

The syntheses of pyridine-functionalized methylidyne-tricobalt nona-carbonyl clusters, their X-ray analyses, and its coordination to Pd(II)¹

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Abstract

Two kinds of methylidyne-tricobalt nonacarbonyls with a pyridine functional group as an apical substituent have been synthesized from trichloromethylpyridine derivatives. The structures of two new clusters have been determined by single crystal X-ray analysis. EH-MO calculations have shown that the atomic charge on the N atom in $\text{NC}_5\text{H}_4\text{-3-CCo}_3(\text{CO})_9$ is close to that of β -picoline. This cluster can coordinate to Pd(II) and *trans*- $\text{PdCl}_2\{\text{NC}_5\text{H}_4\text{-3-CCo}_3(\text{CO})_9\}_2$ with a nanometer dimension has been synthesized as a precursor of molecular dot. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Tricobalt cluster with a pyridine ligand; Single crystal X-ray analysis; Nanometer scale cluster; Molecular dot

1. Introduction

The preparation of nanometer-sized metal clusters with uniform dimensions and shapes has now become a challenging field of chemistry because of their possible applications to nanotechnology [1]. So far, two major methods have been employed to produce nanometer-sized particles, that is, dry methods and wet methods. A typical example of the former methods is the gas phase synthesis from bulk solids by use of the laser ablation and/or the electrical discharge [1] and that of the latter methods is the solution phase synthesis of colloids, alkoxides, and/or metal cluster coordination compounds in solvents [1]. However, both methods meet the size-distribution problem except the synthesis of coordination compounds and the production of uni-

form sized particles with a preparative scale quantity is quite difficult except for some synthetic methods of coordination cluster compounds [1]. Therefore, we have proposed the synthesis of higher-nuclearity clusters in a molecular design fashion by use of the small cluster unit, $-\text{CCo}_3(\text{CO})_9$, as a building block in the previous papers, targeting the synthesis of such nanometer-size clusters. We have successfully synthesized several prototype clusters [2]; a similar idea of linking two cluster units of $\text{CCo}_3(\text{CO})_9$ has already appeared in a previous paper [3]. As an extension of this work, the next target is the synthesis of spherical clusters with a nanometer-size (Scheme 1). We propose calling such a cluster 'a molecular dot'. The key cluster unit to construct such a molecular dot is a pyridine-functionalized tricobalt cluster, $\text{py-CCo}_3(\text{CO})_9$, the synthesis of which has not been reported in spite of the plethora of studies on the synthesis of many kinds of methylidyne-tricobalt nonacarbonyls by Seyferth et al. [4]. The present paper reports on the tailored synthesis of pyridine-functionalized tricobalt clusters, their X-ray structural analyses,

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and the demonstration of the coordination of one of these clusters to a Pd(II) complex.

2. Experimental section

2.1. General comments

All reactions were carried out under an argon atmosphere by standard Schlenk techniques. 3-trichloromethylpyridine, 3-Cl₃C–NC₅H₄ and *trans*-PdCl₂(NCPH)₂ were synthesized by the literature methods [5,6]. The fraction of 3-Cl₃C–NC₅H₄ with b.p. 53–55°C/0.05 mmHg was collected and used for the synthesis of (3-py)CCo₃(CO)₉. ¹H-NMR spectra were recorded on a JEOL EX-270 WB spectrometer. IR spectra were recorded on a JASCO Valor-III FT-IR spectrometer.

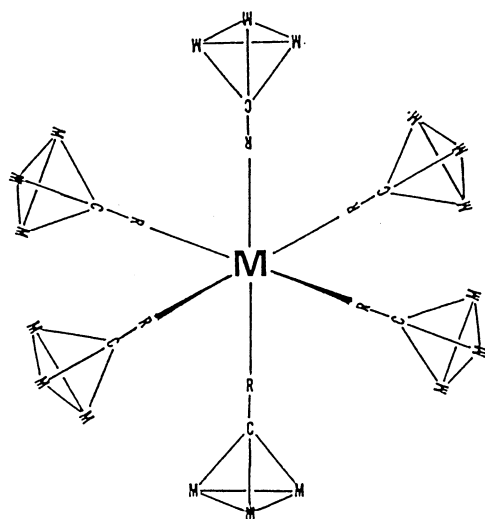
2.2. Synthesis of NC₅H₃-6-Cl-3-CCo₃(CO)₉ (1) and NC₅H₄-3-CCo₃(CO)₉ (2)

A THF solution (30 ml) of Co₂(CO)₈ (920 mg, 2.77 mmol) was stirred at 55°C for 30 min. Then a THF solution (10 ml) of 3-Cl₃C–NC₅H₄ (330 mg) (8 mmol) was added. The mixture was stirred at 55°C for 2.5 h and left standing at room temperature overnight. The brown solution was filtered by use of filter paper and then poured into a 10% HCl solution. The purple-brown product was extracted with each 50 ml of CH₂Cl₂ several times and the solvent was partially distilled under a reduced pressure from the combined extracts. The remaining solution was subjected to a Yamazen YFLC-700 medium pressure liquid chromatography (Wako-gel C-200). A mixed solvent of hexane–benzene (1:1) eluted a small amount of red

