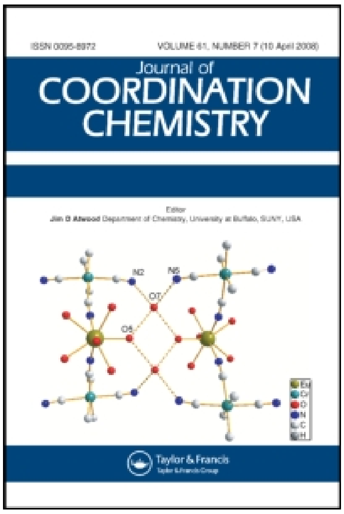

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SYNTHESIS OF HIGHER-NUCLEARITY CLUSTERS BY ASSEMBLING THE -$CCo_3(CO)_9$ UNITS INTO AROMATIC SPACER MOLECULES

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SYNTHESIS OF HIGHER-NUCLEARITY CLUSTERS BY ASSEMBLING THE -$CCo_3(CO)_9$ UNITS INTO AROMATIC SPACER MOLECULES

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p-$[(OC)_9Co_3C]_2C_6H_4$ (**1**) has been synthesized by reacting $Co_2(CO)_8$ with p-$(Cl_3C)_2C_6H_4$. 4,4'-$[(OC)_9Co_3CC(O)]C_6H_4$-$C_6H_4[C(O)CCo_3(CO)_9]$ (**2**) has been synthesized from p-LiC_6H_4-C_6H_4Li and $BrCCo_3(CO)_9$. Similarly m-$[(OC)_9Co_3CC(O)CH_2]_2C_6H_4$ (**3**) has been synthesized from m-$(LiCH_2)_2C_6H_4$ and $BrCCo_3(CO)_9$. X-ray analysis was done for **1** and **2**; both compounds exhibit a stacked structure. Cyclic voltammetry and UV spectra revealed usual behavior for **1**, that is, two cluster units interact strongly through the benzene spacer, which is not the case for clusters **2** and **3**.

KEYWORDS: higher-nuclearity cluster, methylidynetricobalt nano-carbonyl, organic spacer, X-ray structures, interaction between clusters

INTRODUCTION

Transition-metal cluster chemistry has developed in many facets such as catalysts, multi-redox agents, and electronic and optical devices.[1–3] Novel higher-nuclearity clusters have been synthesized serendipitiously by a variety of methods including pyrolysis of small clusters or redox condensation of mononuclear transition metal complexes with an appropriate ligand such as a phosphine.[4–6] However, it is quite difficult to know in advance what will be produced by these traditional methods; unexpected higher-nuclearity clusters are sometimes formed by these methods. We, therefore, have been interested in the construction of higher-nuclearity clusters in a fashion of molecular design by use of the -$CCo_3(CO)_9$ unit as a prospective building block, targeting synthesis of nanometer-size clusters because of their potential application in nanotechnology. By sizing clusters to nanometer-scale, it is expected that exotic properties such as electronic, magnetic or optical characteristics which are not observed in smaller clusters should emerge.[7–9] Our choice of this unit as a building block is as follows; first, $RCCo_3(CO)_9$ is generally stable in air. Second, electrons are delocalized onto the whole molecule and thus $RCCo_3(CO)_9$ is regarded as an electron sink; this feature is important to produce higher-nuclearity clusters

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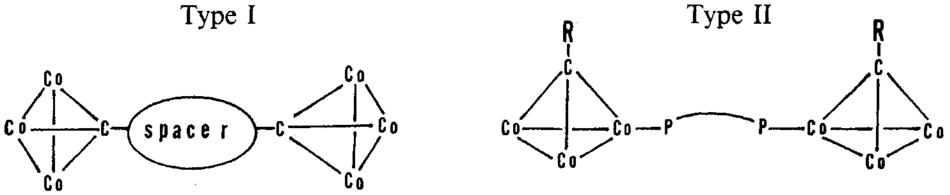
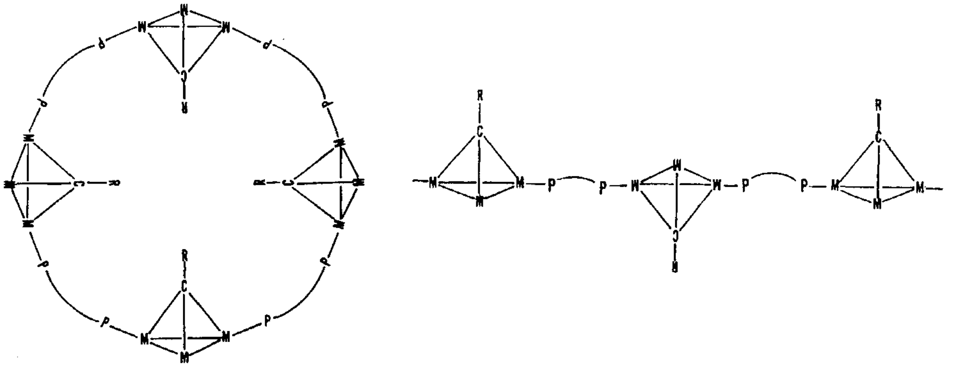


Type I

Type II

Scheme 1



Scheme 2

with long-range electron transfer potential. Third, two positions are available to link $RCCo_3(CO)_9$ units, that is the apical C (type I higher-nuclearity cluster) and the basal Co (type II higher-nuclearity cluster, Scheme 1). Fourth, a variety of substituents can be introduced onto the apical carbon atom.[10] Thus, the apical substituents offer the sphere which will be adequate for effective molecular recognition if these units are linked in an appropriate arrangement (Scheme 2).

