



Effect of anchoring group and valent of cobalt center on the competitive cleavage of C–F or C–H bond activation

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ABSTRACT

Treatment of $\text{CoMe}(\text{PMe}_3)_4$ with 2,6-difluorobenzophenone imine and 2,6-difluorobenzophenone resulted in C–H bond activation complex, $[\text{Co}(2\text{-C}_6\text{H}_4)\text{-(C=NH)}\text{-(2',6''-F}_2\text{C}_6\text{H}_3)(\text{PMe}_3)_3]$ (**2**), and C–F bond activation complex $[\text{Co}(\text{Me})(\text{F})(2\text{-(6-FC}_6\text{H}_3)\text{-(C=O)-C}_6\text{H}_5)(\text{PMe}_3)_2]$ (**3**) respectively. Using $\text{Co}(\text{PMe}_3)_4$ instead of $\text{CoMe}(\text{PMe}_3)_4$ the C–F activation Co(I) complex $[\text{Co}(2\text{-(6-FC}_6\text{H}_3)\text{-(C=NH)-C}_6\text{H}_5)(\text{PMe}_3)_3]$ (**1**), was obtained by the reaction of $\text{Co}(\text{PMe}_3)_4$ with 2,6-difluorobenzophenone imine. In the case of mono-fluorinated aromatic ketone, the reaction of $\text{CoMe}(\text{PMe}_3)_4$ with 2,4'-difluorobenzophenone afforded only C–H bond activation complex, $[\text{Co}(2\text{-(4-FC}_6\text{H}_3)\text{-(C=O)}\text{-(2'-FC}_6\text{H}_4)(\text{PMe}_3)_3]$ (**4**) in comparison with the C–F activation in the di-fluorinated aromatic ketone 2,6-difluorobenzophenone system. The crystal structures of complexes **1**, **3** and **4** were determined by X-ray diffraction. The proposed mechanisms were discussed.

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1. Introduction

The intramolecular selective activation of C–F versus C–H bond has attracted a great deal of attention in recent years because of the requirements of “molecular surgery” in modern synthetic chemistry. The priority of selective activation of C–F versus C–H bond within one molecule is complicated and is related to many factors [1–16]. It has not only thermodynamic but also kinetic reason. A survey of competing C–F activation pathways in the reaction of Pt(0) with fluoropyridines by Perutz was investigated with both computational and experimental methods [17]. In 2008 Klein reported the first regioselective cyclometalation reactions of cobalt in arylketone [18]. It was found that $\text{CoMe}(\text{PMe}_3)_4$ activates *ortho*-(C–H) and *ortho*-(C–F) bonds of aromatic ketones and the *ortho*-(C–F) activation is preferred over the *ortho*-(C–H) activation in 2,3,4,5,6-pentafluorobenzophenone. Recently Johnson published a combined experimental and computational study of unexpected C–F bond activation intermediates and selectivity in the reaction of pentafluorobenzene with a $(\text{PEt}_3)_2\text{Ni}$ synthon [19]. Goldman reported addition at the aryl *meta*- and *para*-positions is kinetically more favorable than at the *ortho*-position, although thermodynamics favor the chelated *ortho*-(C–H) addition for

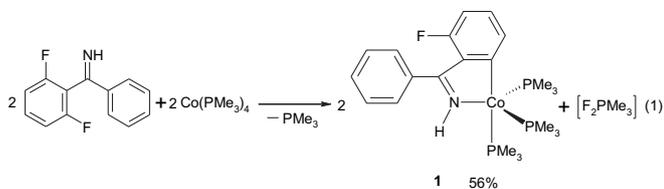
three coordinate d^8 metal complexes [20]. Hydrido osmium is capable of producing the triple C–H bond activation of the cyclohexyl group of cyclohexylmethyl ketone [21]. Esteruelas found that the *ortho*-(C–H) bond activation is preferred over the *ortho*-(C–F) bond activation in aromatic ketones with one aromatic ring by phosphine-supported hexahydride osmium complex [22]. Both C–F and C–H bond activations are favored by an increase of the degree of fluorination of the substrates [23]. We obtained the first organo cobalt(III) complex containing a [C–Co–F] fragment through a cyclometalation reaction involving C–F bond activation at a cobalt(I) center with an aldehyde-N atom as an anchoring group [24]. In this paper we present competitive cleavage of C–F versus C–H bond in the cyclometalation reaction at electron-rich cobalt center with ketone and imine as anchoring group. Through the reaction of $\text{CoMe}(\text{PMe}_3)_4$ with 2,6-difluorobenzophenone, another example of organo cobalt(III) complex, $[\text{Co}(\text{Me})(\text{F})(2\text{-(6-FC}_6\text{H}_3)\text{-(C=O)-C}_6\text{H}_5)(\text{PMe}_3)_2]$ (**3**), containing a [C–Co–F] fragment was obtained.