Table 1
Crystal data

Compound	NC ₅ H ₃ -6-Cl-3-CCo ₃ (CO) ₉ (1)	NC ₅ H ₄ -3-CCo ₃ (CO) ₉ (2)
Formula	C ₁₅ H ₃ ClCo ₃ NO ₉	C ₁₅ H ₄ Co ₃ NO ₉
Formula weight	553.4	519.0
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>
Unit cell dimensions		
<i>a</i> (Å)	10.537(2)	13.518(3)
<i>b</i> (Å)	10.585(2)	29.887(5)
<i>c</i> (Å)	8.781(2)	8.992(1)
α (°)	93.25(2)	90
β (°)	93.13(1)	94.96(2)
γ (°)	86.31(1)	90
<i>V</i> (Å ³)	974.5(3)	3819(1)
<i>Z</i>	2	8
<i>D</i> _{calc} (g cm ^{−3})	1.887	1.832
Crystal dimensions (mm ³)	0.50 × 0.35 × 0.30	0.60 × 0.55 × 0.35
μ (Mo–K α) (cm ^{−1})	14.85	15.10
Scan type	ω -2 θ	ω -2 θ
Scan range	1.50 + 0.35 tan θ	1.30 + 0.35 tan θ
Scan speed (° min ^{−1})	5.0	5.0
2 θ _{max} (°)	55.0	50.0
Temperature (K)	298	298
Unique reflections	4482	6364
Reflections with $ F_o > 3\sigma(F_o)$	4030	5041
No. of parameters refined	277	535
<i>R</i>	0.103	0.0355
<i>R</i> _w	0.116	0.0284

Mo–K α radiation ($\lambda = 0.71073$ Å); $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$; $R_w = [\Sigma (|F_o| - |F_c|)^2 / \Sigma w(F_o)^2]^{1/2}$ where $w = 1/\sigma^2(F)$.



Scheme 1.

band and benzene eluted a huge purple band. Both products were recrystallized from hexane–dichloromethane to afford a purple-red product **1** (from the red band, 20 mg) and a purple-brown product **2** (from the purple band, 220 mg, 30%). Single crystal X-ray analysis has shown that **1** is NC₅H₃-6-Cl-3-CCo₃(CO)₉; IR (ν (CO), Nujol mull): 2105 (m), 2056 (vs), 2046 (s, sh), 2030 (s), 2015 (m), 1999 (m) cm^{−1}. ¹H-NMR (CD₃OD): 8.583 (d, 3 Hz, 1H, C3–H), 7.711 (dd, 3 Hz, 8 Hz, 1H, C6–H), 7.293 (d, 0.6 Hz, 1H, C5–H). Absorption spectrum (CH₂Cl₂ solution) ($\lambda_{\max}$): 390 ($\epsilon = 6.4 \times 10^3$), 515 ($\epsilon = 1.8 \times 10^3$) nm. Single crystal X-ray analysis has shown that **2** is NC₅H₄-3-CCo₃(CO)₉. Anal.Calc. for C₁₅H₄Co₃NO₉(%): C, 34.71; H, 0.78; N, 2.70. Found: C, 34.14; H, 0.79; N, 2.68. IR (ν (CO), Nujol mull): 2105 (m), 2071 (m, sh), 2053 (vs), 2036 (vs), 2019 (s), 2004 (m, sh), 1989 (m) cm^{−1}. ¹H-NMR (CD₃OD): 8.746 (s, 1H, C₁₉–H, C₂₉–H), 8.452 (d, 3 Hz, 1H, C₁₈–H, C₂₈–H), 7.964 (d, 8 Hz, 1H, C₁₆–H, C₂₆–H), 7.430 (dd, 6 Hz, 5 Hz, 1H, C₁₇–H, C₂₇–H). Absorption spectrum (CH₂Cl₂ solution) ($\lambda_{\max}$): 380 ($\epsilon = 5.2 \times 10^3$), 510 ($\epsilon = 1.7 \times 10^3$) nm.

