

Molecular Structure of $\text{Co}_2(\mu\text{-Alkyne})$ Complex Containing $\text{Ph}_2\text{PC}_5\text{F}_6\text{PPh}_2$ Ligand

Makoto Minato*, Yasutada Miyato, Masaki Kakeya

Department of Materials Chemistry, Graduate School of Engineering, Yokohama National University, Yokohama, Japan

Email: minato@ynu.ac.jp

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Abstract

Oxidative-decarbonylation of $\text{Co}_2(\text{CO})_6(\mu\text{-PhC}\equiv\text{CH})$ with Me_3NO in the presence of an electron deficient ligand, $\text{Ph}_2\text{PC}_5\text{F}_6\text{PPh}_2(\text{F}_6\text{FOS})$, produces $\text{Co}_2(\text{CO})_4(\mu\text{-PhC}\equiv\text{CH})(\text{F}_6\text{FOS})$, (**1**). The metrical values of **1** have been compared to those of the closely related cobalt carbonyl alkyne compound **A** containing (*Z*)- $\text{Ph}_2\text{PCH}=\text{CHPPh}_2$ (*Z*-dppe) ligand. Strikingly anomalous is an alkyne $\text{C}\equiv\text{C}$ bond (1.34(1) Å) in **1**, which is somewhat elongated compared to **A** (1.31(1) Å). When taking a strong electron-withdrawing power of fluoride atom into account, F_6FOS ligand appeared to reduce the π -back-donation ability of cobalt atom, making this bond shortened in comparison to the same bond in **A**. Bond lengthening in the alkyne $\text{C}\equiv\text{C}$ bond in **1** is attributed to the enhanced electron donor ability of F_6FOS compared to *Z*-dppe and can be understood by examining resonance structures of F_6FOS ligand.

Keywords

Alkyne-Bridged Cobalt Complex, Electron Deficient Ligand, Crystal Structure, Coordinated Alkyne $\text{C}\equiv\text{C}$ Bond

1. Introduction

We have become interested in ligands of the type $\text{R}_2\text{PC}_5\text{F}_6\text{PR}_2$ ($\text{R} = \text{Ph}$, *cyclo*- C_6H_{11}), which are reported by Cullen (**Chart 1**) [1].

These ligands seem to display unique electronic properties in comparison to typical diphosphine ligands such as DIPHOS ($\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) because they possess a low-lying π^* orbital due to a bridging perfluorocyclopentenyl ring, which is recognized to be a strong electron-withdrawing group [2]. Therefore an organometallic compound with this type of ligand is anticipated to serve as an effective electron reservoir by stabilizing electron

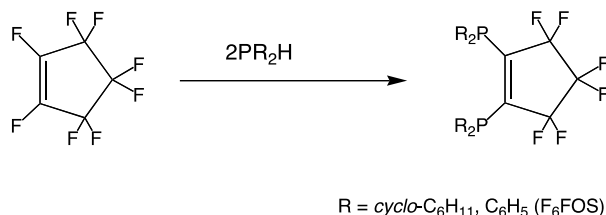


Chart 1. Preparation of diphosphine ligands containing perfluorocyclopentenyl ring.

counts in excess of 18-electrons [3] [4]. To establish the electronic influence of F₆FOS (R = Ph, 1,2-bis(diphenylphosphino)hexafluorocyclopentene) ligand, we wish to report the synthesis and single-crystal X-ray diffraction study of an alkyne-bridged cobalt complex containing F₆FOS.

Energetic investigations of cobalt-alkyne compounds involving various bidentate phosphine ligands have been performed [5]-[10]. For example, Bott and coworkers reported that the rigid diphosphine, (Z)-Ph₂PCH=CHPh₂ (Z-dppe), reacted with Co₂(CO)₆(μ-PhC≡CH) to yield the chelating complex Co₂(CO)₄(μ-PhC≡CH) [(Z)-dppe], (**A**) [11]. On the basis of Bott's results, we set out to prepare the alkyne-bridged cobalt complex **1** containing F₆FOS ligand that would differ from complex **A** in the amount of electron density on the metal center but would be sterically very similar with respect to coordination (**Scheme 1**).

We reckoned that a comparison of the metrical values for **1** and **A** served to elucidate the electronic effect of F₆FOS ligand. In addition, no crystallographic study on F₆FOS appears to have been recorded, and consequently data on this ligand are also briefly reported.

