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## Aromatic ketone as chelating ligand in trimethylphosphine complexes of cobalt through cyclometalation reactions and C-H activation

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### Abstract

Cyclometalation transform barely activated or non-activated C-H bonds of coordinated ligands into C-metal bonds. Metallacyclic species are known for almost all transition elements, and the majority of them contain five-membered rings. <sup>[1, 2]</sup> Since the decisive breakthrough by Murai *et al.*, who achieved a highly efficient ruthenium-catalyzed addition of aromatic C-H bonds to unsaturated substrates this reaction is recognized as a new category of chemistry. The compounds which were synthesized and presented in this work serve as stable models of reactive intermediate. Benzophenone and benzylphenylketone reacts smoothly under mild conditions with CoMe (PMe<sub>3</sub>)<sub>4</sub> by elimination of methane to afford five-membered metallacycles compounds 1, 2 respectively. Iodomethane reactions with compound 1 form iodo-cobalt (III) complex 3 through oxidative addition reaction. 2,3,4,5,6-pentafluorobenzophenone react with Co(I) educts by elimination of methane and C-F activation to afford penta coordinate Co(I), complex 4. All complexes 1-4 obtained were characterized by spectroscopy IR, NMR and their X-ray diffraction was discussed.

**Keywords:** Aromatic ketone; chelating ligand; Trimethylphosphine; Cobalt complexes; Cyclometalation reactions

### Introduction

Organometallic ideas have been useful in interpreting the chemistry of metal surfaces and of metal colloids. The controlled pyrolysis of organometallic species has proved to be a useful way of preparing solid-state material with unusual properties <sup>[3, 4]</sup>. Public concern for the environment has led to the rise of "green chemistry", the purpose of which is to minimize the production of chemical waste in industry and commerce. One way to do this is to use catalysts rather than stoichiometric reagents to bring about reactions. Many commercially important processes that rely on transition metal organometallic complexes as catalysts have been developed, and such applications are likely to gain more importance in the future <sup>[5]</sup>. The carbon – hydrogen bond of alkanes cannot usually be regarded as functional group. Its unique position in organic chemistry is well illustrated by the standard representation of organic molecules: the presence of C-H bonds is indicated simply by the absence of any other bond. C-H bond activations are often classified as proceeding via either nucleophilic (oxidative addition) or electrophilic modes. However, these two classes of C-H activation have much in common, perhaps even more so than the corresponding modes of H<sub>2</sub> activation. Both reactions appear to proceed through a  $\sigma$ -bond intermediate <sup>[6-8]</sup>. Even more striking, putatively electrophilic activations, in most cases, proceed via complete oxidative addition (followed by deprotonation of the resulting metal hydride) <sup>[9]</sup>. The activation of carbon-fluorine bonds is of great importance in organometallic chemistry and catalyst development because this type of reaction contributes to the fundamental understanding of the reactivity of stable bonds and the selective replacement of F atoms <sup>[10-13]</sup>. Reports on C-F activation by first row transition metals are rare <sup>[14]</sup>, and no examples of organo iron or cobalt fluorides containing a C-M-F moiety have been described. The only cobalt-promoted carbon-fluorine bond activation was reported with ionic cobaltocenium fluoride as fluoride source <sup>[15]</sup>.

### Experimental

#### General procedures and materials

All syntheses and manipulations were carried out under an inert atmosphere of argon or nitrogen by using modified Schlenk techniques <sup>[16]</sup>.

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This type of apparatus offers an opportunity of carrying out a complete synthesis in a closed system, and in one run synthesis, transport and storage of chemicals were done under an atmosphere of purified Argon (BTS catalyst) [17]. Solvents (THF, diethyl ether, pentane) were dried according to known procedures and were freshly distilled prior to use. All reagents (Aldrich, Acros, Fluka, or Lancaster) were used as purchased without further purification.

