

# Addition and/or oxidation in the reaction of a tricobalt cluster with silver(I) salts: synthesis, structure and solution properties of $[\text{Co}_3\text{Cp}_3(\mu_3\text{-CPh})_2\{\mu\text{-Ag(X)}\}]$ ( $\text{X} = \text{CF}_3\text{CO}_2, \text{NO}_3$ ) and $[\text{Co}_3\text{Cp}_3(\mu_3\text{-CPh})_2\{\mu\text{-Ag(NCMe)}\}]\text{PF}_6$

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Received 21 August 2003; accepted 29 September 2003

## Abstract

Reactions of the benzyldiene-capped tricobalt cluster  $[\text{Co}_3\text{Cp}_3(\mu_3\text{-CPh})_2]$  (**1**) with various silver salts have been examined. The salts of weakly- or non-coordinating anions (e.g.,  $\text{BF}_4^-$  and  $\text{PF}_6^-$ ) oxidize **1** in  $\text{CH}_2\text{Cl}_2$  to form its cationic radical,  $\mathbf{1}^+$ . Reactions with salts of strongly coordinating anions (e.g.,  $\text{CF}_3\text{CO}_2^-$  and  $\text{NO}_3^-$ ) yield the silver(I) adducts of **1**,  $[\text{Co}_3\text{Cp}_3(\mu_3\text{-CPh})_2\{\mu\text{-Ag(X)}\}]$  (for  $\text{X} = \text{CF}_3\text{CO}_2^-$ : **2** and  $\text{NO}_3^-$ : **3**). Even with  $\text{AgBF}_4$  or  $\text{AgPF}_6$ , the reaction in MeCN produces a silver(I) adduct,  $[\text{Co}_3\text{Cp}_3(\mu_3\text{-CPh})_2\{\mu\text{-Ag(NCMe)}\}]^+$  ( $\mathbf{4}^+$ ). The  $\text{Co}_3\text{Ag}$  skeleton in the structures of **2**, **3**, and  $\mathbf{4}^+$  is similar in each compound. The Co–Co bond bridged by the Ag atom (for **2**, Co–Co = 2.4785(8) Å, for **3**, Co–Co = 2.4837(9) Å, and for  $\mathbf{4}^+$ , Co–Co = 2.4578(7) Å) is longer than the average Co–Co bond length in **1** where  $\langle\text{Co–Co}\rangle_{\text{av}} = 2.382(8)$  Å. The other Co–Co bonds in the compounds are slightly shorter than those in **1**. The  $\text{Co}_2\text{Ag}$  triangle is not coplanar with the  $\text{Co}_3$  triangle; the dihedral angles between these triangles for **2**, **3** and  $\mathbf{4}^+$  are 162.7°, 157.7°, and 151.6°, respectively. Dissolution of  $\mathbf{4PF}_6$  in  $\text{CH}_2\text{Cl}_2$  leads to the formation of  $\mathbf{1}^+$  and the deposition of Ag metal. The  $^1\text{H}$  NMR spectra of **2** and **3** in  $\text{CD}_2\text{Cl}_2$  indicate that the  $\text{AgX}$  group moves over the three Co–Co bonds. The ESR spectra in frozen acetonitrile solutions of **2**, **3**, and  $\mathbf{4PF}_6$  show the existence of a small amount of  $\mathbf{1}^+$ , but the deposition of Ag metal was not observed.

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*Keywords:* Trinuclear clusters; Silver complexes; Cobalt complexes; Metal–metal bonds; X-ray structure analyses

## 1. Introduction

Silver(I) salts are one of the most popular reagents in coordination chemistry. They are used for halogen abstraction and as an oxidant for compounds with low to moderate oxidation potentials. These oxidation potentials depend on the counter anions and solvents [1]. In cluster chemistry, univalent Group 11 metal ions have been used to synthesize higher-nuclearity clusters [2]. In some cases, Group 11 metals bound to the metal–metal bond, similar to a proton. Sometimes complexes with

M–Ag bonds are regarded as being intermediates in the electron-transfer reaction between M and  $\text{Ag}^+$  [3]. We have investigated the electronic structures of Group 9 trinuclear clusters with  $\mu_3$ -benzyldiene ligands,  $[\text{M}_3\text{Cp}_3(\mu_3\text{-CPh})_2]$  (where M = Co or Rh) [4–6]. We attempted to isolate the salts of  $\mathbf{1}^+$  by oxidizing **1** with silver(I) salts. However, we obtained not only  $\mathbf{1}^+$ , but also silver(I) adducts of **1**, depending on the counter anion and the solvent used. In this paper, we describe the synthesis and X-ray structure of the silver(I) adducts: **2**, **3**, and  $\mathbf{4PF}_6$ . The  $^1\text{H}$  NMR spectra of **2** and **3** in dichloromethane indicate that the  $\text{AgX}$  moiety migrates over the Co–Co bonds with moderate rates. In acetonitrile solution of **2**, **3**, and  $\mathbf{4PF}_6$ , there is an equilibrium involving  $\mathbf{1}^+$ .

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## 2. Experimental

### 2.1. General

Dichloromethane, *n*-hexane, and acetonitrile were distilled over CaH<sub>2</sub> before use, and the silver salts were dried under vacuum before use. The starting material **1**, was synthesized using the literature method of Fritch and Vollhardt [7], and purified by recrystallization from *n*-hexane.