2. Experimental Section

2.1. General Considerations

Unless otherwise noted, all reactions were carried out under anaerobic and anhydrous conditions using Ar or N₂ and conventional Schlenk techniques using the general methods. NMR spectra were measured on the following instruments, at the frequencies listed, unless stated otherwise: Jeol JMN-AL 400 and Jeol FX270, ¹H NMR (400 MHz), ³¹P (161.7 MHz), ¹⁹F NMR (376.05 MHz). Chemical shifts are quoted to the following references: ¹H NMR ((CH₃)₄Si, 0 ppm); ³¹P NMR (PPh₃, 0 ppm); ¹⁹F NMR (CF₃COOH, -78.50 ppm).

F₆FOS [1] and Co₂(CO)₆(μ-PhC≡CH) [12] were prepared by following literature procedures.

2.2. Synthesis of Complex 1

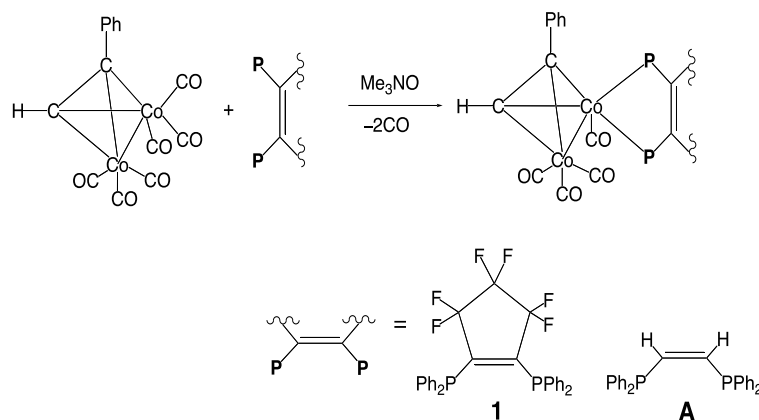
To 0.080 g (0.21 mmol) of Co₂(CO)₆(μ-PhC≡CH) and 0.11 g (0.20 mmol) of F₆FOS in 15 mL of ethanol was added 0.030 mg (0.40 mmol) of Me₃NO₂. The solution was stirred for 24 h at ambient temperature. The dark-red precipitate was formed and the supernatant was removed. The resulting solid was washed with hexane and pumped dry to yield **1** (0.11 g, 62%). Crystals suitable for an X-ray structural analysis were obtained by recrystallization from dichloromethane/*n*-heptane. Complex **1**: ¹H NMR (CDCl₃, 25°C, 400 MHz): δ 4.9 - 5.0 (br m, 1H, ≡CH), 7.0 - 7.8 (m, 25H, Ph protons); ³¹P{¹H} NMR (CDCl₃, 25°C, 160 MHz): δ 69.6 (s, 1P), 80.2 (s, 1P); ¹⁹F NMR (CDCl₃, 25°C, 376.05 MHz) δ -132.61 (dt, *J* = 11, 236 Hz, 1F), -131.29 (dt, *J* = 11, 236 Hz, 1F), -111.34 (d, *J* = 267, 2F), -109.60 (d, *J* = 271, 1F), -109.53 (d, *J* = 267, 1F); IR (KBr, ν (C≡O, cm⁻¹): 1929, 1960, 2012, 2056.

2.3. Single Crystal X-Ray Diffraction

Selected structural details for the structures of F₆FOS ligand and complex **1** are included in **Table 1** and full crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 1052995 and 1052994, respectively. Copies of these data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

3. Results and Discussion

The ligand, F₆FOS, was synthesized from HPPH₂ and octafluorocyclopentene. Complex **1** was synthesized in a



Scheme 1. The reactions of the alkyne-bridged binuclear Co complex with F₆FOS and Z-dppe.

Table 1. Experimental details.