Trimethylphosphine  $\text{PMe}_3$  [18],  $\text{Co}(\text{PMe}_3)_4$  [19],  $\text{CoMe}(\text{PMe}_3)_4$  [20], benzophenone, 2, 3, 4, 5, 6-pentafluorobenzophenone. C, H, P, N analyses of air sensitive solids were carried by H. Kolbe micro-analytical laboratory, Mulheim /Ruhr. Infrared spectra ( $4000\text{--}400\text{ cm}^{-1}$ ), as obtained from Nujol mulls between KBr discs, were recorded on a Bruker FRA106 spectrometer.  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectra were obtained from Bruker AVANCE 500, ARX 300 and AM 200 spectrometers.  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR resonances were obtained with broad-band proton decoupling. Assignment of  $^{13}\text{C}$  signals was supported by DEPT trace. Melting points were measured in capillaries sealed under argon atmosphere.

[2-(Benzoyl- $\kappa\text{O}$ ) phenyl- $\kappa\text{C}$ ] tris-(trimethylphosphine) cobalt (I) (1) 920 mg (2.43 mmol) of  $\text{CoMe}(\text{PMe}_3)_4$  in THF were combined with 443 mg (2.43 mmol) of benzophenone to afford 924 mg of brown crystals of 1 which crystallize at  $4^\circ\text{C}$ .

Yield 81%; M.P  $111 - 113^\circ\text{C}$ . (dec.). IR (Nujol)  $\nu = 3057\text{ w}$  ( $\nu\text{ H-C=C}$ );  $1582\text{ m}$  ( $\nu\text{ C=C}$ );  $1484\text{ m}$  ( $\nu\text{ C=O}$ );  $935\text{ vs}$  ( $\rho_1\text{ PCH}_3$ ).  $^1\text{H}$  NMR (500 MHz,  $[\text{D}_8]$  THF, 300 K):  $\delta = 1.30(\text{d}, ^2J_{\text{P,H}} = 6.5\text{ Hz}, 27\text{ H}, \text{PCH}_3)$ ;  $6.61(\text{dt}, ^4J_{\text{H,H}} = 0.8\text{ Hz}, ^3J_{\text{H,H}} = 7.8\text{ Hz}, 1\text{ H}, \text{Ar-H})$ ;  $7.12(\text{t}, ^3J_{\text{H,H}} = 7.8\text{ Hz}, 2\text{H}, \text{Ar-H})$ ;  $7.33(\text{tt}, ^4J_{\text{H,H}} = 1.2\text{ Hz}, ^3J_{\text{H,H}} = 8.0\text{ Hz}, 1\text{H}, \text{Ar-H})$ ;  $7.46(\text{dt}, ^4J_{\text{H,H}} = 0.9\text{ Hz}, ^3J_{\text{H,H}} = 7.4\text{ Hz}, 1\text{H}, \text{Ar-H})$ .  $^{13}\text{C}$  NMR (125 MHz,  $[\text{D}_8]$  THF, 300 K):  $\delta = 21.3(\text{m}, \text{PCH}_3)$ ;  $118.3(\text{q}, ^4J_{\text{P,C}} = 4.6\text{ Hz}, \text{CH})$ ;  $121.9(\text{s}, \text{CH})$ ;  $122.6(\text{s}, \text{CH})$ ;  $123.7(\text{d}, ^5J_{\text{P,C}} = 2.4\text{ Hz}, \text{CH})$ ;  $124.2(\text{dd}, ^4J_{\text{P,C}} = 3.4\text{ Hz}; 170.8(\text{q}, ^3J_{\text{P,C}} = 11.8\text{ Hz}, \text{C=O})$ ,  $173.9(\text{m}, \text{Co-C})$ .  $^{31}\text{P}$  NMR (202 MHz,  $[\text{D}_8]$  THF, 300 K):  $\delta = 5.1(\text{S}_{\text{br}}, \text{PCH}_3)$ .  $\text{C}_{22}\text{H}_{36}\text{CoOP}_3$  (468.83): Calc C, 56.42; H, 7.75; P, 19.84 Found: C, 56.95; H, 7.53; P, 20.68 %.

