that Hf and Hi protons (total 6H) coalesced to a broad peak, which should be coupled with Hh (3H, triplet), is consistent with the coordination exchange. At 60 °C, Ha, Hb, and Hc protons coalesced to one broad AB pattern, indicating that the chirality on the central cobalt (Δ or Λ) most likely remains unchanged during the coordination exchange process.

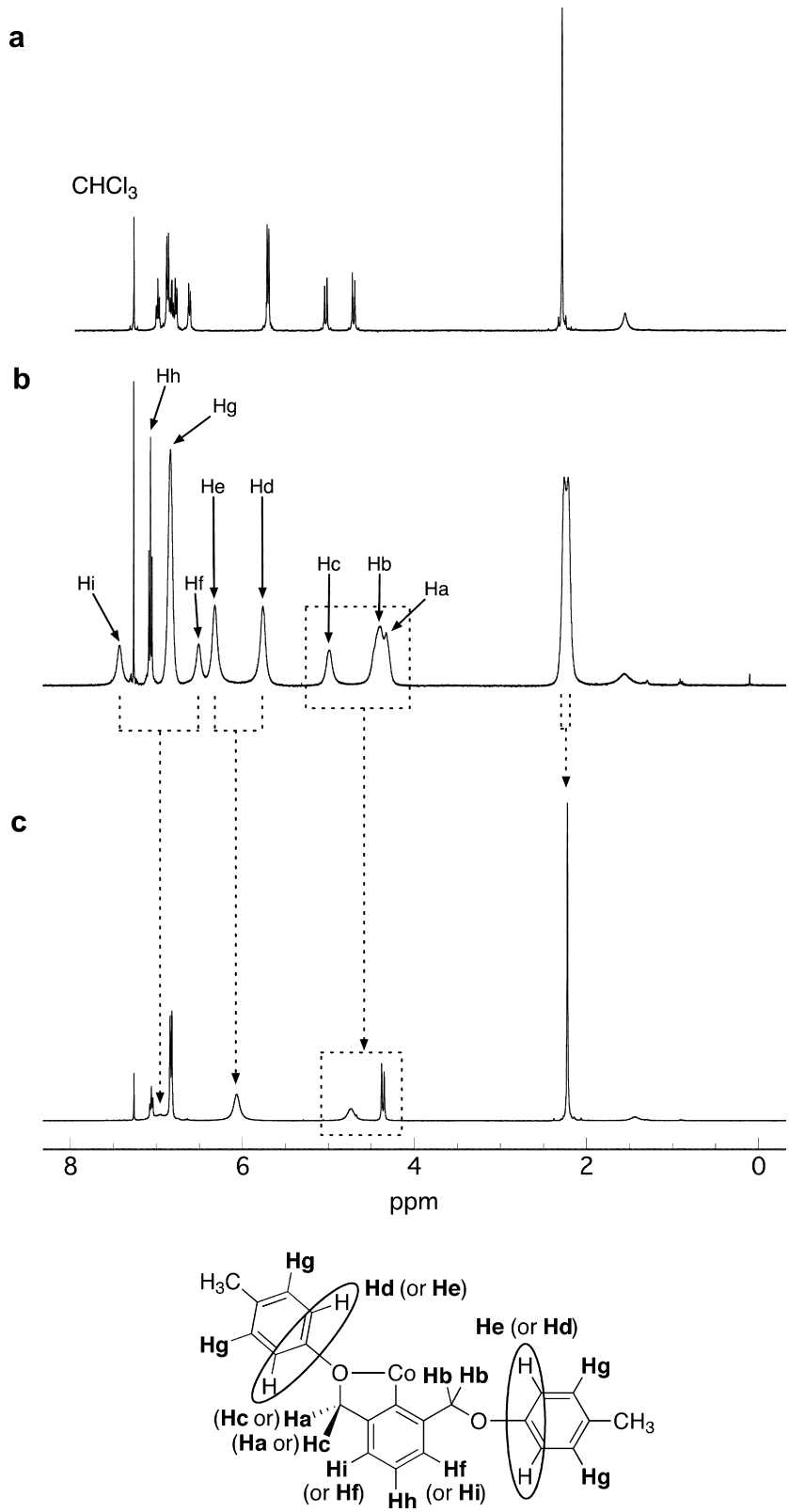
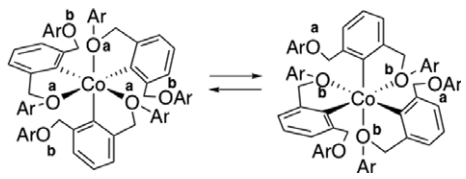


