# Synthesis of fluorophenyl carbonyl cobalt(I) complexes and decarbonylation of 2,4,5-trifluorobenzaldehyde catalyzed by CoMe(PMe₃)₄

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### A B S T R A C T

Three fluorophenyl carbonyl cobalt(I) complexes $Ph_F(PMe_3)_3Co(CO)$ (**1–3**) were synthesized by the reaction of fluoro-benzaldehydes with $CoMe(PMe_3)_4$ via C–H bond activation and decarbonylation reaction. The dicarbonyl cobalt(I) complex $(2,4-F_2C_6H_3)Co(CO)_2(PMe_3)_2$ (**4**) was obtained by reacting of complex **1** with CO. Complex **1** reacted with pentafluorobromobenzene afforded cobalt(II) bromide $(2,4-F_2C_6H_3)Co(Br)(PMe_3)_3$ (**5**) with the formation of perfluorinated diphenyl. The reaction of complex **3** and phenylacetylene delivered the hydrido diethinyl cobalt(III) complex $(PhC{\equiv}C)_2Co(H)(PMe_3)_3$ (**6**) with 1,2,4-trifluorobenzene as a byproduct. The molecular structures of **1**, **4** and **5** were determined by X-ray diffraction. Furthermore, we found that $CoMe(PMe_3)_4$ could be used as a catalyst for the catalytic decarbonylation of 2,4,5-trifluorobenzaldehyde with triethylsilane as a hydrogen source.

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## 1. Introduction

C–H bond activation and decarbonylation reaction of aldehyde mediated by transition metal complexes are of great interest due to their importance in organometallic chemistry and organic synthesis. In the past decades, the C–H bond activation reaction of aldehyde has been studied with various transition metal complexes, such as iron [1], ruthenium [2], osmium [3], rhodium [4], iridium [5,6], platinum [7] and cobalt [8]. The reactions of aromatic aldehydes with $CoMe(PMe_3)_4$ afforded the mono carbonyl complexes through C–H activation followed by a decarbonylation step and a proposed reaction mechanism was also reported [8]. As an early example, Tsuji reported the decarbonylation of aldehydes by stoichiometric amount of Wilkinson's catalyst in 1965 [9]. Since then many research groups made efforts in the field of catalytic decarbonylation of aldehydes [10]. On the one hand, aldehydes can be used as important substrates for the total syntheses through decarbonylation of aldehydes [11]; in addition, the carbon monoxide generated by the decarbonylation of aldehydes can be used as CO sources for the carbonylation reaction [12].

In this paper we report the C–H bond activation and decarbonylation reaction of three fluoro-benzaldehydes with $CoMe(PMe_3)_4$. Three fluorophenyl carbonyl cobalt(I) complexes **1–3** were synthesized. The chemical reactivity of carbonyl cobalt(I)

complexes was studied. The catalytic decarbonylation of 2,4,5-trifluorobenzaldehyde to 1,2,4-trifluorobenzene by $CoMe(PMe_3)_4$ was studied in the presence of triethylsilane.

## 2. Results and discussion

### 2.1. Synthesis of fluorophenyl carbonyl cobalt(I) complexes **1–3**

Three fluorophenyl carbonyl cobalt(I) complexes **1–3** were prepared from the reaction of fluorobenzaldehydes with $CoMe(PMe_3)_4$ through C–H bond activation and decarbonylation of aldehydes (Eq. (1)).



$$\text{(1)}$$
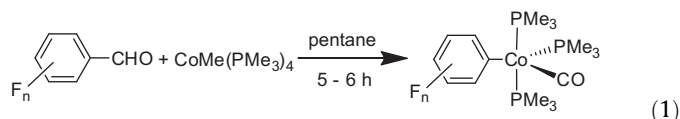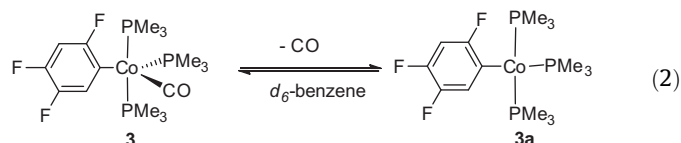
**1**: $F_n$ = 2,4-difluoro-
**2**: $F_n$ = 2,5-difluoro-
**3**: $F_n$ = 2,4,5-trifluoro-