[2-(Benzoyl- $\kappa\text{O}$ ) benzyl- $\kappa\text{C}$ ] tris-(trimethylphosphine) cobalt (I) (2) 1.15 g (3.04 mmol) of  $\text{CoMe}(\text{PMe}_3)_4$  in THF were combined with 0.60 g (3.04 mmol) of benzylphenylketone to afford 0.97 g of brown crystals 2 which crystallize from pentane at  $-27^\circ\text{C}$ . Yield 66%; M.P  $107 - 109^\circ\text{C}$ . (dec.). IR (Nujol)  $\nu = 3048\text{ m}, 3023\text{ m}$  ( $\nu\text{ H-C=C}$ );  $1580\text{ s}, 1570\text{ s}, 1547\text{ s}$ , ( $\nu\text{ C=C}$ );  $1483\text{ m}$  ( $\nu\text{ C=O}$ );  $937\text{ vs}$  ( $\rho_1\text{ PCH}_3$ );  $874\text{ m}$  ( $\rho_2\text{ PCH}_3$ );  $748(\gamma\text{ C-H}_{\text{arom}})$ ;  $712\text{ s}, 698\text{ vs}$  ( $\nu_{\text{as}}\text{ PC}_3$ ).  $^1\text{H}$  NMR (500 MHz,  $[\text{D}_8]$  THF, 300 K):  $\delta = 1.05(\text{S}_{\text{br}}, 27\text{H}, \text{PCH}_3)$ ;  $4.20(\text{s}, 2\text{H}, \text{CH}_2)$ ;  $7.25 - 7.55(\text{m}, 6\text{H}, \text{Ar-H})$ ;  $8.03 - 9.19(\text{m}, 3\text{H}, \text{Ar-H})$ .  $^{13}\text{C}$  NMR (125 MHz,  $[\text{D}_8]$  THF, 300 K):  $\delta = 20.9(\text{m}, \text{PCH}_3)$ ;  $46.1(\text{s}, \text{CH}_2)$ ;  $127.5(\text{s}, \text{CH})$ ;  $129.4(\text{s}, \text{CH})$ ;  $129.6(\text{d}, ^3J_{\text{P,C}} = 8.2\text{ Hz}, \text{CH})$ ;  $130.6(\text{s}, \text{CH})$ ;  $133.8(\text{s}, \text{CH})$ ;  $136.5(\text{s}, \text{CH})$ ;  $138.2(\text{s}, \text{C})$ ;  $151.2(\text{m}, \text{C})$ ;  $158.4(\text{s}, \text{CH})$ ;  $166.1(\text{s}, \text{Co-C=O})$ ;  $183.7(\text{m}, \text{Co-C})$ .  $^{31}\text{P}$  NMR (202 MHz,  $[\text{D}_8]$  THF, 300 K):  $\delta = 1.5(\text{S}_{\text{br}}, 3\text{P}, \text{PCH}_3)$ .  $\text{C}_{23}\text{H}_{38}\text{CoOP}_3$  (482.41): Calc C, 57.27; H, 7.94; P, 19.26 Found: C, 56.49; H, 7.39; P, 19.53 %.

Iodo (methyl) [2-(Benzoyl- $\kappa\text{O}$ ) benzyl- $\kappa\text{C}$ ] bis-(trimethylphosphine) cobalt (III) (3)

540 mg (1.15 mmol) of compound 1 in pentane were combined with 327 mg (1.44 ml, 2.30 mmol) of  $\text{CH}_3\text{I}$  to afford 431 mg of dark orange crystals 3 which crystallize at  $4^\circ\text{C}$ . Yield 67%; M.P  $133 - 135^\circ\text{C}$ . (dec.). IR (Nujol)  $\nu = 3058\text{ vw}, 3034\text{ vw}$  ( $\nu\text{ H-C=C}$ );  $1569\text{ m}$  ( $\nu\text{ C=C}$ );  $1547\text{ m}$  ( $\nu\text{ C=O}$ );  $1158\text{ w}$  ( $\delta_{\text{s}}\text{ Co-CH}_3$ );  $947\text{ vs}$  ( $\rho_1\text{ PCH}_3$ );  $720\text{ m}$  ( $\gamma\text{ C-H}_{\text{arom}}$ );  $706\text{ m}$  ( $\nu_{\text{as}}\text{ PC}_3$ ).  $^1\text{H}$  NMR (500 MHz,  $[\text{D}_8]$  THF, 300