### 2.2. Measurements

The <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on a JEOL α-400 spectrometer. Deuterated solvents over 4 Å molecular sieves that were degassed using several freeze–pump–thaw cycles were transferred to J. Young<sup>®</sup> NMR tubes before use on a vacuum line. The ESR data were measured on a JEOL TE-200X ESR spectrometer. ESR spectra were digitalized and integrated by using a Radical Research Win-RAD ESR Data analyzer.

### 2.3. Preparation of [Co<sub>3</sub>Cp<sub>3</sub>(μ<sub>3</sub>-CPh)<sub>2</sub>{μ-Ag(O<sub>2</sub>CCF<sub>3</sub>)}] (2)

AgO<sub>2</sub>CCF<sub>3</sub> (0.15 g, 0.68 mmol) was added to a CH<sub>2</sub>Cl<sub>2</sub> solution (50 ml) of **1** (0.35 g, 0.64 mmol). After stirring for 24 h, the solution was filtered and evaporated to dryness. The resulting brown solid was washed with *n*-hexane and recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane. Yield: 0.40 g (82%). *Anal. Calc.* for C<sub>31</sub>H<sub>25</sub>AgCo<sub>3</sub>F<sub>3</sub>O<sub>2</sub>: C, 48.28; H, 3.27. Found: C, 48.00; H, 3.21%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, at –60 °C): δ 4.76 (10H, s, AgCoCp), 4.96 (5H, s, CoCp), 7.34 (2H, m, *p*-Ph), 7.40 (4H, m, *m*-Ph), 7.79 (4H, m, *o*-Ph).

### 2.4. Preparation of [Co<sub>3</sub>Cp<sub>3</sub>(μ<sub>3</sub>-CPh)<sub>2</sub>{μ-Ag(NO<sub>3</sub>)}] (3)

AgNO<sub>3</sub> (0.12 g, 0.71 mmol) was added to a CH<sub>2</sub>Cl<sub>2</sub> solution (70 ml) of **1** (0.39 g, 0.71 mmol). After stirring for 24 h at room temperature, the solution was filtered and evaporated to dryness. The resulting brown solid was washed with *n*-hexane and recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane. Yield: 0.40 g (81%). *Anal. Calc.* for C<sub>29</sub>H<sub>25</sub>AgCo<sub>3</sub>NO<sub>3</sub>: C, 48.36; H, 3.50; N 1.94. Found: C, 48.22; H, 3.32; N 1.99%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, at –20 °C): δ 4.76 (10H, s, AgCoCp), 4.99 (5H, s, CoCp), 7.36 (2H, m, *p*-Ph), 7.42 (4H, m, *m*-Ph), 7.85 (4H, m, *o*-Ph).

### 2.5. Preparation of [Co<sub>3</sub>Cp<sub>3</sub>(μ<sub>3</sub>-CPh)<sub>2</sub>{μ-Ag(NCMe)}]PF<sub>6</sub> (4PF<sub>6</sub>)

A CH<sub>2</sub>Cl<sub>2</sub> solution (30 ml) of **1** (0.11 g, 0.20 mmol) was added to an MeCN solution (30 ml) of AgBF<sub>4</sub> (0.10 g, 0.51 mmol) with stirring. After 1 h of stirring at room

temperature, the solution was filtered and evaporated to dryness. LiPF<sub>6</sub> (0.28 g, 1.8 mmol) in MeCN (20 ml) was added to the residue, and the solution was stirred for 5 min. The brown solid obtained by evaporation was washed with water, and recrystallized by slow diffusion of diethylether into its MeCN solution. Yield: 0.060 g (36%). *Anal. Calc.* for C<sub>31</sub>H<sub>28</sub>AgCo<sub>3</sub>F<sub>6</sub>NP: C, 44.11; H, 3.34; N, 1.66. Found: C, 44.21; H, 3.26; N, 1.59%.

### 2.6. X-ray structure determination

Crystals of **2** were obtained by slow evaporation from a CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane solution. Complex **3** was crystallized by slow diffusion of *n*-hexane into a CH<sub>2</sub>Cl<sub>2</sub> solution. Crystals of **4PF<sub>6</sub>** were obtained by vapor diffusion of diethylether into an MeCN/diethylether solution. The X-ray intensity data were collected on a Rigaku AFC7R diffractometer employing graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). The cell dimensions were determined using the least-squares refinement of the diffractometer angles for 25 automatically centered reflections. The scattering factors for the neutral atoms were obtained from Cromer and Waber [8], using anomalous dispersion [9]. The positions of the metal atoms were determined by a direct method employing the SHELXS 86 [10] package. The structures were expanded using the DIRDIF [11] software, and refined using a full matrix least-squares method by the teXsan<sup>®</sup> crystallographic software package [12]. An empirical absorption correction based on six azimuthal scans was applied for **2** [13]. An analytical absorption correction [14] was applied for **3** and **4PF<sub>6</sub>**. The final least-squares cycle included non-hydrogen atoms, with the anisotropic thermal parameters and hydrogen atoms maintained at fixed positions using isotropic thermal parameters that were 1.2 times those of the connected atoms. The crystal data and description of the structure refinement are summarized in Table 1.