**1 - 3**

Cobalt(I) species **1–3** were isolated as red crystals in the yields of 86% (**1**), 53% (**2**) and 40% (**3**) by crystallization from pentane at −20 °C. The yields of complexes **2** and **3** are lower because both complexes did not completely crystallize from the reaction solutions. Crystals **1–3** were relatively stable at room temperature for about 1 h. However, they quickly decomposed when reserved

as solution and exposed in the air. In the IR spectra of complexes **1–3**, the bands of $\nu(C=O)$ were recorded at 1880 (**1**), 1881 (**2**) and 1877 (**3**) cm$^{-1}$. This indicates that the decarbonylation process of aldehyde was followed by coordination of CO to the cobalt atom. In the $^1$H NMR spectra of complexes **1** and **2**, at 0.92 ppm one singlet was found for three thrimethylphosphine ligands. For complex **1** one aromatic proton was registered at 7.19 ppm while the other two aromatic hydrogen were recorded at 6.56 ppm. For complex **2** one aromatic proton was found at 7.22 ppm while the other two aromatic protons were registered at 6.47 ppm. One signal for two kinds of different PMe$_3$ ligands is attributed to the dynamic ligand behavior (Berry type pseudorotation and ligand dissociation) [8]. All of the three $^{19}$F NMR spectra for these three complexes **1–3** were recorded as expected. The $^1$H NMR spectrum of complex **3** indicates that complex **3** looks like a paramagnetic substance. It could be noted that the three F atoms with strong electron-withdrawing effect make the electron density at the cobalt center of complex **3** smaller and the π-backbond from cobalt to CO becomes weaker. Therefore, the CO ligand dissociates more easily than PMe$_3$. In addition, in the $^{31}$P NMR spectrum of **3**, no signal for free PMe$_3$ was observed. It is suggested that in solution the paramagnetic species might be a tetra-coordinate cobalt(I) complex **3a** formed through dissociation of CO from **3** (Eq. (2)). We attempted to isolate complex **3a**, but it was not successful so far.

The molecular structure of complex **1** was confirmed by single crystal X-ray diffraction (Fig. 1). Complex **1** has a distorted trigonal bipyramidal coordination geometry with P1–Co1–P3 (163.8(1)°) in the axial direction. 2,4-difluorophenyl, the carbonyl and the third trimethylphosphine ligand are in the equatorial positions. The phenyl ring is in the equatorial plane. The sum of three bond angles (C1–Co1–P2 = 113.3(3)°, C1–Co1–C2 = 133.0(4)° and C2–Co1–P2 = 113.7(3)°) around the cobalt center in the equatorial plane is 360.0°. This result verifies that the four atoms [Co1C1C2P2] are coplanar. Co1–P2 (2.239(3) Å) is longer than Co1–P3 (2.161(3) Å) and Co1–P1 (2.169(3) Å) owing to the strong influence of the fluorinated phenyl group and the carbonyl ligand. Co1–C2 (2.015(9) Å) and Co1–C1 (1.724(9) Å) are in the normal region of Co–C distances for the typical sp$^2$ and sp hybridized carbon atoms respectively.
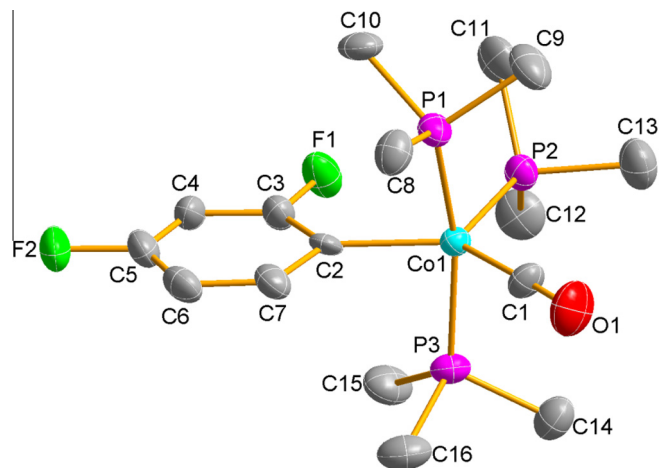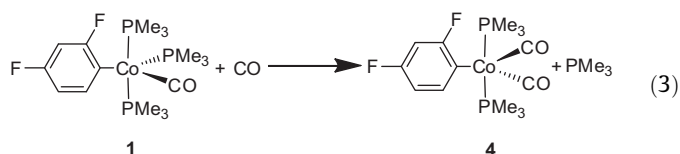
## 2.2. Chemical properties of complexes **1** and **3**

A pentane solution of complex **1** was stirred under 1 bar of CO atmosphere for 12 h to afford complex **4** (Eq. (3)). After work-up complex **4** was isolated as light yellow crystals. In the IR spectrum of **4**, two strong signals of terminal carbonyl ligands were registered at 1956 and 1898 cm$^{-1}$. In the $^1$H NMR spectrum of complex **4**, two PMe$_3$ ligands were recorded as one triplet at 1.03 ppm while the signals for three aromatic protons were observed between 6.74 ppm and 7.17 ppm. In the $^{31}$P NMR spectrum of complex **4**, a singlet at 40.9 ppm was found for the two *trans*-PMe$_3$ ligands. All of the spectroscopic data are consistent with trigonal bipyramidal geometry. This conjecture was confirmed by single crystal X-ray diffraction. The cobalt atom resides in the center of a distorted trigonal bipyramid of coordination atoms (Fig. 2). The axial bond angle (P2–Co1–P3 171.90(4)°) is slightly deviated from idealized geometry (180°). The triangular plane is formed by three coordinated carbon atoms [C1, C13 and C14]. The sum (360.01°) of three bond angles (C1–Co1–C13 = 116.52(2)°, C1–Co1–C14 = 122.74(2)° and C13–Co1–C14 = 120.75(2)°) around the cobalt center illustrates that the four atoms [CoC1C13C14] are in one plane. In comparison with Co1–C1 (2.025(3) Å), the shorter Co–C13 (1.747(4) Å) and Co–C14 (1.752(4) Å) distances are attributed to the synergistic effect of the σ-donating and π-backbonding between cobalt atom and the carbonyl ligands. Co–P bond lengths fall in the normal region [13].