In a previous communication, we reported the synthesis and X-ray molecular structure analysis for p-$[(OC)_9Co_3C]_2C_6H_4$ (type I) and $[MeCCo_3(CO)_8]_2(\mu$-dppfe) (type II).[11] We now focus our attention on the synthesis of $[(OC)_9Co_3C]\cdot$ Ar$\cdot[CCo_3(CO)_9]$ compounds where Ar denotes an aromatic spacer molecule. The present paper reports the detailed procedure for the synthesis and some spectroscopic and electrochemical data for these new clusters.

EXPERIMENTAL

Materials and General Procedures

All manipulations were made under a nitrogen and/or argon atmosphere. p-$(Cl_3C)_2C_6H_4$, p-$[BrC_6H_4]_2$, and m-$(H_3C)_2C_6H_4$ were purchased from Aldrich. $Co_2(CO)_8$ was purchased from Strem Chemicals. m-$(BrH_2C)_2C_6H_4$ was synthesized from m-$(H_3C)_2C_6H_4$ by the literature method.[12]

Syntheses. p-$[(OC)_9Co_3C]_2C_6H_4$ *(1)*

A THF solution (70 mL) containing $Co_2(CO)_8$ (7.283 g, 21.54 mmol) was heated at 50°C for 30 min. Then, a THF solution(20 mL) containing p-$(Cl_3C)_2C_6H_4$ (3.385 g, 11.28 mmol) was added slowly to this solution and the dark brown mixture was stirred at this temperature for 1.5 h. After gas evolution ceased, the mixture was stirred at 50°C for an additional hour. The solvent was vacuum-stripped and the resulting dark-brown solid was suspended into 100 mL of dichloromethane. Then 10% hydrochloric acid (200 mL) was added and the mixture was stirred for 0.5 h. The resulting dark purple-brown precipitate was collected on a frit, washed with 20 mL of dichloromethane several times, and vacuum-dried to yield a brown solid with a metallic sheen. Yield 800 mg. **1** is slightly soluble in THF, CH_2Cl_2, and $CHCl_3$. *Anal.* Calcd. for $C_{26}H_4Co_6O_{18}$ (%): C, 32.60; H, 0.42. Found: C, 32.72; H, 0.53. IR (ν(CO))(THF): 2102(m), 2060(vs), 2040(s) cm^{-1}. ^1H-NMR($CDCl_3$):δ 7.36 (s, 4H, aromatic). ^{13}C-NMR($CDCl_3$):δ 129.8 (aromatic), 181.4 (carbonyl).

4,4'-$[(OC)_9Co_3CC(O)]C_6H_4$-$C_6H_4[C(O)CCo_3(CO)_9](2)$

A hexane solution which contains 1.1 mmol of n-BuLi was added to THF (8 mL) and the mixture was cooled to −90°C. To this was added a THF solution (2 mL) of 4,4'-dibromobiphenyl (156 mg, 0.5 mmol) with stirring during 3 min. to afford a white turbid solution. The solution was stirred at −78°C for an additional 2.5 h. Then the solution was cooled to −90°C and a THF solution (3 mL) containing 521 mg (1 mmol) of $BrCCo_3(CO)_9$ was added with stirring. The resulting green-brown solution was stirred at −78°C for 1.5 h, at −50°C for 1.5 h, and then warmed gradually to room temperature with stirring. The brown solution was poured into ice-cooled hydrochloric acid (10%). The organic layer was extracted with 20 mL of benzene three times and the combined extracts were dried over anhydrous magnesium sulfate. After filtration, benzene was distilled off at reduced pressure and the brown residue was purified by column chromatography (Wako-gel C-200). The brown band was eluted with benzene and the solvent was vacuum-stripped to afford dark brown product. Yield 95 mg. IR(ν(CO))(benzene): 2114(m), 2066(vs), 2048(s), 1600 (m, br) cm^{-1}. SIMS MS:m/z = 1089.8, $[M-H]^+$. ^{13}C-NMR: δ 206.0(-C(O)), 198.6(CO), 138.7(Ph_{C-4}), 128.3-(Ph_{C-3}), 127.1(Ph_{C-2}), and 143.1(Ph_{C-1}).

m-$[(OC)_9Co_3CC(O)CH_2]_2C_6H_4$ *(3)*

A THF solution (15 mL) containing 1.04 g (2.0 mmol) of $BrCCo_3(CO)_9$ was cooled to −90°C. To this was added a hexane solution containing 2.1 mmol of n-BuLi and the resulting green-brown solution was stirred at −90°C for 1 h. Then a THF solution (3 mL) in which 264 mg (1.0 mmol) of m-$(BrCH_2)_2C_6H_4$ was dissolved was added slowly and the mixture was stirred at −78°C for 0.5 h and at −50°C for 0.5 h. Then the temperature was gradually raised to room temperature. The resulting brown solution was poured into ice-cooled 10% hydrochloric acid. The organic layer was extracted with 20 mL of benzene two times. The combined extracts were washed with 50 mL of water and the organic layer was dried over anhydrous magnesium sulfate. After filtration benzene was distilled off at reduced pressure to afford brown powder. This crude product was dissolved into a minimum amount of benzene and loaded on a silica-gel column (Wako-gel C-200). A brown band eluted with hexane-benzene (1:1) was collected and the solvents were distilled off at reduced pressure to give brown microcrystalline product. Yield 50 mg. IR(ν(CO))(KBr): 2116(m), 2080(sh), 2070(sh), 2060(vs), 2045(s), 2030(s), 2020(sh), 1640(m) (-C(O)) cm^{-1}. ^1H-NMR ($CDCl_3$):δ 4.27 (d, J = 19Hz, 4H, benzylic), 7.25(s, 4H, aromatic). ^{13}C-NMR ($CDCl_3$): δ 138.2($Ph_{C\text{-}1,C\text{-}3}$), 129.7($Ph_{C\text{-}2}$), 129.1($Ph_{C\text{-}5}$), 127.8($Ph_{C\text{-}6}$), 33.2 (benzylic), 198.4 (CO), 209.5(-C(O)). SIMS-MS: m/z = 1040 $[M-H]^+$.