K):  $\delta = 0.21(\text{t}, ^3J_{\text{P,H}} = 9.4\text{ Hz}, 3\text{H}, \text{Co-CH}_3)$ ;  $1.11(\text{t}', ^2J_{\text{P,H}} + ^4J_{\text{P,H}} = 7.8\text{ Hz}, 18\text{H}, \text{PCH}_3)$ ;  $6.97(\text{tt}, ^3J_{\text{H,H}} = 7.8\text{ Hz}, ^4J_{\text{H,H}} = 0.9\text{ Hz}, 1\text{H}, \text{Ar-H})$ ;  $7.21(\text{dt}, ^3J_{\text{H,H}} = 7.0\text{ Hz}, ^4J_{\text{H,H}} = 1.5\text{ Hz}, 1\text{H}, \text{Ar-H})$ ;  $7.39(\text{td}, ^3J_{\text{H,H}} = 7.3\text{ Hz}, ^4J_{\text{H,H}} = 3\text{ Hz}, 1\text{H}, \text{Ar-H})$ ;  $7.53(\text{tt}, ^3J_{\text{H,H}} = 7.8\text{ Hz}, ^4J_{\text{H,H}} = 1.5\text{ Hz}, 2\text{H}, \text{Ar-H})$ ;  $7.59(\text{tt}, ^3J_{\text{H,H}} = 7.3\text{ Hz}, ^4J_{\text{H,H}} = 1.3\text{ Hz}, 1\text{H}, \text{Ar-H})$ ;  $7.75 - 7.82(\text{m}, 3\text{H}, \text{Ar-H})$ .  $^{13}\text{C}$  NMR (125 MHz,  $[\text{D}_8]$  THF, 300 K):  $\delta = -10.1(\text{m}, \text{Co-CH}_3)$ ;  $14.6(\text{t}', ^1J_{\text{P,C}} + ^3J_{\text{P,C}} = 27.6\text{ Hz}, \text{PCH}_3)$ ;  $122.2(\text{s}, \text{CH})$ ;  $129.7(\text{s}, \text{CH})$ ;  $130.2(\text{s}, \text{CH})$ ;  $131.6(\text{t}, ^4J_{\text{P,C}} = 2.2\text{ Hz}, \text{CH})$ ;  $132.9(\text{s}, \text{CH})$ ;  $133.5(\text{d}, ^4J_{\text{P,C}} = 2.5\text{ Hz}, \text{CH})$ ;  $138.1(\text{s}, \text{C})$ ;  $139.1(\text{s}, \text{C})$ ;  $144.0(\text{s}, \text{CH})$ ;  $171.8(\text{m}, \text{C=O})$ ;  $188.6(\text{m}, \text{Co-C})$ .  $^{31}\text{P}$  NMR (202 MHz,  $[\text{D}_8]$  THF, 300 K):  $\delta = 2.03(\text{S}_{\text{br}}, 2\text{P}, \text{PCH}_3)$ .  $\text{C}_{20}\text{H}_{30}\text{CoIOP}_2$  (534.24): Calc C, 44.96; H, 5.66; P, 11.60 Found: C, 44.77; H, 5.80; P, 11.66 %.