2. Results

2.1. Reaction of $\text{Co}(\text{PMe}_3)_4$ with 2,6-difluorobenzophenone imine

$\text{Co}(\text{PMe}_3)_4$ was combined with 2,6-difluorobenzophenone imine affording the C–F bond activation complex **1** (eq. (1)).

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Complex **1** forms purple-blue crystals suitable for X-ray diffraction which decompose above 140 °C. In the IR spectra the characteristic $\nu(\text{C}=\text{N})$ band was found at 1603 cm^{-1} . The resonance of the N–H proton in the ^1H NMR spectrum is registered at 8.36 ppm.

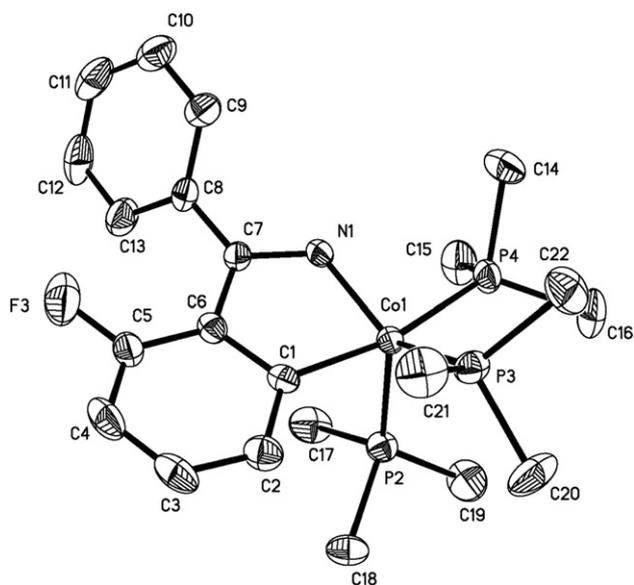
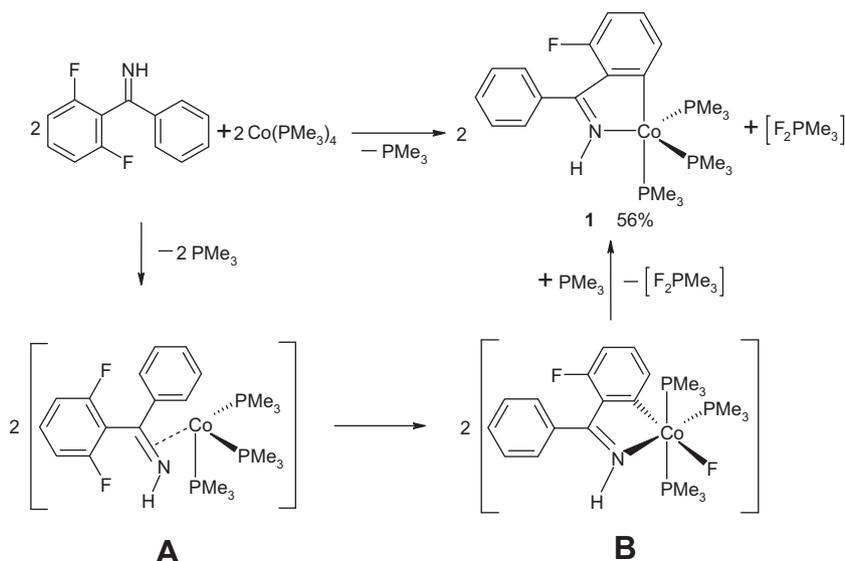