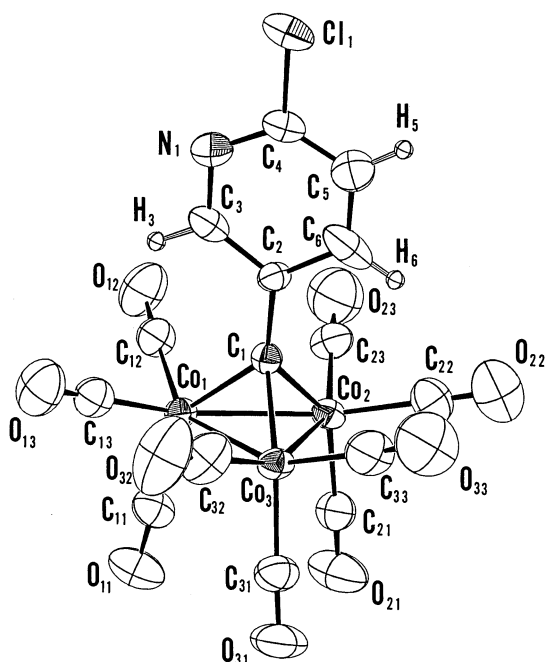


Fig. 1. The molecular structure of $\text{NC}_5\text{H}_3\text{-6-Cl-3CCo}_3(\text{CO})_9$ (**1**).

2.3. Synthesis of $\text{PdCl}_2\{\text{NC}_5\text{H}_4\text{-3-CCo}_3(\text{CO})_9\}_2$ (**3**)

A 74 mg sample of *trans*- $\text{PdCl}_2(\text{NPh})_2$ (0.19 mmol) was dissolved in 50 ml of toluene. To this was added a toluene solution (90 ml) of **2** (200 mg, 0.39 mmol) and the mixture was stirred at room temperature for 3 h and then at 50°C for 1 h. The resulting dark brown precipitates were collected by filtration, washed with a small amount of hexane several times, and dried by suction. Yield 190 mg (82%). Anal. Calc. for $\text{C}_{30}\text{H}_8\text{Cl}_2\text{Co}_6\text{N}_2\text{O}_{18}\text{Pd}$ (%): C, 29.65; H, 0.66, N, 2.31.

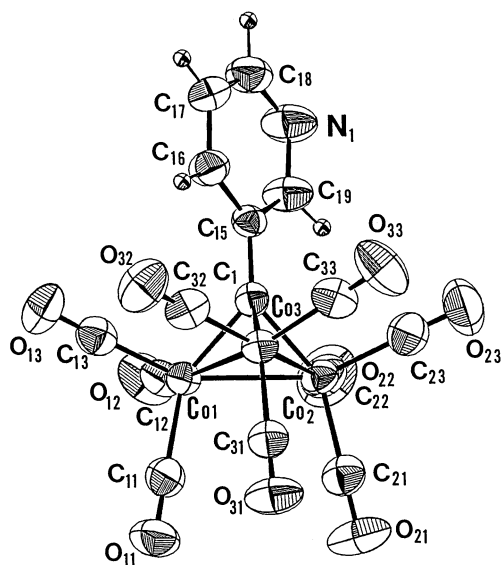


Fig. 2. The molecular structure of molecule 1 of $\text{NC}_5\text{H}_4\text{-3-CCo}_3(\text{CO})_9$ (**2**).

Found: C, 29.36; H, 1.11; N, 2.32. IR ($\nu(\text{CO})$, Nujol mull): 2107 (m), 2059 (s, sh), 2047 (vs), 2037 (s), 2026 (s), 2017 (m, sh), 2005(m, sh) cm^{-1} . Absorption spectrum (CH_2Cl_2 solution) (λ_{max}): 400 ($\epsilon = 9.5 \times 10^4$), 520 ($\epsilon = 3.0 \times 10^4$) nm. All attempts to get single crystals of **3** have so far been unsuccessful because of low solubility to common organic solvents.

2.4. Crystal structure determination

Dark purple brown single crystals of **2** were grown from hexane–dichloromethane (1:1). A crystal with approximate dimensions of $0.60 \times 0.55 \times 0.40 \text{ mm}^3$ was mounted on a MAC MXC³ diffractometer equipped with graphite monochromated Mo- K_α radiation ($\lambda = 0.71073 \text{ \AA}$). Diffraction data were collected at room temperature. Dark brown single crystals of **1** were also grown from hexane–dichloromethane (1:1). A crystal with approximate dimensions of $0.50 \times 0.35 \times 0.30 \text{ mm}^3$ was mounted on a MAC MXC³ diffractometer and diffraction data were similarly measured as above.

The crystal data for **1** and **2** are given in Table 1. The structures were solved by direct methods (Sir 92 for **1** and SHELXS86 for **2**) in a Crystan-G and a Crystan program package provided by MAC Science. All non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms by isotropic thermal parameters. The molecular structures for **1** and **2** are depicted in Figs. 1 and 2, respectively. The atomic coordinates are listed in Table 2 and selected bond lengths and angles are collated in Table 3. The $|F_o| - |F_c|$ tables and anisotropic temperature factor tables are available from the author.