Spectral Measurements

^1H and ^{13}C-NMR spectra were measured with a Varian XL-200 spectrometer in the Fourier-transform mode. The IR spectra were recorded on a JASCO 701G and/or JASCO Valor-III FT-IR spectrometer. UV-vis spectra were measured by use of a Hitachi 220A spectrometer.

Electrochemical Measurements

Cyclic voltammetry was done at 20°C with a BAS CV-50W electrochemical analyzer equipped with a platinum plate electrode for the working electrode and a platinum coil for the auxiliary electrode. A $Ag/AgNO_3$ (0.01M) electrode was employed as the reference electrode with 0.1 M $n\text{-}Bu_4NClO_4$ (TBAP) in CH_2Cl_2 (1 M = 1 $moldm^{-3}$). Approximately a 10^{-3} M solution for each sample was prepared in CH_2Cl_2 which contained 0.1 M TBAP as a supporting electrolyte. A sweep rate of 200 mV/s was generally used for CV. All of the manipulations were carried out under an argon atmosphere. The electrochemical data are tabulated in Table 1.

X-Ray Data Collection and Structure Determination

Purple-brown single crystals of **1** were grown from a hot THF solution and a crystal with approximate dimensions of 0.60×0.13×0.02 mm^3 was mounted on a MAC MXC^3 diffractometer equipped with graphite monochromated Mo Kα radiation (λ = 0.71073Å). Diffraction data were collected at ambient temperature. For **2**, dark brown crystals were grown from hexane-dichloromethane and a crystal with approximate dimensions of 0.50×0.15×0.05 mm^3 was mounted on the same diffractometer. However, diffraction data were collected at −120°C by use of an Oxford Cryostream Cooler to improve the data because the crystal of **2** was of

Table 1 Voltammetric data[a]

Compound	Reduction			
	E_{pc}[b]	E_{pa}[c]	$E_{1/2}$[d]	ΔE[e]
p-$[(OC)_9Co_3C]_2C_6H_4$ (**1**)	−0.96	−0.90	−0.93	
	−1.10	−1.04	−1.07	140[f]
4,4'-$[(OC)_9Co_3CC(O)C_6H_4]_2$ (**2**)	−0.90	−0.77	−0.84	130
m-$[(OC)_9Co_3CC(O)CH_2]_2C_6H_4$ (**3**)	−0.90	−0.80	−0.85	100

[a] a platinum electrode (Ag/Ag^+ standard) with 0.1 M TBAP at 25 °C in 200 mV scan rate. [b] E_{pc} = cathodic peak potential (V). [c] E_{pa} = anodic peak potential (V) [d] $E_{1/2}$ = half-wave potential (V). [e] = peak separation between anodic and cathodic peak potential (mV). [f] peak separation between two $E_{1/2}$ peak potential (mV).

rather poor quality. The crystal data for **1** and **2** are given in Table 2. The structures were solved by a direct method (MULTAN 78 and/or SHELXS 86) and refined by a full-matrix least-squares method on a Sun SPARK2 and/or SP/Classic work station with a Crystan program package provided by MAC Science. Refinements in **1** were made anisotropically for non-hydrogen atoms and isotropically for hydrogen atoms. Refinements for **2** were made anisotropically for non-hydrogen atoms. The molecular structures of **1** and **2** are shown in Fig. 1. The atomic coordinates are listed in Table 3, and selected bond lengths and angles are given in Table 4. The $|F_O|-|F_C|$ tables and anisotropic temperature factor tables are available from the authors.

RESULTS AND DISCUSSION

The most important synthons for the synthesis of $RCCo_3(CO)_9$ are trihalogeno derivatives, RCX_3.[13] However, the reaction of p-$(CCl_3)_2C_6H_4$ with $[Co(CO)_4]^-$ was reported to afford a monocluster derivative, p-$[(OC)_9Co_3C]C_6H_4CHO$ instead of the di-cluster derivative, p-$[(OC)_9Co_3C]_2C_6H_4$.[13] We have reexamined this reaction and found that p-$[(OC)_9Co_3C]_2C_6H_4$ can be synthesized by this method. This product is, however, sparingly soluble in ordinary organic solvents contrary to

Table 2 Crystal data

Compound	p-$[(OC)_9Co_3C]_2C_6H_4$ (**1**)	4,4'-$[(OC)_9Co_3CC(O)]C_6H_4$-C_6H_4 $[C(O)CCo_3(CO)_9]$ (**2**)
Formula	$C_{26}H_4Co_6O_{18}$	$C_{34}H_8Co_6O_{20}$
Formula weight	957.9	1090.0
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	8.680(1)	14.286(7)
b/Å	12.968(2)	16.061(9)
c/Å	7.918(1)	8.939(4)
α/deg	97.81(1)	93.33(4)
β/deg	111.92(2)	91.46(4)
γ/deg	78.89(1)	109.41(4)
V/Å^3	809.6(3)	1929(2)
Z	1	2
d_{calcd}/gcm^{-3}	1.641	1.877
Crystal dimens/mm^3	0.60x0.13x0.02	0.50x0.15x0.05
μ(Mo Kα)/cm^{-1}	16.27	14.4
Scan type	ω-2θ	ω
Scan range/deg	1.38 + 0.35tanθ	1.94 + 0.35tanθ
Scan speed/degmin^{-1}	3	5
$2\theta_{max}$/deg	55	45
Temperature (K)	298	153
Unique reflections	3141	3560
Reflections with $|F_o| > 3\sigma(|F_o|)$	2781	2740
No. of parameters refined	233	547
R	0.0523	0.0944
R_w	0.0348	0.104

Mo Kα radiation (λ = 0.71073 A); $R = \Sigma\||F_o|-|Fc|\| / |F_o|$; $Rw = [\Sigma w(|F_o|-|F_c|)^2/\Sigma\, w(Fo)^2]^{1/2}$ where $w = 1/\sigma^2(F)$.