Fig. 1. Molecular structure of **1** and selected bond distances (Å) and angles (°): Co1–N1 1.885(3), Co1–P2 2.1904(13), Co1–P3 2.2002(12), Co1–P4 2.2159(13), C1–Co1 1.936(4), C7–N1 1.336(5); N1–Co1–C1 80.91(16), N1–Co1–P2 114.11(11), C1–Co1–P2 86.68(12), N1–Co1–P3 133.89(11), C1–Co1–P3 93.66(13), P2–Co1–P3 111.18(5), P2–Co1–P4 97.46(5), P3–Co1–P4 96.03(5), N1–Co1–P4 86.41(11), C1–Co1–P4 167.26(13), C7–N1–Co1 120.9(3), N1–C7–C6 110.9(4), C6–C1–Co1 113.8(3), C1–C6–C7 112.7(3).



Scheme 1. Proposed mechanism for reaction (1).

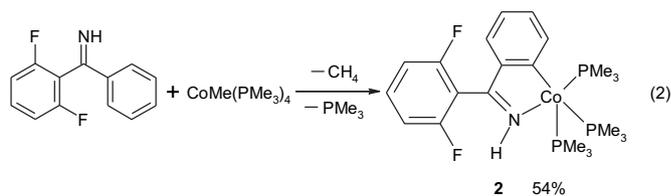
The molecular structure of **1** (Fig. 1) shows a trigonal bipyramidal configuration around cobalt with C1 and P4 on axial direction. The bite angle N1–Co1–C1 $80.91(16)^\circ$ is smaller than that of complex **4**. The sum of internal bond angles of the chelate ring is (539.21°) . The distance of C7–N1 (1.336(5) Å) is close to that (1.337(8) Å) in the reported compound [25]. In comparison with the reaction of $\text{Co}(\text{PMe}_3)_4$ with 2,6-difluorobenzophenone [26], the imine group is a better anchoring group than the keto group. The C–F bond could be activated by the compensation of chelate effect.

In the proposed mechanism (Scheme 1) the π -coordination of $\text{C}=\text{N}$ double bond to the cobalt(0) center is the first step, which makes closing of cobalt center to the *ortho*-(C–F) bond and the formation of the intermediate **A** possible. Oxidative addition between the C–F bond and the cobalt(0) center delivered cobalt(II) intermediate **B**. **B** was reduced to cobalt(I) product **1**.

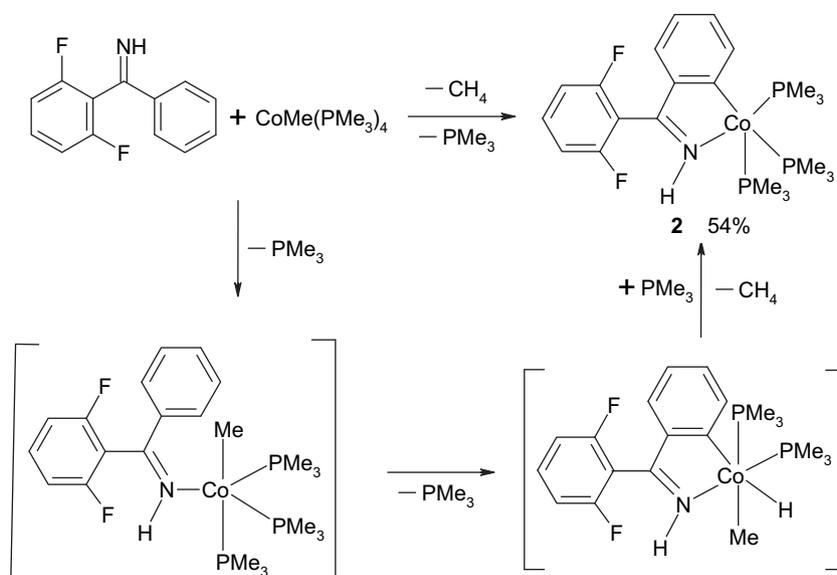
In our early work [27], the formation of F_2PMe_3 in the reaction of perfluorotoluene with $\text{Co}(\text{PMe}_3)_4$ was confirmed via ^{31}P NMR spectroscopy. The fate of the fluorine atom in reaction (1) is not experimentally identifiable.