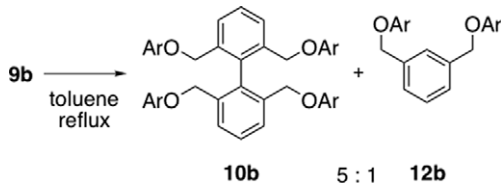
Fig. 4. ^{1}H NMR charts of (a) **9a** at rt, (b) **9b** at rt, and (c) **9b** at 60 °C in $CDCl_3$.

2.4. Reactivity

Compound **9b** was thermally decomposed in refluxing toluene or THF to produce a complex mixture including the dimer of the ligand **10b**, protonated ligand **12b** and undefined black precipitate (Scheme 4). Photoirradiation (313 nm) and reaction with triphenylphosphine or trifluoroacetic acid gave similar results.



Scheme 3. Intramolecular ligand exchange of **9b**.



Scheme 4. Thermal decomposition of **9b**.

3. Conclusion

We presented the first examples of hexacoordinated cobalt(III) complexes bearing *C*,*O*-ligating bidentate ligands. Utilizing the pincer type ligand **8b** as the precursor, the complex **9b** was obtained in 58% yield, whereas the yield of the complex **9a** was very low (19%). The isolated complexes were only *fac*-isomers, and the structures were characterized by single crystal X-ray analyses. Both complexes are stable at rt, and are soluble in chloroalkanes, aromatic solvents and THF. Variable temperature NMR of the compound **9b** clearly indicated the existence of a dynamic ligand exchange process. Some reactions of **9b** mainly resulted in the reductive elimination of the ligand to give the dimer **10b**. Further investigations on the reactivity of these complexes and on application as catalysts are currently under way.

4. Experimental

4.1. General methods

All reactions were performed under N_2. THF was freshly distilled from sodium/benzophenone under an inert atmosphere. Merck silica gel 60 and Merck aluminium oxide 90 active neutral were used for the filtration. Melting points were measured in a sealed capillary using a Yanagimoto micro melting point apparatus. The ^{1}H NMR (400 MHz) spectra were recorded using JEOL EX-400 and AL-400 spectrometers. Chemical shifts (δ) are reported in parts per million from residual $CHCl_3$. The elemental analyses were performed using a Perkin–Elmer 2400 CHN elemental analyzer. Compounds **8a** [10] and **8b** [7e] were prepared by following previously reported procedures.