The reaction of complex **1** with pentafluorophenyl bromide in pentane solution afforded cobalt(II) bromide **5**. Complex **5** was isolated in the form of brown crystals at −20 °C. Furthermore, perfluorobiphenyl was detected in the reaction solution using $^{19}$F NMR (Eq. (4)). The yield of perfluorobiphenyl was 67% determined by $^{19}$F NMR spectroscopy with trifluoromethyltoluene as the external standard. The $^1$H NMR and $^{31}$P NMR spectra illustrate that complex **5** is paramagnetic due to the penta-coordinate cobalt(II) center.

**Fig. 1.** Molecular structure of **1**: selected bond lengths (Å) and angles (°): Co1–C2 2.015(9), Co1–C1 1.724(9), Co1–P1 2.169(3), Co1–P2 2.239(3), Co1–P3 2.161(3); P1–Co1–P3 163.8(1), C1–Co1–P2 113.3(3), C1–Co1–C2 133.0(4), C2–Co1–P2 113.7(3).
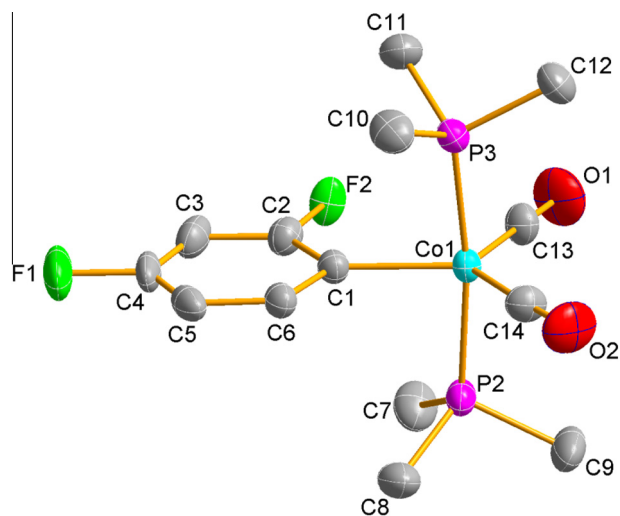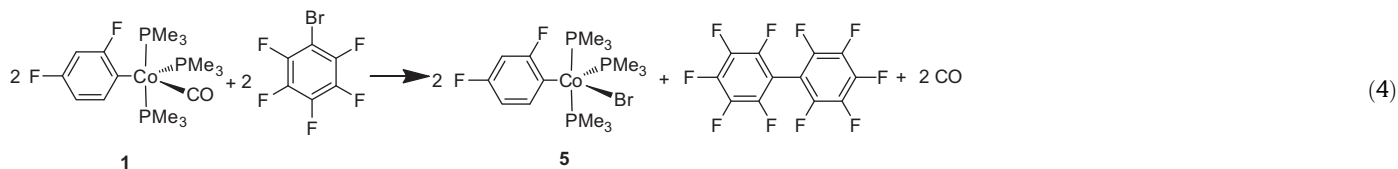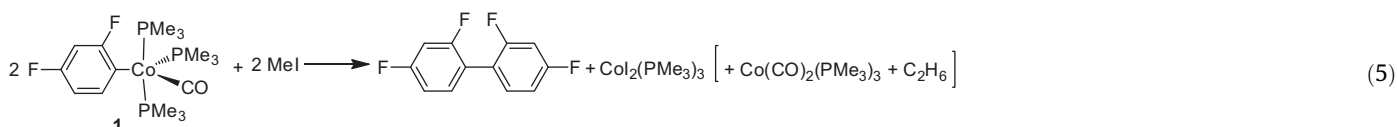
**Fig. 2.** Molecular structure of **4**: selected bond lengths (Å) and angles (°): Co1–C1 2.025(3), Co1–C13 1.747(4), Co1–C14 1.752(4), Co1–P2 2.172(1), Co1–P3 2.174(1); P2–Co1–P3 171.90(4), C1–Co1–C13 116.52(2), C1–Co1–C14 122.74(2), C13–Co1–C14 120.75(2).
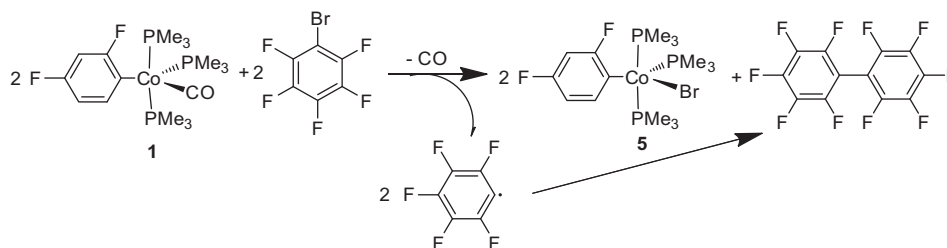
(4)