2.2. Reaction of $\text{CoMe}(\text{PMe}_3)_4$ with 2,6-difluorobenzophenone imine

Instead of cobalt(0) complex $\text{Co}(\text{PMe}_3)_4$, cobalt(I) complex $\text{CoMe}(\text{PMe}_3)_4$ was combined with 2,6-difluorobenzophenone imine affording deep-green crystals of complex **2** through C–H bond activation (eq. (2)).



In the IR spectra $\nu(\text{C}=\text{N})$ absorption was found at 1620 cm^{-1} . The signal of the (NH) group is registered at 8.33 ppm. In the ^{31}P NMR spectra there are three signals for PMe_3 ligands at 43.9, 33.5



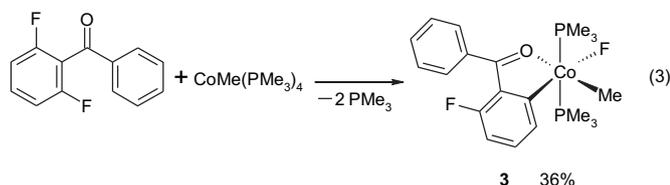
Scheme 2. Proposed mechanism for reaction (2).

and 22.1 ppm with the ratio of 1:1:1. All of the data confirm a trigonal bipyramidal configuration around cobalt. A trial to obtain the crystal and molecular structure information through X-ray diffraction has failed.

A proposed reaction mechanism is described in Scheme 2. The imine-N coordination is the first step. With the cyclometalation effect the *ortho*-(C–H) bond of the phenyl group in the imine ligand is activated affording an active methyl hydrido cobalt(III) intermediate, which affords the product **2** through the escape of methane with reductive elimination.

2.3. Reaction of $\text{CoMe}(\text{PMe}_3)_4$ with 2,6-difluorobenzophenone

In the reaction of 2,6-difluorobenzophenone, an iso-electronic compound of 2,6-difluorobenzophenone imine, with $\text{CoMe}(\text{PMe}_3)_4$, gave rise to complex **3** (eq. (3)) through C–F bond activation. To the best of our knowledge, after the report of the preparation of the first example of organo cobalt(III) complex containing a [C–Co–F] fragment [24], complex **3** is the second example of organo cobalt(III) complex with a [C–Co–F] fragment.



Complex **3** was obtained as violet crystals from pentane at -27°C . In the infrared spectra, there is a strong absorption at 1594 cm^{-1} assigned to $\nu(\text{C}=\text{O})$ bond, a large bathochromic shift comparing with that (1677 cm^{-1}) of the free ligand. In the ^1H NMR spectra the proton resonance of two anisochrom trimethylphosphine ligands is regarded as a singlet at 0.79 ppm, while the signal of Co–CH₃ could be found at 0.30 ppm. ^{31}P NMR data clearly show one signal at 20.4 ppm. Complex **3** crystallized with [Co(2,6-

$\text{F}_2\text{C}_6\text{H}_3\text{-}\eta^2\text{-(C}=\text{O)-C}_6\text{H}_5\text{)}(\text{PMe}_3)_3$] [26] in *P* – 1 space group. The occurrence of complex **3** could be attributed to the impurity of $\text{CoMe}(\text{PMe}_3)_4$ with minor amount of $\text{Co}(\text{PMe}_3)_4$.

The molecular structure (Fig. 2) of complex **3** confirms the octahedral coordination geometry around the Co1 atom with P1 and P2 on axial direction and F2–O1–C7 and C42 in an equatorial plane. The bite angle of C7–Co1–O1 is $82.45(7)^\circ$ which is a little larger than that of the related compounds in early work by Klein et al. [28]. The sum of the angles around the cobalt in metalacycle is 540° . The distance of Co1–O1 (2.0213(13) Å) is longer than that of complex [Co(2,6- $\text{F}_2\text{C}_6\text{H}_3\text{-}\eta^2\text{-(C}=\text{O)-C}_6\text{H}_5\text{)}(\text{PMe}_3)_3$] [26]. The distance of Co1–F2 (1.9316(14) Å) is in the normal region for Co–F bond lengths [24].