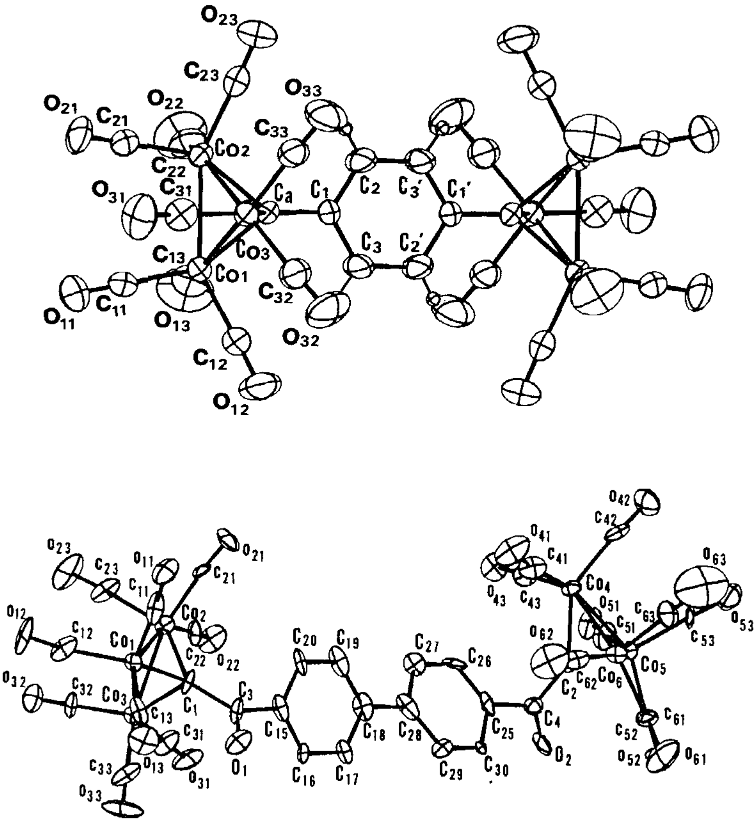


Figure 1 Molecular structures of P-[$(OC)_9Co_3C]_2C_6H_4$ (1) (top) and 4,4'-[$(OC)_9Co_3CC(O)]C_6H_4$-$C_6H_4[C(O)CCo_3(CO)_9]$ (2) (bottom).

congeneric $RCCo_3(CO)_9$ derivatives. This product may have been over-looked previously because of its low solubility.[14] In the case of the biphenyl spacer, an effective synthetic route to bis-CCl_3 substituted derivatives, $(Cl_3C)_2 \cdot Ar$ is not available from the literature to the best of our knowledge and therefore the reaction between $BrCCo_3(CO)_9$ and bis-lithiated aromatics has been examined. Thus, 4,4'-[$(OC)_9Co_3CC(O)]C_6H_4$-C_6H_4-[C(O)C-$Co_3(CO)_9$] (2) has been successfully synthesized as is demonstrated in Fig. 1.[15] In the reaction of $BrCCo_3(CO)_9$ with ROH and/or R_2NH, similar carbonyl insertion was observed[16] and it was suggested that CO migrates from the Co atom. Carbonyl insertion has also been observed in other reactions of $RCCo_3(CO)_9$ with various substrates.[17] Therefore, we suppose that a similar mechanism of CO migration is operative in the present synthesis and two ketone groups are incorporated from the CO groups on the starting cobalt cluster. In the reaction of m-$(LiCH_2)_2C_6H_4$ with $BrCCo_3$-$(CO)_9$, the product with two cluster units, **3**, has been synthesized. The IR band at 1640 cm^{-1} strongly suggests that similar CO insertion has resulted. ^1H- and ^{13}C-NMR spectra and SIMS-MS data have confirmed the synthesis and structure. Similar CO insertion is observed

Table 3 Atomic coordinates and isotropic thermal parameters, $B_{eq}(\text{Å}^2)$ p-$[(OC)_9Co_3C]_2C_6H_4$ **(1)** **4,4'**-$[(OC)_9Co_3CC(O)]C_6H_4$-$C_6H_4[C(O)CCo_3(CO)_9]$ **(2)**