It is proposed that the one-electron oxidative addition of bromo ligand at the cobalt(I) center occurs to form cobalt(II) complex **5** (Scheme 1). Meanwhile, Two pentafluorophenyl radicals combine together to deliver perfluorobiphenyl. Carbon monoxide was formed as a byproduct. This mechanism is different from our early study on the reactions of organometallic complexes with alkyl halogenides. They underwent oxidative addition and reductive elimination to afford metal halogenides [14,15].

The molecular structure of complex **5** with the selected bond distances and angles is shown in Fig. 3. In the molecular structure of **5**, the cobalt atom attains a distorted trigonal bipyramid with P4 and P6 atoms in the axial positions. The axial bond angle is P4–Co2–P6 (166.73(1)°). The C25, P5 and Br1 atoms are in the triangular plane. The sum of three bond angles (C25–Co2–P5 = 115.0(3)°, C25–Co2–Br1 = 137.2(3)° and P5–Co2–Br1 = 107.8(9)°) around the cobalt center in the triangular plane is 360.0°. This indicates that the four atoms [Co2Br1P5C25] are coplanar. The phenyl ring is also in this plane. The dihedral angle between these two planes is 6.87°.

In addition to the reaction (4), complex **1** was also reacted with iodomethane and hexachlorobenzene in order to get the similar cobalt(II) iodide and chloride. However, complex **1** did not react with hexachlorobenzene. The reaction of complex **1** with MeI afforded $CoI_2(PMe_3)_3$, instead of the analogue cobalt(II) iodide. Meanwhile, 2,2′,4,4′-tetrafluorobiphenyl was also detected by *in situ* $^{19}F$ NMR in the reaction solution. This process can be summarized in Eq. (5).
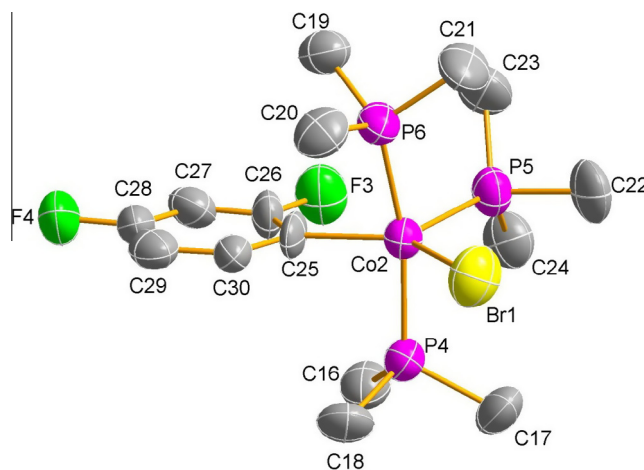


**Fig. 3.** Molecular structure of **5**: selected bond lengths (Å) and angles (°): Co–C25 1.984(7), Co2–P4 2.201(3), Co2–P5 2.273(3), Co2–P6 2.213(3), Co2–Br1 2.456(2); P4–Co2–P6 166.73(1), C25–Co2–P5 115.0(3), C25–Co2–Br1 137.2(3), P5–Co2–Br1 107.8(9).

at −12.3 ppm for the hydrido hydrogen in the $^1H$ NMR spectrum. In addition, the signals of 1,2,4-trifluorobenzene were observed in the reaction solution using $^{19}F$ NMR spectroscopy. Based on these data, it can be inferred that the reaction afforded the hydrido diethinyl cobalt(III) complex $CoH(C\equiv CPh)_2(PMe_3)_3$ (**6**) and 1,2,4-



(5)

Unexpectedly, the reaction of complex **3** with phenylethyne in pentane delivered dialkynyl complex **6** as red crystals. In the IR spectrum of complex **6**, two signals at 2078 and 1889 cm$^{-1}$ were recorded for C≡C and Co–H bond vibration. There is one signal

trifluorobenzene (Eq. (6)). Complex **6** could also be formed with the reaction of $CoBr(PMe_3)_3$ and phenylacetylene [16]. The yield (43%) of 1,2,4-trifluorobenzene was determined by $^{19}F$ NMR spectroscopy with trifluoromethyltoluene as an external standard.