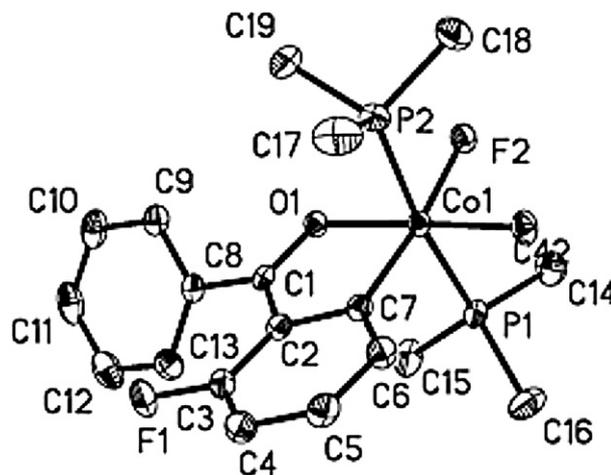
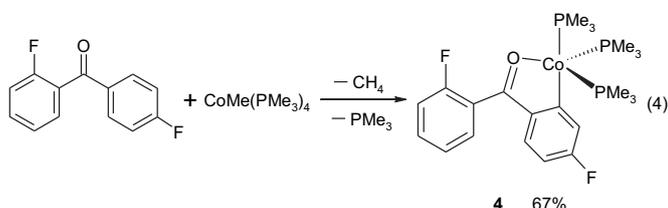


Fig. 2. Molecular structure of **3** and selected bond distances (Å) and angles ($^\circ$): Co1–C7 1.895(2), Co1–F2 1.9316(14), Co1–O1 2.0213(13), Co1–P1 2.2121(11), Co1–P2 2.2138(10), Co1–C42 1.995(2), O1–C1 1.247(2); C7–Co1–F2 172.02(7), C7–Co1–C42 95.73(9), F2–Co1–C42 92.14(8), C7–Co1–O1 82.45(7), F2–Co1–O1 89.71(5), F2–Co1–P1 89.01(5), C42–Co1–O1 177.77(8), C7–Co1–P1 92.52(7), C42–Co1–P1 88.38(9), O1–Co1–P1 90.41(5), C7–Co1–P2 94.16(7), F2–Co1–P2 84.83(5), O1–Co1–P2 93.77(5), P1–Co1–P2 172.53(2).

2.4. Reaction of $\text{CoMe}(\text{PMe}_3)_4$ with 2,4'-difluorobenzophenone

Under similar reaction conditions, the reaction of $\text{CoMe}(\text{PMe}_3)_4$ with 2,4'-difluorobenzophenone afforded the C–H activation complex **4** in the yield of 67.0% (eq. (4)).



From the dark brown solution of diethyl ether complex **4** was obtained as the black needle-shaped crystals. In the IR spectra of complex **4** the absorption at 1596 cm^{-1} belongs to (C=O) group. In the ^{31}P NMR spectra there are two sets of signals with the intensity ratio of 1:2 at 43.9 and 17.5 ppm. The ^{19}F NMR spectrum indicates two signals at -113.2 and -118.8 ppm with the ratio of 1:1. All of the spectroscopic data indicate that the activation of C–H bond is performed instead of C–F bond activation.

The molecular structure of complex **4** was confirmed by X-ray diffraction analysis (Fig. 3). A cobalt atom is centered in a trigonal bipyramid with axial C1 and P2 and a five-membered metallacycle occupying C-axial and O-equatorial position with a bite angle $\text{O1-Co1-C1} = 82.5(2)^\circ$, comparable with that ($82.45(7)^\circ$) in complex **3**. The sum of the internal angles in the cobaltacycle is 539.7° , close to planarity (540°). The distance of P2-Co1 ($2.227(2)\text{ \AA}$) is longer than P3-Co1 ($2.189(2)\text{ \AA}$) and P1-Co1 ($2.184(2)\text{ \AA}$), owing to the stronger *trans*-influence of carbon atom (C1). From reactions ((3) and (4)), in the case of mono-fluorinated aromatic ketone, the reaction of $\text{CoMe}(\text{PMe}_3)_4$ with 2,4'-difluorobenzophenone afforded only C–H activation complex, $[\text{Co}(2\text{-}(4\text{-FC}_6\text{H}_3)\text{-}(\text{C}=\text{O})\text{-}(2'\text{-FC}_6\text{H}_4)(\text{PMe}_3)_3]$ (**4**) in comparison with the C–F activation in the double-fluorinated aromatic ketone, 2,6-difluorobenzophenone system. Increasing the substituted fluoroatoms in phenyl ring is beneficial for the C–F bond activation.