3. Results and discussion

The most important key building block for the synthesis of ‘a molecular dot’ is, in our view, a pyridine-functionalized tricobalt cluster, $\text{py-CCo}_3(\text{CO})_9$. Therefore, we at first attempted the synthesis of $\text{NC}_5\text{H}_4\text{-4-CCo}_3(\text{CO})_9$ from $4\text{-Cl}_3\text{C-NC}_5\text{H}_4$. However, only $\text{HCCo}_3(\text{CO})_9$ has so far been isolated from the similar synthetic procedure as those of **1** and **2** described in Section 2. We have turned our attention to the synthesis of the 3-substituted pyridine cluster from $3\text{-Cl}_3\text{C-NC}_5\text{H}_4$ and successfully obtained the targeted tricobalt cluster with a pyridine functional group as an apical substituent. The synthesis of $\text{NC}_5\text{H}_3\text{-6-Cl-3-CCo}_3(\text{CO})_9$ as a byproduct is well understood because the fraction used to get $3\text{-Cl}_3\text{C-NC}_5\text{H}_4$ contained a small amount of $6\text{-Cl-3-Cl}_3\text{C-NC}_5\text{H}_3$ which is due to the boiling point of the latter liquid being close to that of the former liquid [5]. Before we proceed to the synthesis of a ‘nano cluster’, it seems appropriate to check the molecular structures of **1** and **2** in some

Table 2

Atomic coordinates and isotropic thermal parameters, B_{eq} ($\text{\AA}^2$) for **1** and **2**

Compound 1				
Atom	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
Co1	0.3202(2)	0.3738(2)	0.7576(2)	2.85(6)
Co2	0.2525(2)	0.2676(2)	0.9800(2)	2.84(6)
Co3	0.3200(2)	0.1395(2)	0.7508(2)	3.17(6)
Cl1	−0.3392(4)	0.2738(4)	0.4893(5)	5.0(1)
N1	−0.108(1)	0.352(1)	0.526(2)	4.3(4)
C1	0.182(1)	0.269(1)	0.787(1)	2.6(3)
C2	0.051(1)	0.270(1)	0.712(2)	3.0(4)
C3	0.010(1)	0.349(1)	0.590(2)	4.0(4)
C4	−0.187(1)	0.274(1)	0.581(2)	3.1(4)
C5	−0.157(1)	0.192(2)	0.690(2)	5.4(6)
C6	−0.036(2)	0.194(2)	0.761(2)	4.8(5)
C11	0.484(2)	0.397(1)	0.825(3)	6.6(7)
C12	0.244(1)	0.525(1)	0.808(1)	3.1(4)
C13	0.326(2)	0.389(1)	0.554(2)	4.5(5)
C21	0.404(2)	0.265(1)	1.094(2)	3.7(4)
C22	0.166(1)	0.399(2)	1.066(2)	3.8(4)
C23	0.171(2)	0.150(2)	1.066(2)	3.9(4)
C31	0.484(2)	0.098(1)	0.813(3)	7.6(8)
C32	0.327(2)	0.114(2)	0.552(2)	5.8(6)
C33	0.240(2)	0.000(2)	0.799(3)	8.0(8)
O11	0.586(1)	0.409(1)	0.865(2)	7.1(5)
O12	0.193(1)	0.620(1)	0.842(1)	5.8(4)
O13	0.329(1)	0.401(1)	0.430(1)	6.1(4)
O21	0.496(1)	0.260(1)	1.162(1)	6.3(4)
O22	0.111(1)	0.481(1)	1.133(2)	7.0(5)
O23	0.119(1)	0.076(1)	1.124(2)	8.0(5)
O31	0.583(1)	0.074(1)	0.864(2)	7.8(5)
O32	0.328(2)	0.096(1)	0.423(2)	9.2(6)
O33	0.190(2)	−0.087(1)	0.820(2)	10.8(7)
H3	0.06(2)	0.41(2)	0.54(2)	3.95(0)
H5	−0.23(2)	0.14(2)	0.74(2)	5.31(0)
H6	−0.01(2)	0.14(2)	0.81(2)	4.78(0)
Compound 2				
Molecule 1				
Co1	−0.02997(4)	−0.14187(2)	−0.20489(5)	3.32(2)
Co2	−0.05444(4)	−0.07523(2)	−0.36687(6)	3.43(2)
Co3	−0.19398(3)	−0.10613(2)	−0.23920(5)	3.21(2)
C1	−0.1149(2)	−0.1327(1)	−0.3826(4)	3.08(9)
N1	−0.1216(3)	−0.1800(1)	−0.7708(4)	5.8(1)
C15	−0.1418(2)	−0.1616(1)	−0.5121(4)	3.1(1)
C16	−0.2104(3)	−0.1960(1)	−0.5110(5)	4.2(1)
C17	−0.2334(4)	−0.2218(1)	−0.6364(5)	4.8(1)
C18	−0.1871(4)	−0.2127(2)	−0.7612(5)	5.0(1)
C19	−0.1002(3)	−0.1557(2)	−0.6479(5)	4.7(1)
C11	0.0128(3)	−0.1165(1)	−0.0238(5)	4.2(1)
C12	0.0855(3)	−0.1596(1)	−0.2670(4)	4.2(1)
C13	−0.0679(3)	−0.1961(2)	−0.1455(4)	4.3(1)
C21	−0.0154(3)	−0.0300(1)	−0.2373(5)	4.4(1)
C22	0.0566(3)	−0.0808(2)	−0.4602(5)	5.0(1)
C23	−0.1270(3)	−0.0447(2)	−0.5091(5)	5.0(1)
C31	−0.1860(3)	−0.0684(1)	−0.0765(4)	3.8(1)
C32	−0.2633(3)	−0.1504(1)	−0.1647(5)	4.4(1)
C33	−0.2940(3)	−0.0822(2)	−0.3536(5)	4.7(1)
O11	0.0383(2)	−0.1008(1)	0.0871(3)	6.0(1)
O12	0.1597(2)	−0.1713(1)	−0.3034(3)	6.5(1)
O13	−0.0916(2)	−0.2306(1)	−0.1109(4)	6.3(1)
O21	0.0087(3)	−0.0020(1)	−0.1595(4)	7.4(1)
O22	0.1270(2)	−0.0838(1)	−0.5193(4)	7.9(1)