**Scheme 1.**

$$(6)$$
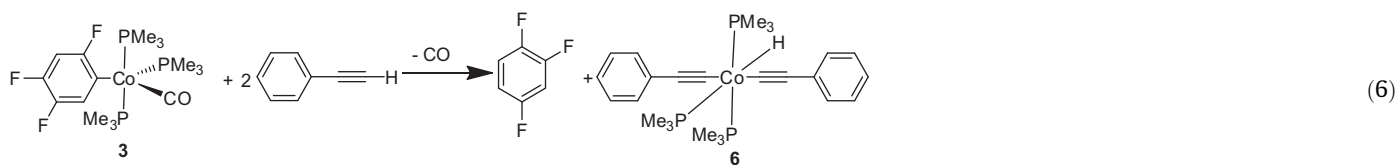
A proposed mechanism of formation of complex **6** was shown in Scheme 2. After dissociation of one carbonyl ligand, the oxidative addition of the C–H bond of phenylacetylene at the cobalt(I) center afforded the hydrido intermediate, cobalt(III) complex **3b**. Intermediate **3b** transforms into intermediate **3c** via reductive elimination with the liberation of one molecule of 1,2,4-trifluorobenzene. The final cobalt(III) complex **6** was formed through the second oxidative addition of the C–H bond of phenylacetylene at the cobalt(I) center of **3c**.

### 2.3. Catalytic decarbonylation of fluorinated benzaldehyde by CoMe (PMe₃)₄

Enlightened by the reactions Eqs. (1) and (6), a catalytic reaction was designed with CoMe(PMe₃)₄ as a catalyst (Eq. (7)). The decarbonylation of 2,4,5-trifluorobenzaldehyde was carried out with triethylsilane as the hydrogen source to afford 1,2,4-trifluorobenzene. The experiments showed that this reduction could be realized under mild conditions at a catalyst loading of 10%.



$$(7)$$
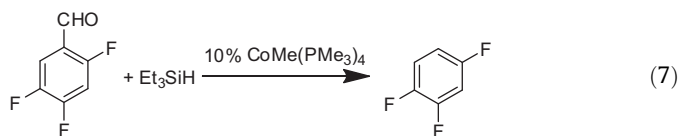
The control experiment illustrated that CoMe(PMe₃)₄ as a catalyst was necessary for this reaction under the given conditions (entry 5, Table 1). Differences of silane species, temperatures, solvents, reaction times and loadings of catalyst were chosen to optimize the reaction condition. The optimized catalytic reaction condition is with Et₃SiH as a hydrogen source in THF at 50 °C for 6 h using 10 mol% of CoMe(PMe₃)₄ and 94% yield could be reached (entry 4, Table 1). The exploration of the applied scope of this catalytic system is ongoing.

In order to reveal the mechanism of this catalytic reaction, some experiments were carried out. Firstly we did a stoichiometric reaction of complex **3** and Et₃SiH in the ratio of 1:1, but found that it

did not react. The crystals of complex **3** were recovered. Secondly Et₃SiH was taken to react with CoMe(PMe₃)₄ in the ratio of 1:1. Co(PMe₃)₄(SiEt₃) was found by NMR in this reaction. The reaction of 1 equivalent of 2,4,5-trifluorobenzaldehyde and 1.2 equivalent of Et₃SiH could be catalyzed by 10% equivalent of Co(PMe₃)₄(SiEt₃). 1,2,4-Trifluorobenzene was found by *in situ* $^{19}$F NMR (Eq. (8)). This indicates that Co(PMe₃)₄(SiEt₃) was the real catalyst in the catalytic decarbonylation reaction (Eq. (7)).



$$(8)$$

**Table 1**
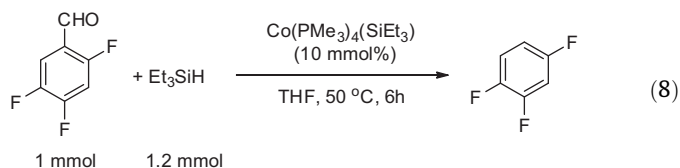Optimization of reaction conditions.[a]

| Entry | Silane | Temperature (°C) | Solvent | Time (h) | Yield (%)[b] |
|---|---|---|---|---|---|
| 1 | Ph₃SiH | 50 | THF | 6 | 80 |
| 2 | PhMe₂SiH | 50 | THF | 6 | 42 |
| 3 | (EtO)₃SiH | 50 | THF | 6 | 73 |
| 4 | Et₃SiH | 50 | THF | 6 | 94 |
| 5[c] | Et₃SiH | 50 | THF | 6 | 0 |
| 6 | Et₃SiH | 30 | THF | 6 | 68 |
| 7 | Et₃SiH | 40 | THF | 6 | 67 |
| 8 | Et₃SiH | 50 | Ether | 6 | 53 |
| 9 | Et₃SiH | 50 | Pentane | 6 | 67 |
| 10 | Et₃SiH | 50 | Toluene | 6 | 56 |
| 11 | Et₃SiH | 50 | THF | 1 | 39 |
| 12 | Et₃SiH | 50 | THF | 2 | 45 |
| 13 | Et₃SiH | 50 | THF | 4 | 71 |
| 14[d] | Et₃SiH | 50 | THF | 6 | 0 |
| 15[e] | Et₃SiH | 50 | THF | 6 | 52 |