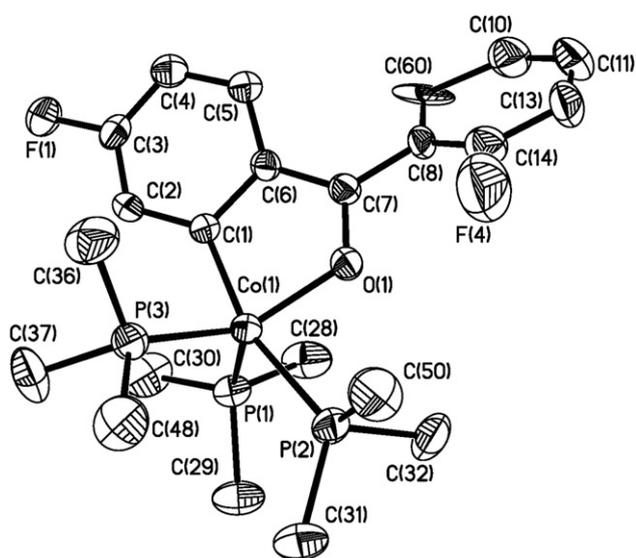


Fig. 3. Molecular structure of **4** and selected bond distances (\AA) and angles ($^\circ$): P3-Co1 $2.189(2)$, P2-Co1 $2.227(2)$; P1-Co1 $2.184(2)$, Co1-O1 $1.905(4)$, Co1-C1 $1.921(6)$, O1-Co1-C1 $82.5(2)$, O1-Co1-P1 $115.91(15)$, C1-Co1-P1 $92.2(2)$, O1-Co1-P3 $131.80(15)$, C1-Co1-P3 $90.78(19)$, P1-Co1-P3 $111.99(8)$, O1-Co1-P2 $80.45(14)$, C1-Co1-P2 $162.7(2)$, P1-Co1-P2 $97.76(9)$, P3-Co1-P2 $98.48(8)$.

3. Conclusions

The C–F or C–H bond of difluorobenzophenone can not be activated by $\text{Co}(\text{PMe}_3)_4$ [26], while the C–F or C–H bond of the difluorobenzophenone are activated by $\text{CoMe}(\text{PMe}_3)_4$. Both $\text{Co}(\text{PMe}_3)_4$ and $\text{CoMe}(\text{PMe}_3)_4$ can activate the C–F or C–H bond with the better anchoring group (C=NH) instead of the keto group. The Co-methyl group is beneficial for the C–H activation because of the thermodynamic contribution of evolution of methane. Increasing the substituted fluoroatoms in phenyl ring is advantageous to the C–F bond activation.

4. Experimental

4.1. General procedures and materials

Standard vacuum techniques were used in manipulations of volatile and air-sensitive materials. Literature method was used in the preparation of $\text{Co}(\text{PMe}_3)_4$ and $\text{CoMe}(\text{PMe}_3)_4$ [29]. 2,4'-difluorobenzophenone were used as purchased. 2,6-difluorobenzophenone and 2,6-difluorobenzophenone imine were prepared by published procedures [30,31]. Melting points were measured in capillaries sealed under argon and were uncorrected. Elemental analyses were carried out on an Elementar Vario EL III. Infrared spectra ($4000 - 400\text{ cm}^{-1}$), as obtained from Nujol mulls between KBr disks, were recorded on a Nicolet 5700. ^1H , ^{19}F and ^{31}P NMR (300, 282 and 121 MHz, respectively) spectra were recorded on a Bruker Avance 300 spectrometer. ^{31}P NMR resonances were obtained with broadband proton decoupling. X-ray crystallography was performed with a Bruker Smart 1000 diffractometer.