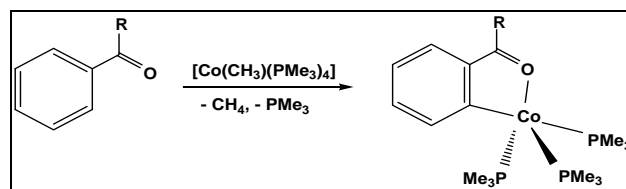
[2-(3, 4, 5, 6-Tetrafluoro-benzoyl- $\kappa\text{O}$ ) phenyl- $\kappa\text{C}$ ] tris-(trimethylphosphine) cobalt (I) (4)

1.20 g (3.17 mmol) of  $\text{CoMe}(\text{PMe}_3)_4$  in THF were combined with 0.86 g (3.17 mmol) of

2, 3, 4, 5, 6-pentafluorobenzophenone to afford 1.08 g of brown crystals 4 which crystallize from pentane at  $-27^\circ\text{C}$ . Yield 63 %; M.P  $152 - 154^\circ\text{C}$ . (dec.). IR (Nujol)  $\nu = 3077\text{ vw}$  ( $\nu\text{ H-C=C}$ );  $1617\text{ m}$  ( $\nu\text{ C=C}$ );  $1590\text{ m}$  ( $\nu\text{ C=C}$ );  $1490\text{ m}$  ( $\nu\text{ C=O}$ );  $1339\text{ s}$  ( $\text{O}$ );  $1339\text{ s}$  ( $\nu\text{ F-C=C}$ );  $939\text{ vs}$  ( $\rho_1\text{ PCH}_3$ );  $830\text{ m}$  ( $\rho_2\text{ PCH}_3$ );  $771\text{ m}, 760\text{ m}$  ( $\gamma\text{ C-H}_{\text{arom}}$ ).  $^1\text{H}$  NMR (500 MHz,  $[\text{D}_8]$  THF, 300 K):  $\delta = 1.32(\text{d}, ^2J_{\text{P,H}} = 6.1\text{ Hz}, 27\text{ H}, \text{PCH}_3)$ ;  $7.09(\text{t}, ^2J_{\text{H,H}} = 7.2\text{ Hz}, 2\text{H}, \text{Ar-H})$ ;  $7.48(\text{t}, ^3J_{\text{H,H}} = 7.0\text{ Hz}, 1\text{H}, \text{Ar-H})$ ;  $7.81(\text{t}, ^3J_{\text{H,H}} = 6.5\text{ Hz}, 2\text{H}, \text{Ar-H})$ .  $^{13}\text{C}$  NMR (125 MHz,  $[\text{D}_8]$  THF, 300 K):  $\delta = 20.5(\text{d}, ^1J_{\text{P,C}} = 20.5\text{ Hz}, \text{PCH}_3)$ ;  $124.0(\text{s}, \text{CH})$ ;  $124.3(\text{s}, \text{CH})$ ;  $128.5(\text{m}, \text{CF})$ ;  $128.8(\text{m}, \text{CF})$ ;  $129.1(\text{s}, \text{CH})$ ;  $129.4(\text{m}, \text{CF})$ ;  $134.5(\text{m}, \text{CF})$ ;  $141.5(\text{m}, \text{C})$ ;  $147.4(\text{s}, \text{C})$ ;  $167.9(\text{s}, \text{C=O})$ ;  $168.7(\text{m}, \text{Co-C})$ .  $^{31}\text{P}$  NMR (202 MHz,  $[\text{D}_8]$  THF, 300 K):  $\delta = 3.6(\text{S}_{\text{br}}, \text{PCH}_3)$ .  $\text{C}_{22}\text{H}_32\text{CoF}_4\text{OP}_3$  (540.34): Calc C 48.90; H 5.97; P 17.20 Found: C 48.58; H 5.70; P 16.88 %.

## Results and discussion

Combining THF solutions of  $\text{CoMe}(\text{PMe}_3)_4$  with benzophenone or benzylphenylketone at  $-70^\circ\text{C}$  after 16 h affords dark brown solutions from which the compounds 1 and 2 were isolated as dark brown crystals in about 81% and 66% yields, respectively [Eq. 1].