## 3. Results and discussion

### 3.1. Reaction of **1** with silver(I) salts

The reaction of **1** with various silver(I) salts yields two types of isolated product: the salts of the cationic radical **1**<sup>+</sup> and the adducts of silver salts. In a previous paper, we reported on the structure of **1**ClO<sub>4</sub> prepared by the electrochemical oxidation of **1** [4]. This salt was also isolated from the reaction of **1** with AgClO<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub>. ESR spectra of solutions of **1** mixed with sufficient amounts of other silver salts of weakly or non-coordinating anions, e.g., PF<sub>6</sub><sup>–</sup>, SbF<sub>6</sub><sup>–</sup>, and BF<sub>4</sub><sup>–</sup>, in CH<sub>2</sub>Cl<sub>2</sub> showed that **1**<sup>+</sup> is quantitatively formed. The reaction of **1** with salts of strongly coordinating anions, e.g., CF<sub>3</sub>CO<sub>2</sub><sup>–</sup> and NO<sub>3</sub><sup>–</sup>, in CH<sub>2</sub>Cl<sub>2</sub> does not show any

Table 1  
Crystal data and refinement description

	2	3	4PF <sub>6</sub>
Chemical formula	C <sub>31</sub> H <sub>25</sub> AgCo <sub>3</sub> F <sub>3</sub> O <sub>2</sub>	C <sub>29</sub> H <sub>25</sub> AgCo <sub>3</sub> NO <sub>3</sub>	C <sub>31</sub> H <sub>28</sub> AgCo <sub>3</sub> F <sub>6</sub> NP
Molecular weight	771.2	720.19	844.20
Crystal size (mm)	0.35 × 0.30 × 0.30	0.25 × 0.15 × 0.10	0.66 × 0.17 × 0.09
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i> (no. 14)	<i>P</i> 2 <sub>1</sub> / <i>c</i> (no. 14)	<i>P</i> 2 <sub>1</sub> / <i>c</i> (no. 14)
<i>a</i> (Å)	12.296(1)	8.730(2)	18.315(1)
<i>b</i> (Å)	17.607(1)	16.806(5)	8.790(2)
<i>c</i> (Å)	12.866(1)	17.248(3)	19.097(2)
$\beta$ (°)	91.351(7)	96.21(2)	95.922(6)
<i>V</i> (Å <sup>3</sup> )	2784.9(3)	2515.7(10)	3058.0(7)
<i>Z</i>	4	4	4
<i>d</i> (calcd) (g cm <sup>-3</sup> )	1.839	1.901	1.833
$\mu$ (mm <sup>-1</sup> )	2.495	2.742	2.341
<i>T</i> (°C)	23	23	23
2 $\theta$ limit (°)	55	55	55
Reflection measured	6919	8600	14969
Reflection unique	6404	5742	7027
Reflections with <i>I</i> > 2 $\sigma$ ( <i>I</i> )	4212	3303	4229
<i>R</i> <sub>1</sub> , <i>R</i> <sub>w</sub> <sup>a</sup>	0.046, 0.104	0.041, 0.100	0.037, 0.086
GOF	1.45	1.47	1.32

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o| \text{ for reflections with } I > 2\sigma(I), R_w = \left[ \frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right]^{1/2} \text{ for all data.}$$

deposition of Ag metal, and X-ray structure analysis of the products reveals that they are the silver salt adducts, **2** and **3**. The cationic radical could not be isolated by reaction in MeCN, even with AgBF<sub>4</sub>. The cationic Ag-adduct **4**<sup>+</sup> was isolated as the PF<sub>6</sub><sup>-</sup> salt by addition of excess LiPF<sub>6</sub> to the solution.

### 3.2. X-ray structural analysis

Fig. 1 shows an ORTEP drawing of **2** including the atom numbering. Selected bond distances and angles are

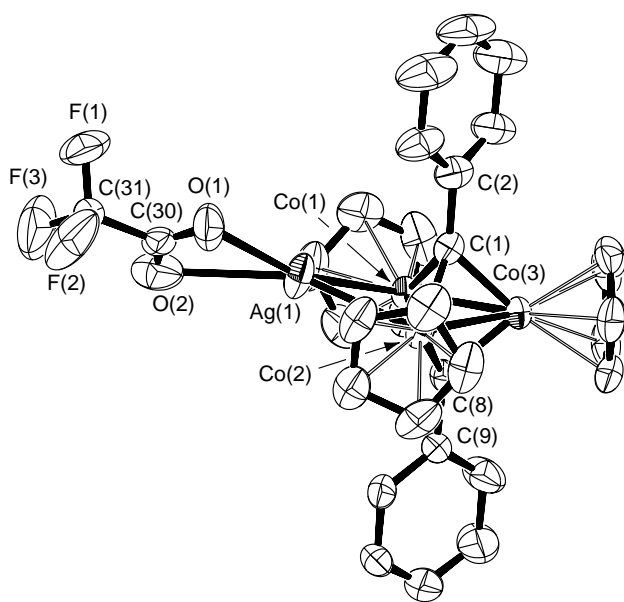


Fig. 1. ORTEP drawing of **2** with 30% probability. Hydrogen atoms are omitted for clarity.

summarized in Table 2. The silver atom coordinated by the oxygen atoms of the trifluoroacetate ion bridges between two of the three cobalt atoms. The structure of **3** and **4PF<sub>6</sub>** are shown in Figs. 2 and 3, respectively, and their selected bond distances and angles are listed in Tables 3 and 4, respectively. The structure of **3** is quite similar to that of **2**. In the structure of **4PF<sub>6</sub>**, the Ag<sup>+</sup> ion is coordinated by a single MeCN molecule, and not by the PF<sub>6</sub><sup>-</sup> ions. The Ag atom in each structure is located out of the Co<sub>3</sub> plane with a dihedral angle of 151.6°–162.7° between the Co<sub>3</sub> and the Co<sub>2</sub>Ag planes.