4.2. Synthesis of *9a*

To a solution of **8a** (831 mg, 3.00 mmol) in THF (60 mL) was dropwise added *n*-BuLi (1.52 M in hexane, 1.92 mL, 3.01 mmol) at −78 °C. After stirring for 1 h at −78 °C, the reaction mixture was transferred to a suspension of $CoCl_2$ (389 mg, 3.00 mmol) in THF (10 mL) at room temperature. The mixture was stirred overnight at room temperature, then filtered through Celite. After removal of the solvents by evaporation, the residue was dissolved in CH_2Cl_2, then filtered through alumina. The solvents were removed by evaporation. The crude mixture, containing **9a** and **10a** (ca. 1:9) was purified by GPC ($ClCH_2CH_2Cl$ eluent, RT = 57.0 min) to afford **9a** as a red solid. Single crystals suitable for an X-ray analysis were obtained from CH_2Cl_2/hexane. Yield of **9a**, 122 mg, 0.188 mmol, 19 %; mp 159–161 °C (decomp); ^{1}H NMR ($CDCl_3$) δ 2.28 (s, 9H), 4.71 (d, 3H, $^2J_{H-H} = 11.2$ Hz), 5.03 (d, 3H, $^2J_{H-H} = 11.2$ Hz), 5.70 (d, 6H, $^3J_{H-H} = 8.0$ Hz), 6.61 (d, 3H, $^3J_{H-H} = 7.6$ Hz), 6.77 (d, 3H, $3J_{H-H} = 8.0$ Hz) 6.82 (t, 3H, $^3J_{H-H} = 7.6$ Hz) 6.87 (d, 6H, $^3J_{H-H} = 8.0$ Hz), 6.98 (t, 3H, $^3J_{H-H} = 7.6$ Hz). Anal. Calc. for $C_{42}H_{39}CoO_3$: C, 77.53; H, 6.04. Found: C, 77.50; H, 6.17%. Compound **10a**: ^{1}H NMR ($CDCl_3$) δ 2.25 (s, 6H), 4.76 (s, 4H), 6.69 (d, 4H, $^3J_{H-H} = 8.2$ Hz), 6.99 (d, 4H, $^3J_{H-H} = 8.2$ Hz), 7.25 (d, 2H, $^3J_{H-H} = 7.2$ Hz), 7.34 (t, 2H,$^3J_{H-H} = 7.2$ Hz), 7.40 (t, 2H,$^3J_{H-H} = 7.2$ Hz), 7.62(d, 2H, $^3J_{H-H} = 7.2$ Hz).

4.3. Synthesis of *9b*

To a solution of **8b** (993 mg, 2.50 mmol) in THF (40 mL) was dropwise added *n*-BuLi (1.52 M in hexane, 1.65 mL, 2.51 mmol) at −78 °C. After stirring for 30 min at −78 °C, the reaction mixture was transferred to a suspension of $CoCl_2$ (328 mg, 2.52 mmol) in THF (15 mL) at room temperature. The mixture was stirred overnight at room temperature, then filtered through Celite. After removal of the solvents by evaporation, the residue was dissolved in CH_2Cl_2, then filtered through silica gel. The solvents were removed by evaporation. The crude mixture was purified by GPC ($ClCH_2CH_2Cl$ eluent, RT = 57.6 min) to afford **9b** as a dark red solid. Single crystals suitable for X-ray analysis were obtained from CH_2Cl_2/hexane. Yield 488 mg, 0.483 mmol, 58%; mp 144–146 °C (decomp); ^{1}H NMR ($CDCl_3$, rt) δ 2.05–2.38 (br, 18H), 4.20–4.55 (br, 9H), 4.86–5.09 (br, 3H), 5.64–5.89 (br, 6H), 6.18–6.42 (br, 6H), 6.42–6.62 (br, 3H), 6.73–6.95 (br, 12H) 7.07 (t, 3H, $^3J_{H-H} = 7.2$ Hz) 7.33–7.55 (br, 3H); ^{1}H NMR ($CDCl_3$, 60 °C) δ 2.22 (s, 18H), 4.37 (d, 6H $^2J_{H-H} = 12.0$ Hz), 4.64–4.84 (br, 6H), 5.93–6.19 (br, 12H), 6.83 (d, 12H, $^3J_{H-H} = 8.0$ Hz), 6.84–7.04 (br, 6H), 7.06 (t, 3H, $^3J_{H-H} = 7.2$ Hz). Anal. Calc. for $C_{66}H_{63}CoO_6$: C, 78.40; H, 6.28. Found: C, 78.50; H, 6.49%. UV–Vis (CH_2Cl_2) λ_{max} ($\log\varepsilon$) 522 (2.76), 408 (2.98), 350–300(sh) (ca. 3.85), 300–240(sh) (ca. 4.56).