4.2. Synthesis of **1**

2,6-difluorobenzophenone imine 0.63 g (2.90 mmol) in pentane (30 mL) was mixed at -80°C with $\text{Co}(\text{PMe}_3)_4$ 1.06 g (2.92 mmol) in 30 mL of pentane. On warming, the reaction mixture turned blue and was stirred for 18 h at 20°C . Crystallization in pentane at -27°C afforded complex **1** as purple-blue crystals. Yield: 0.75 g (56.3%). Dec $>140^\circ\text{C}$. Analysis for **1** $\text{C}_{22}\text{H}_{36}\text{CoFNP}_3$, [found (calculated)]: C, 54.11 (54.44); H, 7.13 (7.48). IR (Nujol): $1603\text{ v}(\text{C}=\text{N})$, $1576\text{ v}(\text{C}=\text{C})$, $3195\text{ v}(\text{N}-\text{H})$, $946\text{ v}(\text{PMe}_3)$. ^1H NMR (300.1 MHz , C_6D_6 , 300 K): δ 0.90 (s(br), 27H , PCH_3), $6.63\text{--}7.77$ (m, 8H , CH_{arom}), 8.36 (s, H, NH). ^{31}P NMR (121.5 MHz , C_6D_6 , 300 K): δ 45.3 (s, P, PCH_3), 14.1 (s, 2P , PCH_3).

4.3. Synthesis of **2**

A solution of 0.69 g (1.82 mmol) of $\text{CoMe}(\text{PMe}_3)_4$ in 30 mL of pentane was combined with a solution of 2,6-difluorobenzophenone imine 0.40 g (1.82 mmol) in pentane (30 mL) at -80°C . The reaction mixture was allowed to warm to ambient temperature and stirred for 18 h , turning green. Crystallization in pentane at -27°C afforded complex **2** as deep-green crystals. Yield: 0.50 g ($54.3.0\%$). Analysis for **2** $\text{C}_{22}\text{H}_{35}\text{CoF}_2\text{NP}_3$, [found (calculated)]: C, 52.15 (52.49); H, 6.83 (7.01). IR (Nujol): $1620\text{ v}(\text{C}=\text{N})$, $1589\text{ v}(\text{C}=\text{C})$, $3193\text{ v}(\text{N}-\text{H})$, $946\text{ v}(\text{PMe}_3)$. ^1H NMR (300.1 MHz , C_6D_6 , 300 K): δ 0.92 (s(br), 27H , PCH_3), $6.65\text{--}7.73$ (m, 7H , CH_{arom}), 8.33 (s, H, NH). ^{31}P NMR (121.5 MHz , C_6D_6 , 300 K): δ 43.9 (s, 1P , PCH_3), 33.5 (s, 1P , PCH_3), 22.1 (s, 1P , PCH_3).

4.4. Synthesis of **3**

A solution of 0.83 g (3.81 mmol) 2,6-difluorobenzophenone in 30 mL pentane was combined with a solution of 1.44 g (3.81 mmol) $\text{CoMe}(\text{PMe}_3)_4$ in 30 mL pentane at -80°C . This reaction mixture was allowed to warm to ambient temperature and stirred for 18 h

to form deep-red solution with green deposition in the bottom. Crystallization from pentane at $-30\text{ }^{\circ}\text{C}$ yielded violet single crystals **3** (0.61 g, yield 36.3%). Analysis for **3** $\text{C}_{20}\text{H}_{29}\text{CoF}_2\text{OP}_2$, [found (calculated)]: C, 53.93 (54.06); H, 6.32 (6.58). Dec $> 150\text{ }^{\circ}\text{C}$. IR (Nujol): 1594 $\nu(\text{C}=\text{O})$, 1541 $\nu(\text{C}=\text{C})$, 944 $\nu(\text{PMe}_3)$. ^1H NMR (300.1 MHz, C_6D_6 , 300 K): δ 0.30 (s, 3H, CH_3), 0.79 (s(br), 18H, PCH_3), 6.33–7.75 (m, 8H, CH_{arom}). ^{31}P NMR (121.5 MHz, C_6D_6 , 300 K): δ 20.4 (s, 2P).