The Ag–Co bond lengths are 2.6150(7)–2.6572(6) Å in **2**, **3** and **4**<sup>+</sup>, respectively. These are similar to those of other complexes with Ag–Co bonds, e.g., 2.589(1)–2.594(1) Å in [ $\{\text{Co}(\text{CO})_4\}_4(\mu\text{-Ag})_4$ ] [15] and 2.600(2)–2.724(2) Å in [ $\{\text{Co}(\text{CNC}_6\text{H}_3\text{Me}_2)_4\}_3\text{Ag}_3$ ] [16]. The Co(Ag)–Co(Ag) distances (2.4785(8) Å for **2**, 2.4837(9) Å for **3**, and 2.4578(7) Å for **4**<sup>+</sup>) are elongated, and the Co–Co(Ag) bonds are slightly shortened from the average Co–Co distance in the parent tricobalt cluster **1** (2.382(8) Å) [4]. The elongation of the M–M bond by the addition of Group 11 metal ions to the M–M edge of the trimetal clusters has also observed in [ $\text{Ru}_3(\text{CO})_9(\mu_3\text{-C}_2\text{Bu})\{\mu\text{-M}'(\text{PPh}_3)\}$ ] (where M' = Cu, Ag, and Au) [17], in [ $\text{Fe}_3(\text{CO})_9(\mu_3\text{-SPr}^i)\{\mu\text{-Au}(\text{PPh}_3)\}$ ] [18,19], and in [ $\text{Fe}_3(\text{CO})_9(\mu_3\text{-Te})\{\mu\text{-Au}(\text{PPh}_3)\}$ ]<sup>-</sup> [20]. In all these clusters, the M'–atom-bridged M–M bonds are elongated by 0.1–0.2 Å, which are similar to those of the present Ag-bridged complexes. For M<sub>3</sub>(μ-M') complexes (where M = Fe, Co, Ru, Os, and Ir; and M' = Cu, Ag, and Au) the dihedral angles between the M<sub>3</sub> and M<sub>2</sub>M' triangles are in the range of 110°–176° [17,19–22]. A complex with two capping ligands, [ $\text{CoFe}_2(\text{CO})_6(\text{Cp})(\mu_3\text{-CO})(\mu_3\text{-$

Table 2

Selected bond distances (Å) and bond and dihedral angles (°) of  $[\text{Co}_3\text{Cp}_3(\mu_3\text{-CPh})_2\{\mu\text{-Ag}(\text{O}_2\text{CCF}_3)\}]$  (**2**)

Bond distances					
Ag(1)–Co(1)	2.6150(7)	Co(2)–C(1)	1.890(4)		
Ag(1)–Co(2)	2.6276(7)	Co(2)–C(8)	1.879(4)		
Ag(1)–O(1)	2.351(4)	Co(3)–C(1)	1.870(4)		
Ag(1)–O(2)	2.719(7)	Co(3)–C(8)	1.868(4)		
Co(1)–Co(2)	2.4785(8)	O(1)–C(30)	1.210(7)		
Co(1)–Co(3)	2.3742(8)	O(2)–C(30)	1.205(6)		
Co(1)–C(1)	1.868(4)	C(1)–C(2)	1.467(6)		
Co(1)–C(8)	1.875(4)	C(8)–C(9)	1.463(6)		
Co(2)–Co(3)	2.3575(8)				
Bond angles					
Co(1)–Ag(1)–Co(2)	56.43(2)	Co(2)–Co(1)–Co(3)	58.08(2)		
Ag(1)–Co(1)–Co(2)	62.04(2)	Co(1)–Co(2)–Co(3)	58.74(2)		
Ag(1)–Co(2)–Co(1)	61.53(2)	Co(1)–Co(3)–Co(2)	63.17(2)		
Dihedral angles <sup>a</sup>					
Plane 1	plane 2		plane 1	plane 2	
Co <sub>3</sub>	Co <sub>2</sub> Ag	162.7	CpCo(1)	CpCo(3)	71.4
CpCo(1)	CpCo(2)	29.9	CpCo(2)	CpCo(3)	79.4

<sup>a</sup> CpCo(*x*) denotes the plane of the cyclopentadienyl ligand bonded to Co(*x*).

COMe) $\{\mu\text{-Au}(\text{PPh}_3)\}$ ], shows a dihedral angle value of 155.4° [22], which is similar to those of the current complexes.