atom	*x*	*y*	*z*	B(eq)
Co1	-0.05921(9)	0.26837(6)	0.3912(1)	2.66(2)
Co2	-0.34725(9)	0.24027(6)	0.1924(1)	2.83(2)
Co3	-0.18266(9)	0.33149(6)	0.0807(1)	2.69(2)
C a	-0.1370(6)	0.1915(4)	0.1590(7)	2.5(2)
C 1	-0.0687(6)	0.0940(4)	0.0807(7)	2.5(2)
C 2	-0.1657(7)	0.0334(6)	-0.056(1)	5.4(2)
C 3	0.1008(8)	0.0571(6)	0.136(1)	5.8(3)
C 11	-0.1068(7)	0.3855(5)	0.5249(8)	3.6(2)
C 12	0.1546(8)	0.2748(5)	0.4201(8)	4.0(2)
C 13	-0.0122(8)	0.1680(5)	0.5448(9)	4.6(2)
C 21	-0.4649(7)	0.3573(5)	0.2706(8)	3.5(2)
C 22	-0.3622(8)	0.1378(5)	0.312(1)	4.8(2)
C 23	-0.5041(8)	0.2056(5)	-0.0222(9)	4.1(2)
C 31	-0.2587(7)	0.4676(5)	0.1361(8)	3.8(2)
C 32	0.0076(8)	0.3401(5)	0.0480(8)	4.3(2)
C 33	-0.3002(6)	0.3101(5)	-0.1543(8)	3.9(2)
0 11	-0.1359(5)	0.4602(3)	0.6099(6)	5.9(2)
O 12	0.2888(5)	0.2769(4)	0.4388(6)	6.5(2)
O 13	0.0228(7)	0.1038(4)	0.6419(7)	8.5(2)
O 21	-0.5360(5)	0.4320(3)	0.3137(6)	5.6(2)
O 22	-0.3760(7)	0.0721(4)	0.3838(8)	8.8(2)
O 23	-0.6038(5)	0.1836(4)	-0.1536(6)	6.4(2)
O 31	-0.3063(6)	0.5518(3)	0.1737(6)	6.2(2)
O 32	0.1252(6)	0.3439(4)	0.0206(7)	8.0(2)
O 33	-0.3681(6)	0.2948(4)	-0.3065(6)	6.8(2)
H 2	-0.266(9)	0.056(6)	-0.10(1)	5.54(0)
H 3	0.160(9)	0.092(6)	0.23(1)	5.91(0)
Co1	-0.3991(2)	-0.2525(2)	0.4298(3)	1.8(1)
Co2	-0.4735(2)	-0.2436(2)	0.1815(3)	1.9(1)
Co3	-0.3579(2)	-0.3277(2)	0.2048(3)	2.0(1)
Co4	0.2525(2)	-0.2673(2)	-0.2341(3)	1.8(1)
Co5	0.1221(2)	-0.3020(2)	-0.0496(3)	1.6(1)
Co6	0.0760(2)	-0.3439(2)	-0.3189(3)	1.9(1)
C 1	-0.338(2)	-0.206(1)	0.255(2)	1.5(7)
C 2	0.140(2)	-0.228(1)	-0.213(2)	1.2(6)
C 3	-0.240(2)	-0.137(1)	0.228(2)	1.2(6)
C 4	0.106(1)	-0.155(1)	-0.239(2)	1.0(6)
O 1	-0.168(1)	-0.124(1)	0.318(2)	2.8(5)
O 2	-0.051(1)	0.134(1)	-0.846(2)	2.9(6)
C 15	-0.224(2)	-0.093(2)	0.086(2)	2.3(8)
C 16	-0.138(2)	-0.090(1)	0.007(2)	1.2(6)
C 17	-0.120(2)	-0.047(1)	-0.128(2)	1.4(6)
C 18	-0.187(2)	-0.013(1)	-0.196(2)	1.7(7)
C 19	-0.272(2)	-0.018(1)	-0.113(2)	1.8(7)
C 20	-0.289(2)	-0.055(1)	0.021(2)	1.9(7)
C 25	-0.133(2)	0.108(1)	-0.616(2)	2.4(8)
C 26	-0.228(2)	0.076(2)	-0.569(3)	2.5(8)
C 27	-0.246(2)	0.038(1)	-0.429(2)	1.7(7)
C 28	-0.166(2)	0.031(1)	-0.341(2)	2.4(8)
C 29	-0.067(2)	0.065(1)	-0.389(2)	1.8(7)
C 30	-0.051(1)	0.100(1)	-0.529(2)	1.2(6)
C 11	-0.441(2)	-0.170(2)	0.526(2)	2.2(8)
C 12	-0.489(2)	-0.356(2)	0.494(3)	3.3(9)
C 13	-0.288(2)	-0.232(1)	0.553(2)	1.8(8)

Table 3 (Continued)

C 21	-0.508(2)	-0.144(2)	0.228(2)	2.0(7)
C 22	-0.467(2)	-0.242(2)	-0.021(3)	2.2(8)
C 23	-0.595(2)	-0.332(2)	0.197(2)	2.4(8)
C 31	-0.311(2)	-0.325(2)	0.022(3)	3.1(9)
C 32	-0.450(2)	-0.438(2)	0.195(3)	2.2(8)
C 33	-0.249(2)	-0.341(2)	0.303(3)	3.4(9)
C 41	0.290(2)	-0.254(2)	-0.430(3)	2.3(8)
C 42	0.297(2)	-0.360(2)	-0.187(3)	2.6(8)
C 43	0.345(2)	-0.170(2)	-0.151(3)	1.9(7)
C 51	0.203(2)	-0.229(2)	0.093(3)	3.2(9)
C 52	0.007(2)	-0.290(2)	0.022(2)	1.8(7)
C 53	0.119(1)	-0.408(1)	0.012(3)	1.9(7)
C 61	-0.057(2)	-0.367(1)	-0.296(2)	1.7(7)
C 62	0.075(2)	-0.316(2)	-0.514(3)	2.4(8)
C 63	0.079(2)	-0.454(2)	-0.331(3)	4(1)
O 11	-0.474(1)	-0.122(1)	0.586(2)	3.4(6)
O 12	-0.548(1)	-0.413(1)	0.535(2)	4.4(7)
O 13	-0.219(1)	-0.217(1)	0.630(2)	3.9(6)
O 21	-0.520(1)	-0.079(1)	0.255(2)	3.3(6)
O 22	-0.463(1)	-0.245(1)	-0.148(2)	3.7(6)
O 23	-0.666(1)	-0.389(1)	0.207(2)	4.6(7)
O 31	-0.284(1)	-0.324(1)	-0.100(2)	4.0(6)
O 32	-0.508(1)	-0.508(1)	0.183(2)	3.4(6)
O 33	-0.183(2)	-0.346(1)	0.364(2)	6.0(8)
O 41	0.318(1)	-0.251(1)	-0.543(2)	4.4(7)
O 42	0.318(1)	-0.418(1)	-0.161(2)	4.1(7)
O 43	0.404(1)	-0.105(1)	-0.097(2)	3.1(6)
O 51	0.260(1)	-0.185(1)	0.185(2)	3.3(6)
O 52	-0.063(1)	-0.285(1)	0.065(2)	4.4(7)
O 53	0.114(1)	-0.475(1)	0.058(2)	4.1(6)
O 61	-0.138(1)	-0.380(1)	-0.291(2)	4.4(7)
O 62	0.078(2)	-0.299(2)	-0.636(2)	5.9(9)
O 63	0.084(2)	-0.523(1)	-0.326(3)	7.5(9)