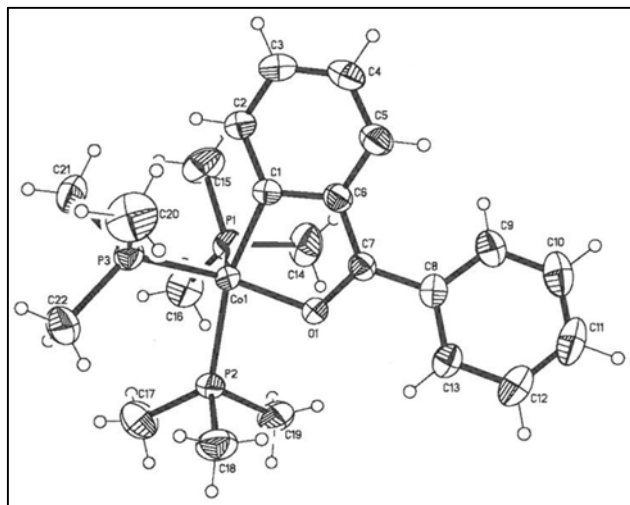
**R = C<sub>6</sub>H<sub>5</sub> 1**

**R = CH<sub>2</sub> (C<sub>6</sub>H<sub>5</sub>) 2**

Compounds 1 and 2, form pentacoordinate molecular complexes which decompose around  $110^\circ\text{C}$ . Elemental analyses confirm the composition after elimination of methane and one of trimethylphosphine ligands. The infrared absorptions of the acyl groups coordinated through oxygen to the cobalt show the expected hypsochromic shifts. They have absorbance's in lower energies than the free ketone,  $1484\text{cm}^{-1}$  ( $\nu\text{ C=O}$ ) 1 and  $1483\text{ cm}^{-1}$  ( $\nu\text{ C=O}$ ) 2.

In  $^1\text{H}$  NMR experiment trimethylphosphine protons resonate at 1.3 ppm as a doublet ( $^2J_{\text{P,H}} = 6.5\text{ Hz}, 27\text{ H}$ ); 1) and at 1.05 ppm as a broad singlet (27 H; 2) due to the ligand dynamics in trigonal bipyramidal systems. In  $^{31}\text{P}$  NMR spectrum three phosphorus nuclei resonate at 5.1 ppm in 1 and at 1.5 ppm in

2 as broad singlets. There can be two reasons for this exchange broadening in trigonal bipyramidal systems: we have either dissociation of trimethylphosphine groups or fast exchange of ligand positions in a pseudorotation process. In the slow exchange limit, we should observe in  $^{13}\text{C}$  spectrum a quartet due to P,C coupling. Only in complex 1 we can clearly locate the C=O resonance as quartet at 170.8 ppm ( $^3J_{\text{P,C}} = 11.8$  Hz). The acyl group in complex 2 resonates at 166.1 ppm as singlet. Coordinated acyl groups appear at higher energies in both compounds than in the ketones; C=O resonates in benzophenone at 196.50 ppm and in benzyl phenyl ketone at 197.43 ppm.  $^{121}$   $^{13}\text{C}$  NMR data confirms the cyclometalation, as metalated carbon atoms resonate at 173.9 ppm (1) and 183.7 ppm (2).



**Fig 1:** Molecular structure of complex 1. Selected bond lengths [Å] and angles [°]: Co1-O1 1.9051(12), Co1-C1 1.9339(18), Co1-P1 2.1786(6), Co1-P3 2.1852(6), Co1-P2 2.2401(5), C7-O1 1.297(2), C6-C7 1.430(3), C7-C8 1.460(3), O1-Co1-C1 83.49(7), C1-Co1-P2 163.52(6), C1-Co1-P1 90.33(6), O1-Co1-P3 137.94(5), C1-Co1-P3 91.46(6), P1-Co1-P3 110.77(2), P1-Co1-P2 97.73(2), P3-Co1-P2 99.01(2), O1-Co1-P2 81.21(4), O1-Co1-P1 110.84(5), C7-O1-Co1 117.51(11).