In the structure of **2**, the trifluoroacetate group is non-symmetrically connected to the Ag atom, with the two Ag–O distances being 2.351(4) and 2.719(7) Å. The

trifluoroacetate group in  $[\text{Rh}_2\text{Cp}_2(\mu\text{-CO})(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)\{\mu\text{-Ag}(\text{O}_2\text{CCF}_3)\}]$  is a bidentate ligand with Ag–O distances of 2.522(9) Å [23], which are close to the average Ag–O bond distances of **2**. The nitrate ion in **3** chelates with the Ag atom. The difference between the two Ag–O bond distances in **3** ( $\Delta_{\text{AgO}} = 0.194$  Å) is smaller than that observed in **2** ( $\Delta_{\text{AgO}} = 0.368$  Å).

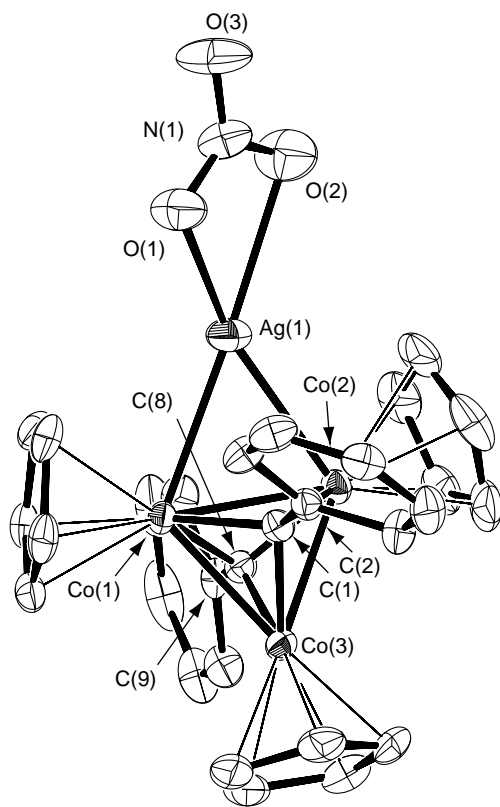


Fig. 2. ORTEP drawing of **3** with 30% probability. Hydrogen atoms are omitted for clarity.

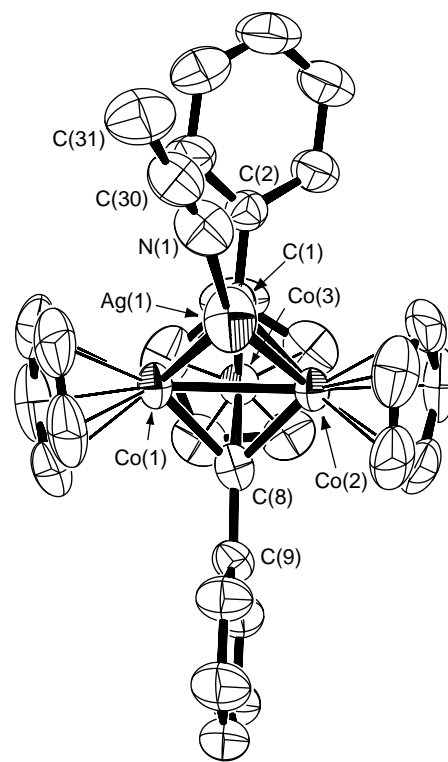


Fig. 3. ORTEP drawing of **4PF<sub>6</sub>** with 30% probability. Hydrogen atoms are omitted for clarity.

Table 3

Selected bond distances (Å) and bond and dihedral angles (°) of  $[\text{Co}_3\text{Cp}_3(\mu_3\text{-CPh})_2\{\mu\text{-Ag}(\text{NO}_3)\}]$  (**3**)

<i>Bond distances</i>					
Ag(1)–Co(1)	2.6483(8)		Co(2)–C(1)		1.893(5)
Ag(1)–Co(2)	2.6449(8)		Co(2)–C(8)		1.865(5)
Ag(1)–O(1)	2.374(5)		Co(3)–C(1)		1.891(5)
Ag(1)–O(2)	2.568(5)		Co(3)–C(8)		1.866(5)
Co(1)–Co(2)	2.4837(9)		O(1)–N(1)		1.229(7)
Co(1)–Co(3)	2.3684(9)		O(2)–N(1)		1.230(6)
Co(1)–C(1)	1.881(5)		O(3)–N(1)		1.227(6)
Co(1)–C(8)	1.882(5)		C(1)–C(2)		1.470(7)
Co(2)–Co(3)	2.3662(9)		C(8)–C(9)		1.478(7)
<i>Bond angles</i>					
Co(1)–Ag(1)–Co(2)	55.97(2)		Co(2)–Co(1)–Co(3)		58.32(3)
Ag(1)–Co(1)–Co(2)	61.95(2)		Co(1)–Co(2)–Co(3)		58.40(3)
Ag(1)–Co(2)–Co(1)	62.08(2)		Co(1)–Co(3)–Co(2)		63.28(3)
<i>Dihedral angles<sup>a</sup></i>					
Plane 1	plane 2		plane 1	plane 2	
Co <sub>3</sub>	Co <sub>2</sub> Ag	157.7	CpCo(1)	CpCo(3)	76.9
CpCo(1)	CpCo(2)	30.1	CpCo(2)	CpCo(3)	74.3

<sup>a</sup> CpCo(*x*) denotes the plane of the cyclopentadienyl ligand bonded to Co(*x*).