in the reactions of 1-$LiC_{10}H_7$ and 1,5-$Li_2C_{10}H_6$ with $BrCCo_3(CO)_9$ in THF; a ν(CO) peak appears at around 1620 cm^{-1} for each product.[18]

The results from the structural analysis for **1** and **2** (Fig. 1) have shown the center of inversion is positioned at the center of the benzene ring for **1** and the twist angle of the two benzene rings in **2** is rather smaller (23.0°) and thus the molecule **2** does not have a center of inversion. In Table 4, important bond lengths and angles are compared for **1** and **2**. As seen from this table, the Co-Co, Co-C_a, and the C-C (in the phenyl group) bond-lengths in **1** are considerably longer than those in **2**. This issue will be discussed later. Figure 2 shows the molecular packing in each crystal; **1** is stacked along the *a* axis (*a* = 8.680 Å) and **2** is stacked along the *c* axis (c = 8.939 Å). This finding suggests some interaction among the higher-nuclearity Co_6 clusters in the crystals of **1** and **2**.

One of our objectives for the present study is to synthesize higher-nuclearity clusters which possess some interaction between two $CCo_3(CO)_9$ units through the spacer molecule. The absorption spectrum of **1** (Fig. 3) is quite interesting; the absorption around 500 nm for $RCCo_3(C)_9$, which is assigned to $\sigma\ (Co_3) \rightarrow a_2$ transition[19], shifts to shorter wave length and splits into two peaks (440 and 460 nm) with enhanced molar absorption coefficients (about 10 times greater than those

Table 4 Selected interatomic distances(Å) and angles (deg).

p-$[(OC)_9Co_3C]_2C_6H_4$(**1**)			
Bond-length			
Co1-Co3	2.471(1)	C1-C2	1.356(8)
Co1-Co2	2.474(1)	C1-C3	1.374(8)
Co2-Co3	2.470(1)	C2-C3	1.38(1)
Co1-Ca	1.914(5)	C11-O11	1.144(7)
Co2-Ca	1.916(5)	C12-O12	1.124(8)
Co3-Ca	1.919(5)	C13-O13	1.131(9)
Co1-C11	1.802(6)	C21-O21	1.127(7)
Co1-C12	1.800(7)	C22-O22	1.13(1)
Co1-C13	1.788(7)	C23-O23	1.121(7)
Co2-C21	1.830(6)	C31-O31	1.131(7)
Co2-C22	1.784(8)	C32-O32	1.13(1)
Co2-C23	1.801(5)	C33-O33	1.136(7)
Co3-C31	1.817(6)	C2-H2	0.82(7)
Co3-C32	1.789(7)	C3-H3	0.86(6)
Co3-C33	1.770(6)		
Ca-C1	1.451(7)		
Bond-angle			
Co3-Co1-Co2	59.95(3)	Co2-Co3-Co1	60.08(3)
Co3-Co2-Co1	59.97(3)	C2-Ca-C3	55.4(2)
C13-Co1-C12	96.8(3)	C21-Co2-Ca	141.5(2)
C13-Co1-C11	102.1(3)	C33-Co3-C32	95.0(3)
C13-Co1-Ca	101.7(2)	C33-Co3-C31	103.9(2)
C12-Co1-C11	101.0(3)	C33-Co3-Ca	100.9(2)
C12-Co1-Ca	102.4(2)	C32-Co3-C31	103.1(3)
C11-Co1-Ca	144.1(2)	C32-Co3-Ca	101.7(3)
C22-Co2-C23	95.9(3)	C31-Co3-Ca	142.9(3)
C22-Co2-C21	103.6(3)	Co1-Ca-Co2	80.4(2)
C22-Co2-Ca	102.2(3)	Co1-Ca-Co3	80.3(2)
C23-Co2-C21	100.4(2)	Co2-Ca-Co3	80.2(2)
C23-Co2-Ca	104.8(3)		
C13-Co1-C12	96.8(3)	C1-C2-C3	123.2(5)
C13-Co1-C11	102.1(3)	O11-C11-Co1	179.5(5)
C12-Co1-C11	101.0(3)	O12-C12-Co1	178.7(6)
C22-Co2-C23	95.9(3)	O13-C13-Co1	177.7(6)
C22-Co2-C21	103.6(3)	O21-C21-Co2	176.9(6)
C23-Co2-C21	100.4(2)	O22-C22-Co2	177.8(6)
C33-Co3-C32	95.0(3)	O23-C23-Co2	178.4(8)
C33-Co3-C31	103.9(2)	O31-C31-Co3	178.6(6)
C32-Co3-C31	103.1(3)	O32-C32-Co3	177.3(6)
C2-C1-Ca	123.0(5)	O33-C33-Co3	176.5(6)
C2-C1-C3	114.5(5)	C3-C1-Ca	122.4(5)
4,4'-$[(OC)_9Co_3CC(O)]C_6H_4$-$C_6H_4[C(O)CCo_3(CO)_9]$(**2**)			
Bond-length			
Co1-Co2	2.455(4)	Co6-C61	1.82(2)
Co1-Co3	2.459(4)	Co6-C62	1.82(3)
Co2-Co3	2.458(5)	Co6-C63	1.76(3)
Co4-Co5	2.456(4)	C11-O11	1.14(4)
Co4-Co6	2.468(4)	C12-O12	1.10(3)
Co5-Co6	2.459(4)	C13-O13	1.12(3)
Co1-C1	1.87(2)	C21-O21	1.13(3)
Co2-C1	1.90(2)	C22-O22	1.13(3)
Co3-C1	1.90(2)	C23-O23	1.12(3)