Crystal data	Complex 1	F ₆ FOS
Chemical formula	C ₄₁ H ₂₆ Co ₂ F ₆ O ₄ P ₂	C ₂₉ H ₂₀ F ₆ P ₂
Formula weight	876.46	544.41
Crystal system, space group	Triclinic, P-1 (#2)	Triclinic, P-1 (#2)
Temperature (K)	-113	-113
<i>a</i> , <i>b</i> , <i>c</i> (Å)	11.472 (2), 18.752 (3), 19.004 (3)	9.818 (2), 10.028 (2), 13.505 (4)
<i>α</i> , <i>β</i> , <i>γ</i> (°)	68.083 (6), 84.063 (9), 81.256 (8)	80.307 (10), 82.954 (10), 73.805 (10)
<i>V</i> (Å ³)	3743.8 (11)	1254.6 (5)
<i>Z</i>	4	2
Radiation type	MoKα (<i>I</i> = 0.71070 Å)	MoKα (<i>I</i> = 0.71070 Å)
<i>μ</i> (mm ⁻¹)	1.0438	0.2350
Crystal size (mm)	0.12 × 0.05 × 0.04	0.32 × 0.21 × 0.10
Data collection		
Diffractometer	Rigaku Saturn CCD area detector	Rigaku Saturn CCD area detector
Absorption correction	Multi-scan (CrystalClear; Rigaku, 1999)	Multi-scan (CrystalClear; Rigaku, 1999)
<i>T</i> _{min} , <i>T</i> _{max}	0.855, 0.959	0.573, 0.977
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	27592, 15685, 8015	9167, 5304, 2742
<i>R</i> _{int}	0.059	0.078
(sinθ/λ) _{max} (Å ⁻¹)	0.650	0.650
Refinement		
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.0793, 0.1849, 1.004	0.0565, 0.1390, 1.033
No. of reflections	15685	5304
No. of parameters	1045	354
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H-atom parameters constrained
□□ _{max} , Δρ _{min} (e Å ⁻³)	1.68, -0.68	0.48, 0.52

Data were collected and processed using CrystalClear (Rigaku).

straightforward fashion from $\text{Co}_2(\text{CO})_6(\mu\text{-PhC}\equiv\text{CH})$ and F_6FOS in the presence of the oxidative-decarbonylation reagent Me_3NO . The IR spectrum of **1** shows three strong CO absorptions in the range of 1900 - 2100 cm^{-1} . In the ^1H NMR spectrum of **1**, the alkyne proton resonance occurs at δ 5.0 ppm, which is 0.8 ppm upfield approximately from that of the parent complex $\text{Co}_2(\text{CO})_6(\mu\text{-PhC}\equiv\text{CH})$. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **1** displays two phosphorus signals at δ 69 ppm and δ 80 ppm, showing a downfield coordination shift (δ -15 ppm in F_6FOS). In contrast to F_6FOS ligand (giving two sets of fluorine resonances in a 2:1 intensity ratio), **1** shows five types of inequivalent fluorine atoms in the ^{19}F NMR spectrum due to the asymmetry imposed by the formation of the chelate ring. There are two doublets of pseudotriplets at δ -132.61 ($J(\text{FF}) = 236$ and 11 Hz) and -131.29 ppm ($J(\text{FF}) = 236$ and 11 Hz), which may be assigned to the central two fluorine atoms in the C_5F_6 ring. In addition, the three pseudodoublets at δ -109.53 ($J(\text{FF}) = 267$ Hz), -109.60 ($J(\text{FF}) = 271$ Hz), and -111.34 ppm ($J(\text{FF}) = 267$ Hz) are attributable to rest of the four fluorine atoms in the ring. This spectrum also indicates strong germinal coupling between fluorine atoms above and below the plane of the ring.

The molecular structures of **1** and F_6FOS are shown in **Figure 1** and **Figure 2**. Pertinent structural parameters for F_6FOS and **1** are compared in **Table 2**.

Complex **1** crystallizes in the triclinic space P-1 (#2). The alkyne portion of **1** is coordinated through its π -bond to Co1 and Co2, while F_6FOS ligand is coordinated to Co1. In the structure, there is a distorted octahedral geometry about each cobalt atom, the two alkyne carbons and two cobalt atoms forming a tetrahedral unit.

It is instructive to compare the geometry about the F_6FOS fragment in **1** to that of the parent F_6FOS ligand. Upon coordination to cobalt atom, the bond lengths and angles of the ligand itself alter significantly. The mean P-C bond distance in **1** at 1.834 Å is somewhat longer than the corresponding value of 1.824 Å in F_6FOS while the C=C bond distance at 1.34(1) Å in the C_5F_6 ring of **1** is slightly shorter than that observed in F_6FOS ligand itself, 1.370(8) Å. This may be explained by a substantial decrease of degree of π -bonding between the phos-

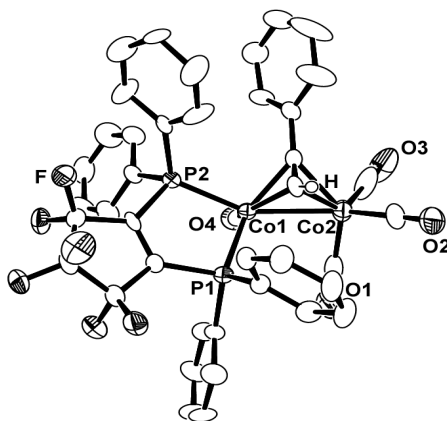


Figure 1. The molecular structure of complex **1**.