The structural data for complex 1 shows trigonal bipyramidal geometry of ligands around the central cobalt atom (C-Co1-P angle near  $163^\circ$ ). The two axial positions are occupied by the metalated carbon atom and a phosphine ligand while two  $\text{PMe}_3$  groups and the oxygen donor of the benzophenone group reside in equatorial positions. The Co-O and Co-C distances (Co1-O1 = 1.9051(12) and Co1-C1 = 1.9339(18) Å) correspond with literature values  $^{[22]}$ . The Co1-P2 distance is elongated (Co1-P2 = 2.2401(5) Å), due to the trans influence of the carbon atom while the other Co-P and P-C bond lengths are close to the average of reported values in arylcobalt compounds. The sum of the internal angles in the five membered metallacycle ( $540^\circ$ ) equals that of a regular pentagon. Benzophenone and benzyl phenyl ketone react with  $\text{Co}(\text{CH}_3)(\text{PMe}_3)_4$  to give ortho-metalated Co(I) complexes 1 and 2.

Coordination of the carbonyl oxygen of aromatic ketones to cobalt is the origin of the high ortho selectivity, which induces breaking of the closest ortho C-H bond. Complex 1 reacts with iodomethane in pentane by dissociation and quarternization of a trimethylphosphine [Eq.2] to afford the octahedral Co (III) complex 3.

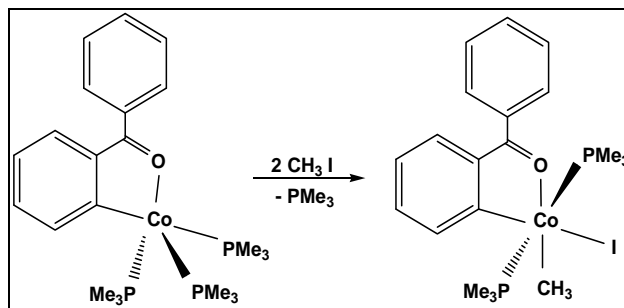


Fig 2

Fig 3

The dark orange crystals of 3 are air stable and under argon decompose above  $133^\circ\text{C}$ . Elemental analysis data support the loss of trimethylphosphine group and coordination of iodomethane. Spectroscopic data are consistent with an octahedral coordination around the cobalt atom. In the IR spectrum, Co-CH<sub>3</sub> group shows a bending vibration at  $1158\text{ cm}^{-1}$  ( $\delta_s$  Co-CH<sub>3</sub>). In the  $^1\text{H}$  NMR spectrum, they resonate as a triplet at 0.21 ppm ( $^3J_{\text{P,H}} = 9.4$  Hz) and as a multiplet at  $-10.1$  ppm, in  $^{13}\text{C}$  NMR spectrum. The protons of *trans* trimethylphosphine groups give a resonance as pseudo triplet at 1.11 ppm ( $t', |^2J_{\text{P,H}} + ^4J_{\text{P,H}}| = 7.8$  Hz, 18H, PCH<sub>3</sub>) in  $^1\text{H}$  NMR and at 14.6 ppm ( $t', |^1J_{\text{P,C}} + ^3J_{\text{P,C}}| = 27.6$  Hz, PCH<sub>3</sub>) in  $^{13}\text{C}$  NMR. In the  $^{31}\text{P}$  NMR spectrum a broad singlet at 2.03 ppm is observed for them. Acyl carbon and metalated carbon have  $^{13}\text{C}$  NMR multiplets at 171.8 ppm and 188.6 ppm. Oxidative addition reaction of 3 form a Co (III) complex which is a very stable solid and their spectra fully consistent with octahedral geometry and two *trans* disposed trimethylphosphine groups. Methyl and Iodide groups occupy *cis* positions and are coplanar with the metallacycle. An intramolecular C-F activation by cobalt complexes has not been reported. After obtaining the first ortho-metalated complex of cobalt 1 with benzophenone, 2, 3, 4, 5, 6 – pentafluoro-benzophenone was used to study the preference for the C-H or C-F activation in aromatic ketones.  $\text{CoMe}(\text{PMe}_3)_4$  was combined with 2,3,4,5,6 – pentafluoro-benzophenone to afford pentacoordinate cobalt (I) complex 4 which crystallizes from pentane at  $-27^\circ\text{C}$  [Eq.3].