Table 2 (Continued)

Compound **2**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
O23	−0.1733(3)	−0.0255(1)	−0.5980(4)	8.2(1)
O31	−0.1819(2)	0.0452(1)	0.0218(3)	6.0(1)
O32	−0.3105(2)	−0.1770(1)	−0.1159(4)	6.7(1)
O33	−0.3592(2)	−0.0671(1)	−0.4238(4)	7.9(1)
H16	−0.244(3)	−0.202(2)	−0.422(5)	4.20(0)
H17	−0.278(4)	−0.245(2)	−0.634(5)	4.84(0)
H18	−0.201(3)	−0.232(2)	−0.853(5)	5.02(0)
H19	−0.056(3)	−0.130(2)	−0.661(5)	4.69(0)
Molecule 2				
Co4	−0.49497(3)	−0.14643(2)	0.23739(5)	3.21(2)
Co5	−0.59545(4)	−0.07970(2)	0.28433(5)	3.18(2)
Co6	−0.58371(4)	−0.10625(2)	0.02663(5)	3.46(2)
C2	−0.6335(2)	−0.1356(1)	0.1933(3)	2.78(8)
N2	−0.8535(2)	−0.2080(1)	0.0815(4)	5.4(1)
C25	−0.7197(2)	−0.1647(1)	0.2059(4)	2.88(9)
C26	−0.7506(3)	−0.1782(2)	0.3414(5)	5.1(1)
C27	−0.8326(4)	−0.2061(2)	0.3432(6)	6.0(2)
C28	−0.8810(3)	−0.2196(2)	0.2126(6)	4.8(1)
C29	−0.7749(3)	−0.1812(2)	0.0811(5)	4.6(1)
C41	−0.3732(3)	−0.1205(1)	0.2264(5)	4.5(1)
C42	−0.4816(3)	−0.1666(1)	0.4254(5)	4.4(1)
C43	−0.4817(3)	−0.1999(2)	0.1507(5)	4.6(1)
C51	−0.4998(3)	−0.0363(1)	0.2937(5)	4.6(1)
C52	−0.6071(3)	−0.0881(1)	0.4800(5)	4.4(1)
C53	−0.7078(3)	−0.0480(1)	0.2480(4)	4.3(1)
C61	−0.4850(3)	−0.0691(2)	−0.0280(4)	4.4(1)
C62	−0.5779(3)	−0.1511(2)	−0.1039(5)	5.1(1)
C63	−0.6923(3)	−0.0797(2)	−0.0620(4)	4.7(1)
O41	−0.2998(2)	−0.1034(1)	0.2195(4)	7.1(1)
O42	−0.4702(3)	−0.1793(1)	0.5435(4)	7.59(1)
O43	−0.4745(3)	−0.2341(1)	0.0989(4)	7.2(1)
O51	−0.4401(3)	−0.0097(1)	0.2972(4)	7.3(1)
O52	−0.6166(3)	−0.0931(1)	0.6016(4)	7.4(1)
O53	−0.7796(2)	−0.0292(1)	0.2282(4)	7.0(1)
O61	−0.4243(2)	−0.0465(1)	−0.0613(4)	7.3(1)
O62	−0.5763(3)	−0.1800(1)	−0.1855(4)	7.5(1)
O63	−0.7613(2)	−0.0640(1)	−0.1194(4)	7.3(1)
H26	−0.714(3)	−0.171(2)	0.433(5)	5.11(0)
H27	−0.844(4)	−0.218(2)	0.436(6)	5.92(0)
H28	−0.940(3)	−0.240(2)	0.209(5)	4.78(0)
H29	−0.753(3)	−0.171(2)	−0.011(5)	4.56(0)

detail. There are two independent molecules in an asymmetric unit for **2**, whereas there is one molecule in an asymmetric unit for **1**. The geometrical parameters for two independent molecules of **2** are quite close for each other. However, the rotational angle of the pyridine ring about the axis which passes through the apical carbon and the center of the Co_3 triangle is somewhat different as is seen in Fig. 3; the pyridine ring in the molecule **2** almost bisects the Co–Co bond whereas the pyridine ring in the molecule **1** rotates a little bit about the axis mentioned above. The N atom side of the pyridine ring tends to direct one of the cobalt atoms. The same result is observed for **1** and the rotation of the apical pyridine ring is close to that of