Table 4 (Continued)

4,4'-[$(OC)_9Co_3CC(O)$]C_6H_4-C_6H_4[$C(O)CCo_3(CO)_9$](4)			
Bond-length			
Co4-C2	1.91(2)	C31-O31	1.16(3)
Co5-C2	1.90(2)	C32-O32	1.14(3)
Co6-C2	1.94(2)	C33-O33	1.10(3)
C1-C3	1.49(3)	C41-O41	1.08(3)
C2-C4	1.44(3)	C42-O42	1.10(4)
C3-C15	1.48(3)	C43-O43	1.17(2)
C4-C25	1.52(3)	C51-O51	1.15(3)
C3-O1	1.24(3)	C52-O52	1.10(3)
C4-O2	1.21(3)	C53-O53	1.14(3)
C18-C28	1.50(3)	C61-O61	1.11(3)
Co1-C11	1.80(3)	C62-O62	1.14(3)
Co1-C13	1.83(3)	C15-C16	1.40(3)
Co2-C21	1.83(3)	C15-C20	1.39(4)
Co2-C22	1.81(2)	C16-C17	1.40(3)
Co2-C23	1.85(2)	C17-C18	1.39(4)
Co3-C31	1.77(2)	C18-C19	1.41(3)
Co3-C32	1.81(2)	C19-C20	1.36(3)
Co3-C33	1.83(3)	C25-C26	1.36(3)
Co4-C41	1.85(3)	C25-C30	1.42(3)
Co4-C42	1.86(3)	C26-C27	1.42(3)
Co4-C43	1.77(2)	C27-C28	1.39(4)
Co5-C51	1.78(2)	C28-C29	1.41(3)
Co5-C52	1.84(3)	C29-C30	1.39(3)
Co5-C53	1.81(2)		
Bond-angle			
Co1-Co2-Co3	60.1(1)	C3-C1-Co1	133(1)
Co2-Co3-Co1	59.9(1)	C3-C1-Co2	139(2)
Co3-Co1-Co2	60.0(1)	C3-C1-Co3	119(2)
Co4-Co5-Co6	60.3(1)	C4-C2-Co4	142(1)
Co5-Co6-Co4	59.8(1)	C4-C2-C5	131(2)
Co6-Co4-Co5	59.9(1)	C4-C2-Co6	121(1)
Co1-C1-Co2	81.3(8)	C1-Co1-C11	108(1)
Co1-C2-Co3	81.4(8)	C1-Co1-C12	141(1)
Co2-C1-Co3	80.8(7)	C1-Co1-C13	99(1)
Co4-C2-Co5	80(1)	C1-Co2-C21	102(1)
Co4-C2-Co6	79.7(9)	C1-Co2-C22	102(1)
Co5-C2-Co6	79.8(8)	C1-Co2-C23	142(1)
C1-C3-C15	121(2)	C1-Co3-C31	102(1)
C2-C4-C25	118(2)	C1-Co3-C32	143(1)
C1-C3-O1	120(2)	C1-Co3-C33	102(1)
C2-C4-O2	121(2)	C2-Co4-C41	108(1)
O1-C3-C15	119(2)	C2-Co4-C42	141.3(9)
O2-C4-C25	120(2)	C2-Co4-C43	98(1)
C2-Co5-C51	102(1)	C2-Co5-C52	99(1)
C2-Co5-C53	146(1)	C2-Co6-C61	104(1)
C2-Co6-C62	102.1(9)	C2-Co6-C63	142(1)

of $PhCCo_3(CO)_9$, **2**, and **3**). Cyclic voltammograms (Fig. 4) demonstrate another unusual behavior of **1**; two *quasi*-reversible reduction peaks are observed around −1.0 V (Ag/Ag^+) for $\mathbf{1}^{20}$, while only one reversible peak is recorded for $RCCo_3(CO)_9$, **2**, and **3**. Coulometry of **1** has confirmed that the electrochemical