[a] Conditions: 2,4,5-trifluoro-benzaldehyde (1 mmol), silane (1.2 mmol), CoMe (PMe₃)₄ (0.1 mmol), solvent (2 mL), N₂ atmosphere.
[b] Determined by $^{19}$F NMR spectroscopy with trifluoromethyltoluene as the external standard.
[c] No catalyst.
[d] CoMe(PMe₃)₄ (0.01 mmol).
[e] CoMe(PMe₃)₄ (0.05 mmol).
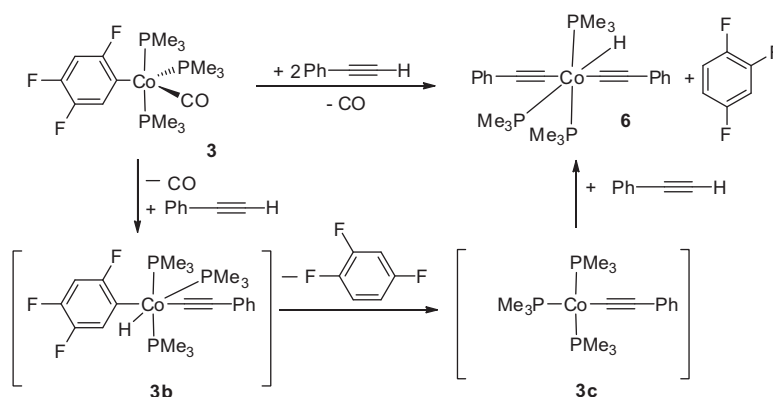


**Scheme 2.**

## 3. Conclusions

In conclusion, the reaction of fluoroaldehydes with CoMe $(PMe_3)_4$ afforded the corresponding fluorophenyl carbonyl cobalt (I) complexes **1–3**. The reactions of complex **1** with CO and pentafluorophenyl bromide provided dicarbonyl cobalt(I) complex **4** and cobalt(II) bromide **5** with the formation of perfluorinated diphenyl while the combination of complex **3** with phenylacetylene delivered hydrido diethinyl cobalt(III) complex **6** with 1,2,4-trifluorobenzene as byproduct. The molecular structures of **1**, **4** and **5** were determined by single crystal X-ray diffraction. The catalytic decarbonylation of 2,4,5-trifluoro-benzaldehyde to 1,2,4-trifluorobenzene by CoMe$(PMe_3)_4$ was explored.

## 4. Experimental

### 4.1. General procedures and materials

Standard vacuum techniques were used in manipulations of volatile and air sensitive materials. Solvents were dried by known procedures and distilled under nitrogen before use. Literature methods were used in the preparation of CoMe$(PMe_3)_4$. [17] Infrared spectra (4000–400 cm$^{-1}$), as obtained from Nujol mulls between KBr disks, were recorded on a Bruker ALPHA FT-IR Spectrometer. $^1$H, $^{13}$C, $^{31}$P and $^{19}$F NMR spectra (300, 75, 121 and 282 MHz, respectively) were recorded on a Bruker Avance 300 spectrometer. $^{13}$C and $^{31}$P NMR resonances were obtained with broadband proton decoupling. Elemental analyses were carried out on an Elementar Vario EL III. Melting points were measured in capillaries sealed under N$_2$ and were uncorrected.

### 4.2. Synthesis of complex 1

2,4-Difluoro-benzaldehyde (0.36 g, 2.53 mmol) was added dropwise to a solution of CoMe$(PMe_3)_4$ (0.96 g, 2.53 mmol) in 30 mL of pentane at −80 °C. This mixture was allowed to warm to ambient temperature to form a red mixture with powders, the powders were dissolved when stirred for 6 h sequentially. The dark red reaction solution was then filtered. Complex **1** (0.93 g, 2.17 mmol) was isolated as red crystals in 86% yield from pentane at 20 °C. m.p.: 105–107 °C. *Anal.* Calc. for C$_{16}$H$_{30}$CoF$_2$OP$_3$ (428.26 g/mol): C, 44.87; H, 7.06. Found: C, 45.03; H, 7.01%. IR (Nujol mull, cm$^{-1}$): 1880 $v$(C=O), 1572 $v$(C=C), 940 $\rho$(PMe$_3$). $^1$H NMR (C$_6$D$_6$, 300 K, ppm): 0.92 (s, 27H, P$Me_3$), 6.56 (s broad, 2H, Ar–$H$), 7.19 (s broad, 1H, Ar–$H$); $^{31}$P NMR (C$_6$D$_6$, 300 K, ppm): 19.0 (s, $P$CH$_3$). $^{19}$F NMR (C$_6$D$_6$, 300 K, ppm): −77.8 (s, 1F), −121.9 (d, $J$ = 8.46 Hz, 1F).