Table 3
Selected bond lengths (Å) and angles (°)

Compound 1		Compound 2			
		Molecule 1		Molecule 2	
Co1–Co2	2.468(3)	Co1–Co2	2.4725(8)	Co4–Co5	2.4695(8)
Co1–Co3	2.478(2)	Co1–Co3	2.4558(7)	Co4–Co6	2.4653(7)
Co2–Co3	2.473(3)	Co2–Co3	2.4706(7)	Co5–Co6	2.4677(7)
C1–Co1	1.92(1)	C1–Co1	1.905(3)	C2–Co4	1.908(3)
C1–Co2	1.82(1)	C1–Co2	1.901(4)	C2–Co5	1.912(3)
C1–Co3	1.96(1)	C1–Co3	1.916(4)	C2–Co6	1.909(3)
C1–C2	1.49(2)	C1–C15	1.471(5)	C2–C25	1.465(5)
Co1–C11	1.83(2)	Co1–C11	1.843(4)	Co4–C41	1.829(4)
Co1–C12	1.79(1)	Co1–C12	1.783(4)	Co4–C42	1.789(4)
Co1–C13	1.80(2)	Co1–C13	1.794(4)	Co4–C43	1.793(4)
Co2–C21	1.83(2)	Co2–C21	1.831(4)	Co5–C51	1.827(4)
Co2–C22	1.77(2)	Co2–C22	1.790(5)	Co5–C52	1.798(4)
Co2–C23	1.78(2)	Co2–C23	1.792(4)	Co5–C53	1.796(4)
Co3–C31	1.81(2)	Co3–C31	1.844(4)	Co6–C61	1.835(4)
Co3–C32	1.75(2)	Co3–C32	1.786(4)	Co6–C62	1.787(5)
Co3–C33	1.82(2)	Co3–C33	1.777(4)	Co6–C63	1.794(4)
N1–C3	1.33(2)	N1–C18	1.327(6)	N2–C28	1.313(6)
N1–C4	1.34(2)	N1–C19	1.333(6)	N2–C29	1.330(6)
C2–C3	1.43(2)	C15–C16	1.383(5)	C25–C26	1.382(6)
C2–C6	1.37(2)	C15–C19	1.400(6)	C25–C29	1.384(5)
C4–C5	1.33(2)	C16–C17	1.379(6)	C26–C27	1.390(7)
C5–C6	1.39(2)	C17–C18	1.359(7)	C27–C28	1.355(7)
C11–C4	1.75(1)				
Co1–Co2–Co3	60.19(8)	Co1–Co2–Co3	59.58(2)	Co4–Co5–Co6	59.91(2)
Co2–Co3–Co1	59.81(8)	Co2–Co3–Co1	60.15(2)	Co5–Co6–Co4	60.08(2)
Co3–Co1–Co2	59.99(8)	Co3–Co1–Co2	60.17(2)	Co6–Co4–Co5	60.01(2)
C1–Co1–Co2	46.8(4)	C1–Co1–Co2	49.4(1)	C2–Co4–Co5	49.8(1)
C1–Co1–Co3	51.1(4)	C1–Co1–Co3	50.2(1)	C2–Co4–Co6	49.8(1)
C1–Co2–Co1	50.6(4)	C1–Co2–Co1	49.6(1)	C2–Co5–Co4	49.6(1)
C1–Co3–Co1	49.7(4)	C1–Co3–Co1	49.8(1)	C2–Co6–Co4	49.8(1)
C1–Co3–Co2	46.6(4)	C1–Co3–Co2	49.4(1)	C2–Co6–Co5	49.8(1)
C2–C1–Co1	130(1)	C15–C1–Co1	132.0(2)	C25–C2–Co4	131.0(2)
C2–C1–Co2	137(1)	C15–C1–Co2	131.7(2)	C25–C2–Co5	132.2(2)
C2–C1–Co3	125.6(9)	C15–C1–Co3	131.5(2)	C25–C2–Co6	132.1(2)
C1–Co1–C11	141.1(7)	C1–Co1–C11	143.3(2)	C2–Co4–C41	142.0(2)
C1–Co1–C12	98.7(6)	C1–Co1–C12	105.1(2)	C2–Co4–C42	105.7(2)
C1–Co1–C13	106.9(6)	C1–Co1–C13	102.3(2)	C2–Co4–C43	101.2(2)
C1–Co2–C21	144.1(6)	C1–Co2–C21	144.2(2)	C2–Co5–C51	143.4(2)
C1–Co2–C22	100.1(6)	C1–Co2–C22	104.7(2)	C2–Co5–C52	104.7(2)
C1–Co2–C23	103.9(6)	C1–Co2–C23	101.6(2)	C2–Co5–C53	101.0(2)
C1–Co3–C31	140.9(7)	C1–Co3–C31	142.2(1)	C2–Co6–C61	143.4(2)
C1–Co3–C32	106.8(7)	C1–Co3–C32	106.6(2)	C2–Co6–C62	102.1(2)
C1–Co3–C33	99.1(7)	C1–Co3–C33	102.6(2)	C2–Co6–C63	102.8(2)