### 3.3. Equilibrium of the Ag adducts in solution

The stabilities and the conversion to  $\mathbf{1}^+$  of the silver adducts in solution depend strongly on the solvents.

#### 3.3.1. ESR study

Dissolution of  $\mathbf{4PF}_6$  in  $\text{CD}_2\text{Cl}_2$  showed deposition of Ag metal. A broad isotropic singlet ESR signal of  $g = 2.19$  was observed at 77 K for the resulting solution. It is the same as the signal of  $\mathbf{1ClO}_4$  in  $\text{CH}_2\text{Cl}_2$  at 77 K [4]. The integrated intensity of the signal indicates that the silver adduct converted quantitatively to the cation radical,  $\mathbf{1}^+$ . On the other hand, a  $\text{CH}_2\text{Cl}_2$  solution of **2** showed neither deposition of Ag metal nor ESR signal.

Contrary to the behavior in  $\text{CD}_2\text{Cl}_2$ , complex  $\mathbf{4PF}_6$  dissolves into MeCN with no deposition of silver metal.

Its frozen solution at 77 K showed a weak broad axially symmetric ESR signal of  $g_{\perp} = 2.22$  and  $g_{\parallel} = 2.11$ . This  $g$  tensor is the same as that of  $\mathbf{1}^+$  in MeCN with 0.1 M  ${}^n\text{Bu}_4\text{NClO}_4$  ( $M = \text{mol dm}^{-3}$ ) [4]. An MeCN solution of **2** showed the same ESR spectrum, but with slightly weaker intensity. Comparison of integrated intensities of ESR signals of **2** and  $\mathbf{4PF}_6$  in MeCN with that of  $\mathbf{1}^+$  in MeCN containing 0.1 M  ${}^n\text{Bu}_4\text{NClO}_4$  revealed that 1–2% of **2** and  $\mathbf{4PF}_6$  converts to  $\mathbf{1}^+$  in MeCN solutions.

#### 3.3.2. ${}^1\text{H}$ NMR study in $\text{CD}_2\text{Cl}_2$

Fig. 4 shows the  ${}^1\text{H}$  NMR spectra of **2** (9 mM) in  $\text{CD}_2\text{Cl}_2$ . At  $-60$  °C, two singlet peaks assigned to the cyclopentadienyl groups were observed at 4.76 ppm (10H) and 4.99 ppm (5H). Their intensity ratio shows that the former and the latter signals are due to the

Table 4

Selected bond distances (Å) and bond and dihedral angles (°) of  $[\text{Co}_3\text{Cp}_3(\mu_3\text{-CPh})_2\{\mu\text{-Ag}(\text{NCMe})\}]\text{PF}_6$  ( $\mathbf{4PF}_6$ )

<i>Bond distances</i>					
Ag(1)–Co(1)	2.6572(6)		Co(2)–Co(3)		2.3812(7)
Ag(1)–Co(2)	2.6330(6)		Co(2)–C(1)		1.891(4)
Ag(1)–N(1)	2.168(4)		Co(2)–C(8)		1.872(4)
Co(1)–Co(2)	2.4578(7)		Co(3)–C(1)		1.873(4)
Co(1)–Co(3)	2.3612(7)		Co(3)–C(8)		1.862(4)
Co(1)–C(1)	1.891(4)		C(1)–C(2)		1.481(5)
Co(1)–C(8)	1.872(4)		C(8)–C(9)		1.473(5)
<i>Bond angles</i>					
Co(1)–Ag(1)–Co(2)	55.37(2)		Co(2)–Co(1)–Co(3)		59.18(2)
Ag(1)–Co(1)–Co(2)	61.82(2)		Co(1)–Co(2)–Co(3)		58.39(2)
Ag(1)–Co(2)–Co(1)	62.82(2)		Co(1)–Co(3)–Co(2)		62.43(2)
<i>Dihedral angles<sup>a</sup></i>					
Plane 1	plane 2		plane 1	plane 2	
Co <sub>3</sub>	Co <sub>2</sub> Ag	151.6	CpCo(1)	CpCo(3)	76.0
CpCo(1)	CpCo(2)	33.9	CpCo(2)	CpCo(3)	71.8

<sup>a</sup> CpCo(*x*) denotes the plane of the cyclopentadienyl ligand bonded to Co(*x*).

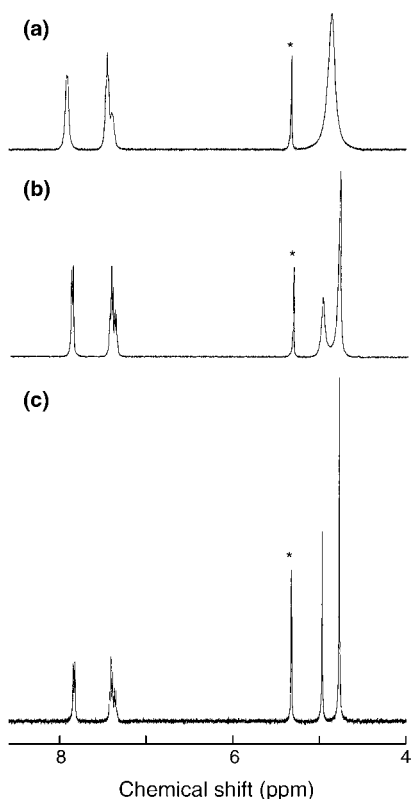


Fig. 4.  $^1\text{H}$  NMR spectra of **2** in  $\text{CD}_2\text{Cl}_2$  at: (a) 20 °C, (b) 0 °C, and (c) -60 °C. The asterisk denotes  $\text{CHDCl}_2$ .