4.5. Synthesis of **4**

A solution of 0.50 g (1.32 mmol) of $\text{CoMe}(\text{PMe}_3)_4$ in 30 mL of pentane was combined with a solution of 2,4'-difluorobenzophenone 0.28 g (1.32 mmol) in pentane (30 ml) at $-80\text{ }^{\circ}\text{C}$. The reaction mixture was allowed to warm to ambient temperature and stirred for 18 h, turning deep-brown. Crystallization in pentane at $-27\text{ }^{\circ}\text{C}$ afforded complex **4** as red-brown crystals. Yield: 0.60 g (67.0%). Analysis for **4** $\text{C}_{22}\text{H}_{34}\text{CoF}_2\text{OP}_3$, [found (calculated)]: C, 52.11 (52.39); H, 6.52 (6.79). IR (Nujol): 1596 $\nu(\text{C}=\text{O})$, 1572 $\nu(\text{C}=\text{C})$, 936 $\nu(\text{PMe}_3)$. ^1H NMR (300.1 MHz, C_6D_6 , 300 K): δ 0.81–1.04 (s(br), 27H, PCH_3), 6.50–8.18 (m, 7H, CH_{arom}). ^{31}P NMR (121.5 MHz, C_6D_6 , 300 K): δ 43.9 (s, P, PCH_3), 17.5 (s, 2P, PCH_3). ^{19}F NMR (282.4 MHz, C_6D_6 , 300 K): δ -113.2 (s, 1F), -118.8 (s, 1F).

4.6. X-ray structure determinations

Intensity data were collected on a Bruker SMART diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$). Crystallographic data for complexes **1**, **3** + $\text{Co}(2,6\text{-C}_6\text{H}_3\text{F}_2\text{-CO}(\eta^2)\text{-C}_6\text{H}_5)(\text{PMe}_3)_3$ [26], and **4** are summarized in Table 1. The structures

Table 1
Crystallographic data for complexes **1**, **3** + $\text{C}_{22}\text{H}_{35}\text{CoF}_2\text{OP}_3$ [26], and **4**.

	1	3 + $\text{C}_{22}\text{H}_{35}\text{CoF}_2\text{OP}_3$ [26]	4
Mol wt	$\text{C}_{22}\text{H}_{36}\text{CoFNP}_3$	$\text{C}_{42}\text{H}_{64}\text{Co}_2\text{F}_4\text{O}_2\text{P}_5$	$\text{C}_{22}\text{H}_{34}\text{CoF}_2\text{OP}_3$
FW	485.36	949.64	504.33
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P-1$	$P-1$	$P2(1)/c$
<i>a</i> (Å)	9.291 (2)	9.0550 (18)	8.531 (3)
<i>b</i> (Å)	10.688 (3)	16.355 (3)	17.705 (5)
<i>c</i> (Å)	13.338 (3)	18.032 (4)	33.660 (10)
α ($^{\circ}$)	94.001 (4)	64.23 (3)	90
β ($^{\circ}$)	102.089 (4)	79.46 (3)	92.237 (6)
γ ($^{\circ}$)	99.587 (4)	79.30 (3)	90
<i>V</i> (Å ³)	1269.4 (5)	2347.2 (8)	5081 (3)
<i>Z</i>	2	2	2
T, K	273	273	273
Crystal size (mm)	$0.25 \times 0.20 \times 0.20$	$0.34 \times 0.25 \times 0.27$	$0.32 \times 0.36 \times 0.28$
<i>D_c</i> (g cm ⁻³)	1.270	1.344	1.319
No. of rflns collections	7568	15,085	25,565
No. of independent rflns	5612	9113	9732
Parameters	262	587	523
<i>R</i> _{int}	0.0259	0.0774	0.0681
θ_{max} ($^{\circ}$)	28.00	26.81	25.63
<i>R1</i> ($I > 2\sigma(I)$)	0.0661	0.0408	0.0797
<i>wR2</i> (all data)	0.2142	0.1244	0.2638

were solved by direct methods and refined with full matrix least-squares on all F^2 (SHELXL-97) with non-hydrogen atoms anisotropic.

Acknowledgment

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Appendix A. Supplementary materials

CCDC 742942, 742940 and 742943 contain the supplementary crystallographic data for complexes **1**, **3** + $\text{C}_{22}\text{H}_{35}\text{CoF}_2\text{OP}_3$ [26], and **4**. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data-request/cif.

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