the molecule 2 in **2**. The drawing of the crystal packing (Fig. 4) and the intermolecular distance calculation show that the C18–H18 and C28–H28 bonds direct to the pyridine ring of the other molecule at almost right angles suggesting the existence of a C–H $\cdots\pi$ interaction. However, such a C–H $\cdots\pi$ interaction is not the case for **1**. The comparison of the geometrical parameters between **1** and **2** has shown that the average Co–CO bond length for **2** (2.467 Å) is slightly shorter than that of **1** (2.473 Å). The average apical C–Co bond length for **2** (1.909 Å) is essentially same as that of **1** (1.90 Å). The *ipso*-carbon-apical carbon bond length (C1–C15 and

C2–C25) for **2** (1.471(5) and 1.465(5) Å) is shorter than that of **1** (1.49(2) Å). The average Co–Co bond length for **2** (1.805 Å) is only slightly longer than that of **1** (1.798 Å). The average C–O bond length for **2** (1.128 Å) is slightly shorter than that of **1** (1.132 Å). The general trend in the bond-lengths including the Co–Co bonds suggests that the electron-withdrawing substituent, Cl at the *para*-position with respect to the cluster in the pyridine ring affects, if any, only slightly the electron density of the $-\text{CCo}_3(\text{CO})_9$ core [7,8]. The observation is in accord with the knowledge that the $-\text{CCo}_3(\text{CO})_9$ core is an excellent electron sink [2,4,9].

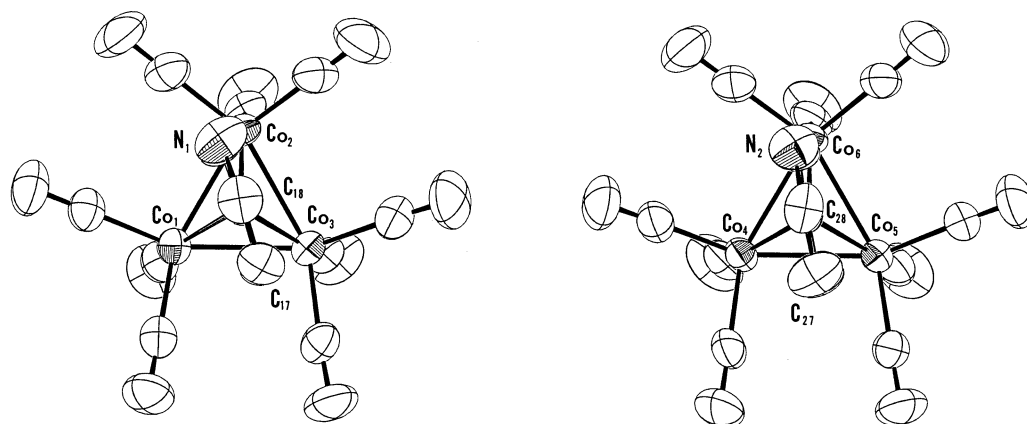


Fig. 3. The rotation of the apical pyridine ring toward the basal tricobalt triangle in **2** (left, molecule 1; right, molecule 2).

Next we investigated the potential of the coordination of the cluster to transition metals by calculating the net atomic charge on the N atom; EH-MO calculations have been made based on the atomic coordinates from the present study by use of CAChe [10]. The atomic charge on the N atom is -0.971 , -0.900 , and -0.820 a.u. for 3-CH₃-NC₅H₄ (β -picoline), **2**, and **1** respectively; the reason for the choice of β -picoline as a standard for the comparison is that it is the typical and the most frequently employed ligand as a pyridine ligand with a substituent at the 3-position. The calculation suggests that the coordinating ability of **2** is close to that of β -picoline in terms of atomic net charge. Therefore, we have examined the reaction of **2** with *trans*-PdCl₂(NCPh)₂ in toluene. As is described in Section 2, a dark brown product is obtained. This product is characterized as *trans*-PdCl₂{NC₅H₄-3-CCO₃(CO)₉}₂ (**3**) by elemental analyses, IR, and the absorption spectrum; there is no reason to doubt that **3** has a *trans*

geometry because *trans*-PdCl₂(NCPh)₂ was used as a Pd source. Upon coordination, **3** shows a slight shift of $\nu(\text{CO})$'s to a higher energy and a slight shift of the absorption peaks in the visible region to a longer wave length with the increased molecular absorption coefficients (more than ten times greater than those of **2**). Attempts to grow single crystals of **3** have so far been unsuccessful due to quite low solubility in common organic solvents. Therefore, we have estimated the molecular dimension of **3** from a molecular model, which suggests that **3** has an approximately 1.5 nm diameter. As a square-planar configuration is suggested for the palladium (II) center in **3**, the molecular shape of **3** should not be spherical. Thus, our efforts to create a supracluster with a spherical shape, that is a molecular dot, are continuing by introducing **2** into a metal center which has a tetrahedral and/or octahedral configuration.