$\text{Cp}(\text{CoAg})$  and  $\text{Cp}(\text{Co})$  protons, respectively. With increasing temperature, these peaks broaden (Fig. 4(b)), and finally average into a broad singlet peak (Fig. 4(a)). This result indicates that the bridging Ag atom is moving over the three Co–Co edges in  $\text{CD}_2\text{Cl}_2$  intramolecularly or intermolecularly. Similar fluxional behavior has been observed in the protonated species of alkylidyne-capped clusters [24–26]. The phenyl groups on the capping carbon atoms of **2** are non-equivalent due to the non-planar structure of the  $\text{Co}_3\text{Ag}$  core in the crystal. However, the two phenyl groups are equivalent in the  $^1\text{H}$  NMR spectrum, even at -60 °C. This should be so, because the difference in their chemical shifts is smaller than the rate of jumping of the Ag group between both the sides of the  $\text{Co}_3$  plane. The chemical shifts of **3** in  $\text{CD}_2\text{Cl}_2$  are listed in Table 5 together with those of related complexes. A similar temperature dependence of the  $^1\text{H}$  NMR spectra was observed for **3**.

### 3.3.3. $^1\text{H}$ NMR study in $\text{CD}_3\text{CN}$

When dissolved in  $\text{CH}_2\text{Cl}_2$ ,  $4\text{PF}_6$  converts quantitatively to  $\mathbf{1}^+$  with deposition of  $\text{Ag}^0$ . However, the ESR study in the previous section shows that a small portion of the silver adduct dissolved in MeCN has converted to the cationic radical,  $\mathbf{1}^+$ . To see the fate of the main portion of  $4\text{PF}_6$  dissolved in acetonitrile, we examine its  $^1\text{H}$  NMR. Fig. 5(a) shows the  $^1\text{H}$  NMR spectrum of

Table 5  
 $^1\text{H}$  NMR chemical shift (ppm) for **2**, **3**, and  $4\text{PF}_6$  in  $\text{CD}_2\text{Cl}_2$  and  $\text{CD}_3\text{CN}^a$

Complex	Temperature (°C)	<i>o</i> -Ph	<i>m</i> -Ph	<i>p</i> -Ph	Cp
In $\text{CD}_2\text{Cl}_2$					
<b>2</b>	20	7.90	7.44	7.39	4.83
	-60	7.81	7.40	7.34	4.76, 4.99
<b>3</b>	20	7.85	7.42	7.36	4.76, 4.99
	-20	7.85	7.42	7.36	4.76, 4.99
In $\text{CD}_3\text{CN}$					
<b>2</b>	20	7.98	7.47	7.27	4.62
	-40	7.98	7.43	7.35	4.71
<b>3</b>	20	7.88	7.50	7.20	4.55
	20	7.88	7.50	7.20	4.55
$4\text{PF}_6$	20	7.75	7.52	7.07	4.44
$\mathbf{1}^b$	20	8.30	7.53	7.43	4.46
$\text{IClO}_4^b$	20	-7.77	9.67	-8.43	-5.72

<sup>a</sup> Concentration of the sample is 9–11 mM in  $\text{CD}_2\text{Cl}_2$  and 5–7 mM in  $\text{CD}_3\text{CN}$ .

<sup>b</sup> Ref. [4].

$4\text{PF}_6$  (5 mM) in  $\text{CD}_3\text{CN}$  at 20 °C. In the Cp region, there is a singlet peak at 4.44 ppm. The single peak of the Cp ligands suggests that there is a rapid exchange equilibrium between  $\mathbf{1}^+$  and  $\mathbf{4}^+$ . The peaks of the phenyl protons exist as broad singlets for *o*-Ph (7.75 ppm) and *p*-Ph (7.07 ppm), and as a relatively sharp triplet for *m*-Ph protons (7.52 ppm). The broadening of the *o*-Ph and *p*-Ph signals and the sharp signal of the *m*-Ph are also due to rapid exchange reaction between  $\mathbf{1}^+$  and  $\mathbf{4}^+$ . Signals of *o*-Ph, *p*-Ph, and *m*-Ph of  $\mathbf{1}^+$  are paramagnetically shifted and have been observed at -7.77, -8.43, and 9.67 ppm, respectively, at 20 °C [4]. The difference of the chemical shift of the *m*-Ph proton between  $\mathbf{1}^+$  and  $\mathbf{4}^+$  is far smaller than those of the *o*-Ph and *p*-Ph peaks. This is the origin of the line width differences between *m*-Ph and *o*- and *p*-Ph  $^1\text{H}$  signals. The  $^1\text{H}$  NMR and the ESR spectra showed no detectable changes upon aging of the  $4\text{PF}_6$  solution. This suggests that the equilibrium including  $\mathbf{1}^+$  is established in solution. Fig. 5(b) shows