### 4.3. Synthesis of complex 2

Complex **2** was synthesized according to the method given above for complex **1**.

Complex **2**: Yield: 52.8%. m.p.: 102–104 °C. *Anal.* Calc. for C$_{16}$H$_{30}$CoF$_2$OP$_3$ (428.26 g/mol): C, 44.87; H, 7.06. Found: C, 45.03; H, 6.96%. IR (Nujol mull, cm$^{-1}$): 1881 $v$(C=O), 1591 $v$(C=C), 938 $\rho$(PMe$_3$). $^1$H NMR (C$_6$D$_6$, 300 K, ppm): 0.92 (s, 27H, P$Me_3$), 6.47 (d, 2H, Ar–$H$), 7.22 (s broad, 1H, Ar–$H$); $^{31}$P NMR (C$_6$D$_6$, 300 K, ppm): 18.3 (s, $P$CH$_3$). $^{19}$F NMR (C$_6$D$_6$, 300 K, ppm): −124.0 (d, $J$ = 22.56 Hz, 1F), −88.6 (d, $J$ = 19.74 Hz, 1F).

### 4.4. Synthesis of complex 3

Complex **3** was synthesized according to the method given above for complex **1**.

Complex **3**: Yield: 39.8%. m.p.: 98–100 °C. *Anal.* Calc. for C$_{16}$H$_{29}$CoF$_3$OP$_3$ (446.25 g/mol): C, 43.06; H, 6.55. Found: C, 43.18; H,

6.42%. IR (Nujol mull, cm$^{-1}$): 1877 $v$(C=O), 1601 $v$(C=C), 934 $\rho$ (PMe$_3$). $^1$H NMR (C$_6$D$_6$, 300 K, ppm): 0.87 (s, P$Me_3$), 1.22 (s, P$Me_3$), 6.47 (s broad, Ar–$H$), 7.20 (s broad, Ar–$H$); $^{31}$P NMR (C$_6$D$_6$, 300 K, ppm): 18.6 (s, $P$CH$_3$). $^{19}$F NMR (C$_6$D$_6$, 300 K, ppm): −147.7 (t, $J$ = 19.74 Hz, 1F), −144.7 (d, $J$ = 19.74 Hz, 1F), −83.6 (s, 1F).

### 4.5. Synthesis of complex 4

A sample of **1** (0.46 g, 1.07 mmol) in 50 mL of pentane at room temperature was stirred under 1 bar of CO for 12 h, and the red solution slowly turned yellow. The reaction solution was then filtered. Crystallization at −20 °C afforded light yellow crystals of **4** (0.21 g, 51.2%). m.p.: 110–112 °C. *Anal.* Calc. for C$_{14}$H$_{21}$CoF$_2$O$_2$P$_2$ (380.19 g/mol): C, 44.23; H, 5.57. Found: C, 44.38; H, 5.44%. IR (Nujol mull, cm$^{-1}$): 1956 $v$(C=O), 1898 $v$(C=O) 1610 $v$(C=C), 947 $\rho$(PMe$_3$). $^1$H NMR (C$_6$D$_6$, 300 K, ppm): 1.03 (t′, |$^2J$(P,H) + $^4J$(P,H)| = 9 Hz, 18H, P$Me_3$), 6.47(m, 2H, Ar–$H$), 7.17 (s broad, 1H, Ar–$H$); $^{31}$P NMR (C$_6$D$_6$, 300 K, ppm): 40.9 (s, $P$CH$_3$). $^{19}$F NMR (C$_6$D$_6$, 300 K, ppm): −120.1 (d, $J$ = 5.64 Hz, 1F), −79.1 (d, $J$ = 5.64 Hz, 1F). $^{13}$C NMR (C$_6$D$_6$, 300 K, ppm): 147.48 (d, $J$ = 19.50 Hz), 110.40 (d, $J$ = 19.50 Hz), 101.70 (dd, $J$ = 38.25, 22.5 Hz), 30.17(s), 18.86 (t′, $J$ = 33 Hz).