4.4. Thermal decomposition of *9b*

A toluene (5 mL) solution of **9b** (51.4 mg, 0.051 mol) was heated at reflux for 6 h. The mixture was filtered through Celite to remove the insoluble precipitate, then

evaporated to dryness. The residue contained **10b** and **12b** (5:1) based on the ^{1}H NMR analysis. Compound **10a**: ^{1}H NMR ($CDCl_3$) δ 2.24 (s, 12H), 4.66 (s, 8H), 6.65 (d, 8H, $^3J_{H-H} = 8.6$ Hz), 6.96 (d, 8H, $^3J_{H-H} = 8.6$ Hz), 7.42 (t, 2H, $^3J_{H-H} = 8.0$ Hz), 7.56 (d, 4H, $^3J_{H-H} = 7.6$ Hz). Compound **12a**: ^{1}H NMR ($CDCl_3$) δ 2.30 (s, 6H), 5.06 (s, 4H), 6.87 (d, 4H, $^3J_{H-H} = 8.6$ Hz), 7.08 (d, 4H, $^3J_{H-H} = 8.6$ Hz), 7.38 (s, 3H), 7.49 (s, 1H).

4.5. Single crystal X-ray analysis of *9a* and *9b*

Crystals suitable for the X-ray structural determination were mounted on a Mac Science DIP2030 imaging plate diffractometer and irradiated with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) for the data collection. The unit cell parameters were determined by separately autoindexing several images in each data set using the DENZO program (Mac Science) [11]. For each data set, the rotation images were collected in 3° increments with a total rotation of 180° about the ϕ axis. The data were processed using SCALEPACK. The structure was solved by a direct method with the SHELX-97 program [12]. Refinement on F^2 was carried out using full-matrix least-squares using the SHELX-97 program [12]. All non-hydrogen atoms were refined using anisotropic thermal parameters. The hydrogen atoms were included in the refinement along with the isotropic thermal parameters. The crystallographic data are summarized in Table 2.

Table 2
Crystallographic data for **9a** and **9b**

	9a	**9b**
Formula	$C_{42}H_{39}CoO_3$	$C_{66}H_{63}CoO_6$
Molecular weight	650.66	1011.09
Crystal system	Orthorhombic	Monoclinic
Space group	*Pna*2$_1$	*Pn*
Color	Red	Dark red
Habit	Plate	Plate
Crystal dimension (mm)	0.20, 0.15, 0.15	0.20, 0.15, 0.15
a (Å)	10.9770(2)	15.9380(3)
b (Å)	14.7690(4)	10.4220(2)
c (Å)	21.2650(3)	16.1940(3)
α (°)	90	90
β (°)	90	105.1420(10)
γ (°)	90	90
V (Å^3)	3447.47(12)	2596.53(8)
Z	4	2
D_{calc} (g cm^{-3})	1.562	1.293
Absolute coefficient (mm^{-1})	0.535	0.385
F(000)	1368	1068
Radiation: λ (Å)	Mo Kα, 0.71073	Mo Kα, 0.71073
Temperature (°C)	23	−78
Data collected	$+h, +k, +l$	$+h, +k, \pm l$
Reflections collected	3993	6187
Independent reflections	3993	6187
Number of parameters refined	418	664
$R_1(I > 2\sigma(I))$	0.0602	0.0384
wR_2 (all data)	0.2003	0.1351
Goodness-of-fit	1.142	1.235
Maximum shift in final cycle	0.001	0.001
Final diff map, max (e/Å)	0.548	0.490

5. Supplementary material

CCDC 609210 and 609211 contain the supplementary crystallographic data for **9a** and **9b**. The data can be obtained free of charge via htpp://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +(44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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