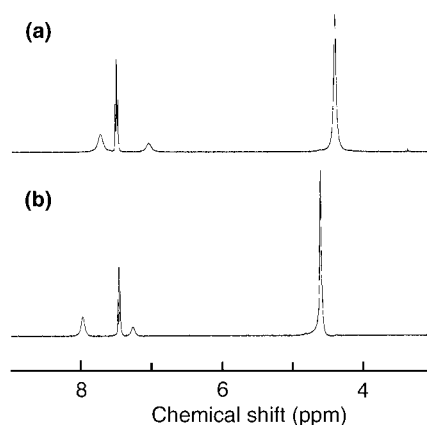


Fig. 5.  $^1\text{H}$  NMR spectra of: (a)  $4\text{PF}_6$  and (b) **2** in  $\text{CD}_3\text{CN}$  at 20 °C. The concentrations of the complexes are 5 mM.

Table 6

Qualitative summary of product or equilibrium mixture from the reaction of  $[\text{Co}_3\text{Cp}_3(\mu\text{-Ph})_2]$  (**1**) and silver salt<sup>a</sup>

Ag salt	In $\text{CH}_2\text{Cl}_2$	In MeCN
$\text{AgPF}_6$ $\text{AgClO}_4$ $\text{AgBF}_4$	$1^+$	$[\text{Co}_3\text{Ag}]^+ + 1^+$
$\text{AgO}_2\text{CCF}_3$ $\text{AgNO}_3$	$[\text{Co}_3\text{Ag}]^+$	$[\text{Co}_3\text{Ag}]^+ + 1^+$

<sup>a</sup> $[\text{Co}_3\text{Ag}]^+$  represents a  $\text{Ag}^+$  adduct of **1**.

the  $^1\text{H}$  NMR spectrum of **2** in  $\text{CD}_3\text{CN}$ . The NMR spectrum of **2** in  $\text{CD}_3\text{CN}$  (Fig. 5(b)) differs from that of **4PF<sub>6</sub>** (Fig. 5(a)). This shows that the  $\text{CF}_3\text{CO}_2^-$  ion in **2** does not dissociate completely. If the  $\text{CF}_3\text{CO}_2$  ligand bound to the Ag atom of **2** were completely replaced by MeCN, the NMR spectrum of **2** in acetonitrile must be the same as that of **4PF<sub>6</sub>**. When the temperature was lowered to  $-40^\circ\text{C}$ , the Cp signal shifted to the lower field and the peak width broadened. It means that the rate of the exchange equilibrium including **2** and  $1^+$  is still rapid at this temperature. A  $\text{CD}_3\text{CN}$  solution of **3** shows similar  $^1\text{H}$  NMR spectra to those of **2**.

For the MeCN solutions of **2**, **3**, and **4PF<sub>6</sub>**, deposition of Ag metal was not observed, although the oxidation of **1** to its cationic radical was detected by ESR (vide supra). Silver ion might be an only possible oxidant in the solution. We suppose that a soluble  $\text{Ag}^0$  species is included in the equilibrium in the MeCN solution. Mononuclear silver(0) species should have one odd electron. However, no such ESR signal was detected in all the solutions of the  $\text{Co}_3\text{Ag}$  complexes. A dinuclear  $\text{Ag}^0$  complex with the  $S=0$  spin state might be a possible candidate in the equilibrium.

#### 4. Concluding remarks

The formation of two types of products (the cationic radical  $1^+$  and the Ag-adducts), depends on the reduction potential of the  $\text{Ag}^+$  ion [1]. The oxidation potential of **1** is  $-0.05\text{ V}$  versus  $\text{Fc}^+/\text{Fc}$  in  $\text{CH}_2\text{Cl}_2$ , and  $-0.06\text{ V}$  versus  $\text{Fc}^+/\text{Fc}$  in MeCN [4]. In  $\text{CH}_2\text{Cl}_2$ ,  $\text{Ag}^+$  is a relatively strong oxidizing reagent, whose reduction potential has been estimated as being  $0.65\text{ V}$  versus  $\text{Fc}^+/\text{Fc}$  [1]. The  $\text{Ag}^+$  reduction potential is expected to shift to a negative value when  $\text{CF}_3\text{CO}_2^-$  or  $\text{NO}_3^-$  coordinates to  $\text{Ag}^+$ , and anion-coordinated  $\text{Ag}^+$  cannot oxidize **1**. The  $\text{Ag}^+$  ion in MeCN is a weaker oxidizing reagent than the  $\text{Ag}^+$  ion in  $\text{CH}_2\text{Cl}_2$ , since the  $\text{Ag}^+$  ion is coordinated by MeCN molecules. Although the formation of  $1^+$  was detected in MeCN,  $1^+$  is only a minor component in the equilibrium with the silver adduct. Observed reactions of **1** with various silver(I) salts in  $\text{CH}_2\text{Cl}_2$  and MeCN are summarized qualitatively in Table 6.

#### 5. Supplementary material

Crystallographic data (excluding structural factors) for the structural analysis of **2**, **3**, and **4PF<sub>6</sub>** have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 217788, 217789, and 217790. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

#### Acknowledgements

This work was supported by Grants-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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