### 4.6. Synthesis of complex 5

A sample of 1-bromo-2,3,4,5,6-pentafluoro-benzene (0.30 g, 1.21 mmol) in 20 mL of pentane was slowly combined with a solution of **1** (0.52 g, 1.21 mmol) in 20 mL pentane at −80 °C. This mixture was allowed to warm to 20 °C and stirred for 48 h to form a brown solution. The reaction solution was then filtered. Crystallization at −20 °C afforded brown crystals of **5** (0.26 g, 44.6%). m.p.: 120–122 °C. *Anal.* Calc. for C$_{15}$H$_{30}$BrCoF$_2$P$_3$ (480.15 g/mol): C, 37.52; H, 6.30. Found: C, 37.67; H, 6.15%. IR (Nujol mull, cm$^{-1}$): 1576 $v$(C=C), 944 $\rho$(PMe$_3$). The signals of $^1$H NMR (C$_6$D$_6$, 300 K, ppm) and $^{31}$P NMR (C$_6$D$_6$, 300 K, ppm) were strongly broadened. $^{19}$F NMR (C$_6$D$_6$, 300 K, ppm): −77.8 (s, 1F), −121.8 (d, $J$ = 5.64 Hz, 1F) ppm. The yield of perfluorobiphenyl was 67.2% determined by $^{19}$F NMR spectroscopy with trifluoromethyltoluene as the external standard.

### 4.7. The reaction of complex 3 with phenylethyne

A sample of phenylethyne (0.21 g, 2.06 mmol) in 20 mL of pentane was slowly combined with a solution of complex **3** (0.46 g, 1.03 mmol) in 20 mL of pentane at −80 °C. This mixture was allowed to warm to 20 °C and stirred for 24 h, the solution color became dark-red from red. The reaction solution was then filtered. Crystallization at −20 °C afforded red crystals of **6** [16]. The yield (43%) of 1,2,4-trifluoro-benzene in reaction mixture was determined by $^{19}$F NMR spectra with trifluoromethyltoluene as the external standard.

### 4.8. Procedure for catalytic reaction

In a 25 mL Schlenk tube containing a solution of CoMe$(PMe_3)_4$ (37.8 mg, 0.1 mmol) in 2 mL of THF were added to 2,4,5-triflouro-benzaldehyde (1.6 mg, 1.0 mmol), then Et$_3$SiH (0.14 g, 1.2 mmol) were added to the system. The reaction mixture was stirred at 60 °C for 6 h. The yield of product was determined by $^{19}$F NMR spectra using trifluoromethyltoluene as an external standard.

### 4.9. X-ray crystal-structure determinations

The single-crystal X-ray diffraction data of the complexes were collected with a Bruker SMART Apex II CCD diffractometer

equipped with a graphite-monochromated Mo Kα radiation source ($\lambda$ = 0.71073 Å). The structures were solved by direct or Patterson methods with the SHELXS-97 program and refined on $F^2$ with SHELXTL. All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions and refined by using a riding model.

### 4.10. Crystallographic data of complex 1

$C_{16}H_{30}CoF_2OP_3$, Mr. = 428.24, monoclinic, space group $P2(1)/c$, $a$ = 9.722(3) Å,   $b$ = 8.873(2) Å,   $c$ = 24.443(7) Å,   $\beta$ = 94.14(2)°, $V$ = 2103.0(10) Å$^3$,   $T$ = 180 K,   $Z$ = 4,   Dcalc = 1.353 mg cm$^{-3}$, $\mu$ = 1.353. A total of 9472 reflections were collected, 3578 unique ($R_{int}$ = 0.0826), $R_1$ = 0.1049 (for 9472 reflections with $I > 2\sigma(I)$), $\omega R_2$ = 0.0391 (all data).

### 4.11. Crystallographic data of complex 4

$C_{14}H_{21}CoF_2O_2P_2$, Mr. = 380.20, monoclinic, space group $P2(1)/c$, $a$ = 11.937(2) Å,   $b$ = 8.707(2) Å,   $c$ = 17.751(3) Å,   $\beta$ = 103.31(1)°, $V$ = 1795.4(6) Å$^3$,   $T$ = 296 K,   $Z$ = 4,   Dcalc = 1.407 mg cm$^{-3}$, $\mu$ = 1.407. A total of 9447 reflections were collected, 2903 unique ($R_{int}$ = 0.0463), $R_1$ = 0.0416 (for 9447 reflections with $I > 2\sigma(I)$), $\omega R_2$ = 0.1263 (all data).

### 4.12. Crystallographic data of complex 5

$C_{15}H_{30}BrCoF_2P_3$, Mr. = 480.16, orthorhombic, space group $Pcab$, $a$ = 13.435(4) Å, $b$ = 24.437(5) Å, $c$ = 26.154(6) Å, $\beta$ = 90°, $V$ = 8586.4 (4) Å$^3$, T = 293 K, Z = 16, Dcalc = 1.486 mg cm$^{-3}$, $\mu$ = 1.486. A total of 47068 reflections were collected, 6958 unique ($R_{int}$ = 0.1174), $R_1$ = 0.1247 (for 9472 reflections with $I > 2\sigma(I)$), $\omega R_2$ = 0.3459 (all data).

### Acknowledgments

### Appendix A. Supplementary material

CCDC 1046655 (for **1**), 1046656 (for **4**), and 1046657 (for **5**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2015.10.006.

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