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References

- [1] (a) I.J. De Jongh (Ed.), *Physics and Chemistry of Metal Cluster Compounds*, Kluwer, Dordrecht, 1994. (b) G. Schmid (Ed.), *Clusters and Colloids—From Theory to Applications*, VCH, Weinheim, 1994; V.E. Borisenko, A.B. Filonov, S.V. Gaponenko, V.S. Gurin (Eds), *Physics, Chemistry and Application of Nanostructures*, World Scientific, Singapore, 1997. (c) F. Träger, G. Zu Putlitz (Eds), *Metal Clusters*, Springer, Berlin, 1986.
- [2] (a) S. Onaka, M. Otsuka, A. Mizuno, S. Takagi, K. Sako, M. Otomo, *Chem. Lett.* (1994) 45. (b) S. Onaka, M. Otsuka, *Chem. Lett.* (1995) 269. (c) S. Onaka, M. Otsuka, S. Takagi, K. Sako, *J. Coord. Chem.* 137 (1996) 151.

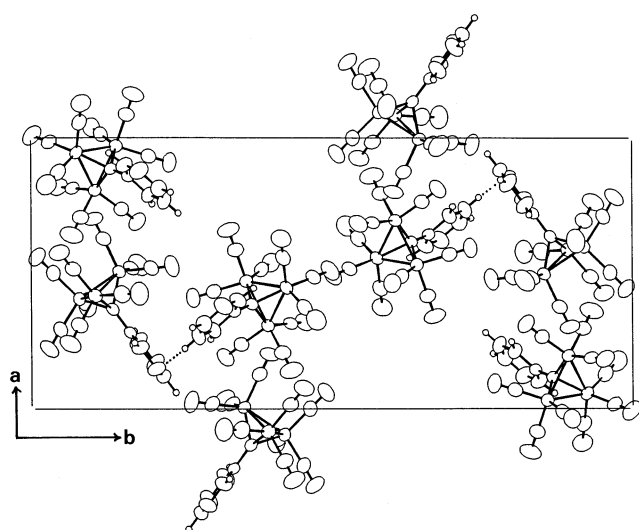


Fig. 4. A projection of the crystal **2** along the *c* axis, which indicates C-H $\cdots\pi$ interactions.

- [3] B.R. Penfold, B.H. Robinson, *Acc. Chem. Res.* 6 (1973) 73.
- [4] (a) D. Seyferth, J.E. Hallgren, R.J. Spohn, *J. Organomet. Chem.* 23 (1970) C55. (b) D. Seyferth, J. Hallgren, *J. Organomet. Chem.* 49 (1973) C41. (c) D. Seyferth, M.O. Nestle, C.S. Eschbach, *J. Am. Chem. Soc.* 98 (1976) 6724. (d) D. Seyferth, G.H. Williams, C.L. Nivert, *Inorg. Chem.* 16 (1977) 758. (e) D. Seyferth, C.N. Rudie, *J. Organomet. Chem.* 184 (1980) 365. (f) D. Seyferth, C.N. Rudie, J.S. Merola, R.H. Berry, *J. Organomet. Chem.* 187 (1980) 91 and references therein.
- [5] R.S. Daintier, T. Jackson, A.H.H. Omar, H. Suschitzky, B.J. Wakefield, N. Hughes, A.J. Nelson, *J. Chem. Soc. Perkin Trans.* 1 (1989) 283.
- [6] R.J. Angelici (Ed.), *Inorg. Synth.*, vol. 28, John Wiley, New York, 1990, p. 61.
- [7] (a) S. Onaka, *Bull. Chem. Soc. Jp.* 44 (1971) 2135. (b) S. Onaka, *Bull. Chem. Soc. Jp.* 46 (1973) 2444. (c) S. Onaka, *Bull. Chem. Soc. Jp.* 48 (1975) 310. (d) S. Onaka, Y. Kondo, M. Yamashita, Y. Tatematsu, Y. Kato, M. Goto, T. Ito, *Inorg. Chem.* 24 (1985) 1070 and references therein.
- [8] M.L. Katcher, G.L. Simon, *Inorg. Chem.* 11 (1972) 1651.
- [9] G. Palyi, F. Piacenti, L. Marko, *Inorg. Chim. Acta, Reviews* (1970) 109.
- [10] CAChe version 3.8 provided by CAChe Scientific, Oxford Molecular Group Inc., 1995.