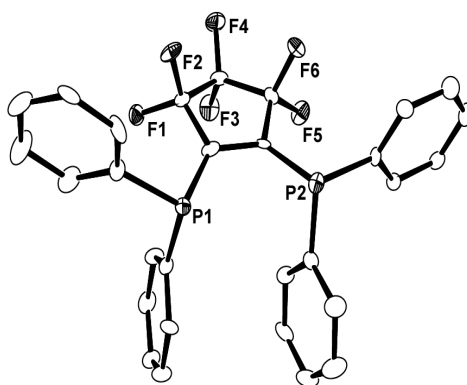
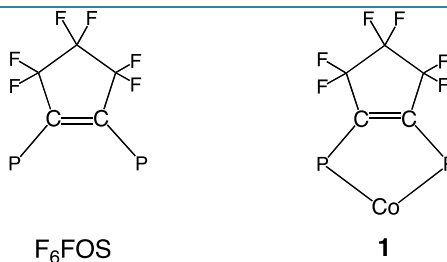


Figure 2. The molecular structure of ligand F_6FOS .

Table 2. Comparison of structural parameters for F₆FOS ligand and Complex **1**.

	P-C bond (av., Å)	C=C bond (Å)	P-P-C-C angle (av., deg.)
F ₆ FOS	1.824	1.370 (8)	123.4
Complex 1	1.834	1.34 (1)	119.0



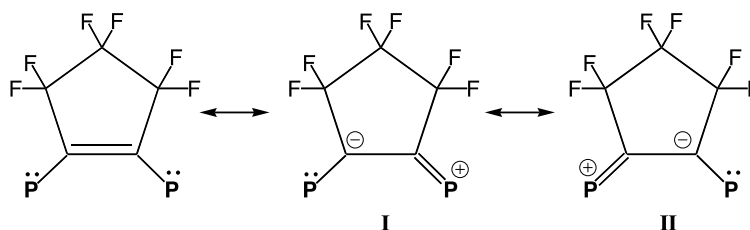
phorus lone-pair orbitals and π -orbital of the C=C bond in **1**. For F₆FOS ligand, three resonance forms may be drawn as shown in [Scheme 2](#).

The structure **I** or **II** makes a considerable contribution to the hybrid because the strong electron-withdrawing effect of fluoride substituents decreases the electron density at the charge-bearing carbons. This structural feature accommodates some degree of P-C multiple bonding. Consequently, this gives the C=C bond of F₆FOS a partial single-bond character and lengthens it. Then, coordination of the ligand to cobalt atom would lead to reduce π -donation from the electron pairs on phosphorus atoms. As expected, the mean endocyclic P-C=C bond angle of 119.0° in **1** is smaller than that of 123.4° in F₆FOS ligand.

Our major objective of this study is to establish how the substitution of Z-dppe for F₆FOS affects the structure of the rest of the complex. Since complexes **1** and **A** were expected to be sterically very similar with respect to the polyhedral Co₂ core, it could be argued that any observed structural differences would have their origin in the electronic properties inherent to each ancillary diphosphine ligand.

To begin with, we verified the bonding geometry about Co^I atoms in **1** and **A**. [Table 3](#) compares pertinent distances and bond angles of **1** and **A**. The P²-Co^I-P¹ bite angle in **1** is 90.4(1)° and, the Co^I-P¹ bond with a bond length of 2.216(3) and Co^I-P² bond with a bond length of 2.175(3) average at 2.196 Å. These values are analogous to those reported for **A** (88.39(8)° and 2.188 Å, respectively). Furthermore, the Co^I-CO bond distance of 1.769(9) Å in **1** is essentially consistent with the value that observed in **A** (1.769(8) Å). It may be inferred from these facts that **A** and **1** are sterically very similar with respect to coordination around Co^I, and therefore, the steric effects from the substituents (H versus C₃F₆ frame) of the C³=C⁴ bonds on the nature of the rest of the molecules are rather weak. As a result, only the electronic effect will be at the origin of any variations in the measured parameters.