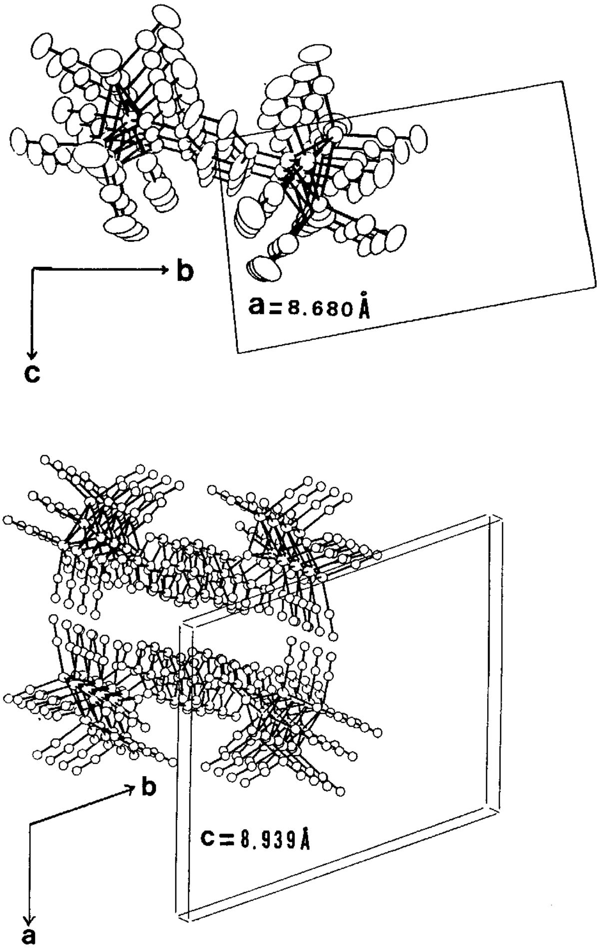


Figure 2 A perspective projection of the molecules along a crystal axis; a view down the **a** axis for **1** (top) and a view down the **c** axis for **2** (bottom).

process around −1.0 V is composed of two apparent one-electron processes, **1**/**1**$^+$ and **1**$^+$/**1**$^{2+}$, and each process is separated by *ca.* 140 mV. This separation is comparable with Δ $E_{1/2}$ values (130 mV) for $C_{15}H_{12}Cr(CO)_3$ ($C_{15}H_{12}$ is 9,10-dihydro-9,10-methanoanthracene) reported by Geiger *et al.*;[21] they have concluded that the monocation of this complex has a trapped valence state and has been categorized as class II mixed valent.[22] From UV and CV data, we conclude that the two redox sites, -$CCo_3(CO)_9$, interact significantly through the π-bond system of the spacer benzene ring. ^{13}C-NMR resonances for CO groups in **1** show a high-field shift of 17 ppm compared with those of **2** and **3**, indicating that CO groups in **1** are strongly shielded. As mentioned above, the Co-Co, Co-C (apical), and C-C (benzene) bond-lengths in **1** are longer than those of **2**. These findings also lend support for electron delocalization in **1**. The rather broad peak at 1600 cm^{-1}

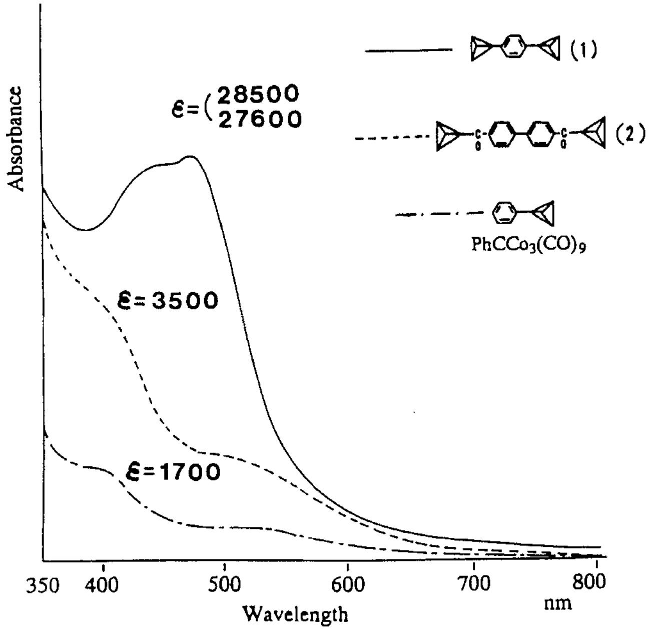


Figure 3 Electronic spectra of **1**, **2**, and $C_6H_5CCo_3(CO)_9$ in THF.

observed in **2** is assigned to ν(CO) (ketone group). This is the lowest frequency ketonic CO group among the analogous $RC(O)CCo_3(CO)_9$ derivatives, where R denotes a simple aromatic molecule.[10,16,17] Presumably this lowering results from π-electron delocalization which extends over each $C_6H_4C(O)CCo_3(CO)_9$ unit, but the delocalization does not extend over two cluster units because of the twist of two phenyl rings. UV spectra and cyclic voltammograms for **2** and **3** are typical for $RCCo_3(CO)_9$ and do not suggest an interaction between the two cluster units for **2** and **3**.

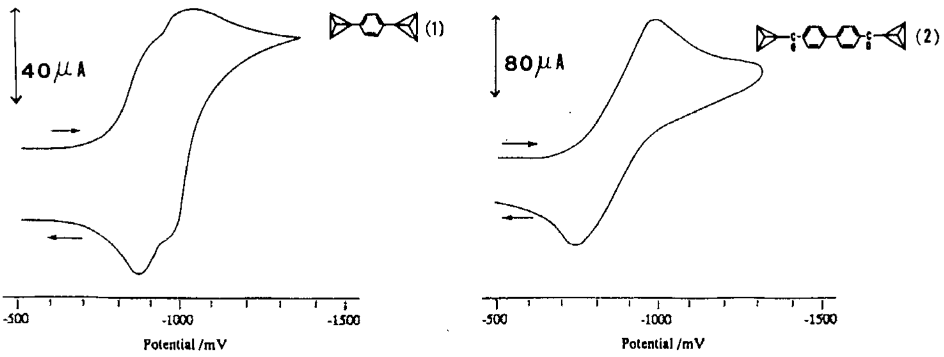


Figure 4 Cyclic voltammograms of **1** (left) and **2** (right) in CH_2Cl_2 at 25°C; 200 mV/s, Pt plate (working electrode), Ag/Ag^+ in CH_3CN (reference electro de).

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