Interestingly, the C³=C⁴ bond distance at 1.34(1) Å in the C₅F₆ ring of **1** is somewhat longer than the corresponding bond distance in **A** (1.328(9) Å). This behavior confirms that the C³=C⁴ bond in **1** still has partial single-bond character, as stated above. One might think the alkyne C¹≡C² bond length is a better criterion for Co(π^* C) interaction due to the bond weakening resulting from back donation of d-electrons on the Co atom into an empty π^* orbital. The alkyne C¹≡C² distance of **1** is found to be 1.34(1) Å. Contrary to our expectation, this distance is slightly longer than that in **A** (1.31(1) Å) and is equal to a value found for the C³=C⁴ bond in **1**. We envisaged that electron-withdrawing C₅F₆ ring in F₆FOS should decrease in the amount of electron density of Co^I atom in **1**, which reduces the π^* -back-donation ability of the atom, making this bond closer to the triple bond in free PhC≡CH. As a consequence, in the case of **1** the alkyne C¹≡C² bond was expected to be shortened in comparison to the same bond in **A**. However, the lengthening of the alkyne C¹≡C² distance in **1** relative to **A** is observed. The result provides evidence that the Co^I atom in **1** may be acting as a better donor of electron density than the corresponding cobalt atom in **A**. As described above, the C³=C⁴ bond distance in the C₅F₆ ring of **1** has partial single-bond character, suggesting that the C³ and C⁴ atoms have sp^3 character to some extent. It is well known that electronegativity values vary with the bond order [13]. So the phosphorus atoms in **1** may have a greater σ -donating ability than those in **A** because carbon atoms with sp^2 bonding generally have a greater electron-withdrawing power than those with sp^3 bonding. Hence, it can be concluded that by substitution of Z-dppe by F₆FOS the electron density on the cobalt atom has not indeed decreased, but rather resulting in more

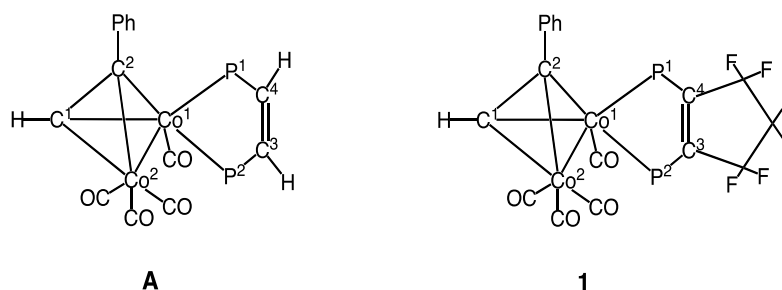


Scheme 2. The resonance forms of F_6FOS .

Table 3. Comparison of structural parameters for **A** and Complex **1**.

	A ^a	Complex 1
P-Co ¹ bond (av., Å)	2.188	2.196
P ² -Co ¹ -P ¹ angle (deg.)	90.4(1)	88.39(8)
Co ¹ -CO bond (Å)	1.769(8)	1.769(9)
C ³ =C ⁴ bond (Å)	1.328(9)	1.34(1)
C ¹ ≡C ² bond (Å)	1.31(1)	1.34(1)
Co ¹ -C ¹ bond (Å)	1.920(8)	1.92(1)
Co ¹ -C ² bond (Å)	1.929(7)	1.962(8)
Co ² -C ¹ bond (Å)	1.991(9)	2.004(7)
Co ² -C ² bond (Å)	1.983(8)	2.000(8)
Co ² -CO bond (av., Å)	1.765	1.773

^a Reference [11].



π -back-donation to the alkyne ligand.

This lengthened the alkyne $C^1\equiv C^2$ distance in **1** is counter-balanced by the short Co^1-Co^2 distance of 2.471(2) Å, somewhat shorter than the corresponding bond length of 2.495(2) Å found in **A**. In addition, the $Co-C$ (alkyne) distances in **1** are meaningfully longer than the same bond distances in **A** (1.92(1) versus 1.920(8), 1.962(8) versus 1.929(7), 2.000(8) versus 1.983(8), 2.004(7) versus 1.991(9) Å, respectively). In comparison to **A**, it thus appears that in **1** the alkyne ligand remains directed away from Co^1 atom, whereas the $Co^2(CO)_3$ fragment is located more close to Co^1 . The Co^2-CO bond lengths in **1** average to 1.773 Å, which is close to the value reported in (**A**) (1.765 Å).

4. Concluding Remarks

The bidentate ligand F_6FOS displaces two carbonyl groups from $Co_2(CO)_6(\mu-PhC\equiv CH)$ to give $Co_2(CO)_4(\mu-PhC\equiv CH)(F_6FOS)$ (**1**), the structure of which is compared with that of a closely related cobalt carbonyl alkyne compound (**A**). The crystal structure of **1** confirms that the electron-withdrawing C_5F_6 group in F_6FOS makes the alkyne $C\equiv C$ lengthened in comparison to the same bond in **A**.

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