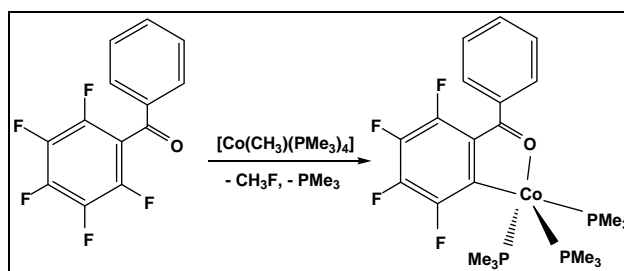
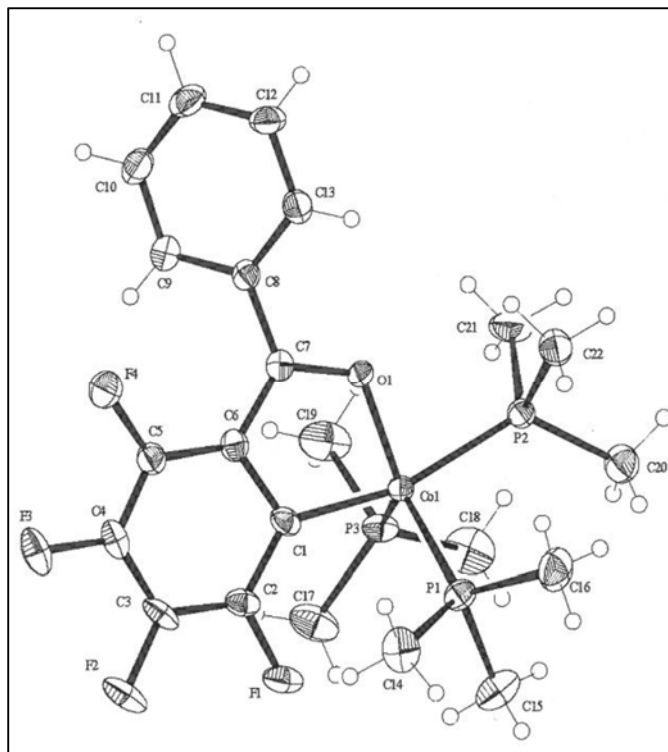


Fig 4

The brown crystals of 4 start to decompose at  $152^\circ\text{C}$  which is  $40^\circ\text{C}$  higher than 1. Elemental analysis confirms the expected constitution of 4 with three trimethylphosphine groups and loss of one fluorine atom. The IR spectra show a  $\nu(\text{C}=\text{O})$  vibration at  $1490\text{ cm}^{-1}$  which lies by  $6\text{ cm}^{-1}$  to higher energy than that in 1, along with a strong  $\nu(\text{F}-\text{C})$  vibration at  $1339\text{ cm}^{-1}$ . In the  $^1\text{H}$  NMR spectrum the protons of trimethylphosphine groups resonate at 1.32 ppm as a doublet  $n(^2J_{\text{P,H}} = 6.1$  Hz) indicating ligand mobility. In  $^{31}\text{P}$  NMR as a broad singlet at 3.6 ppm is recorded. Five aromatic protons on the phenyl ring resonate at 7.09 ppm ( $t', ^3J_{\text{H,H}} = 7.2$  Hz, 2H), 7.48

ppm ( $t, {}^3J_{\text{H,H}}=7.0$  Hz, 1H) and 7.81 ppm ( $t, {}^3J_{\text{H,H}}=6.5$  Hz, 2H), respectively. Highly concentrated solution of 4 was prepared in order to see the fluorinated carbon atoms in a  ${}^{13}\text{C}$   $\{^1\text{H}\}$  NMR spectrum (see Experimental Part). The metalated carbon atom is detected resonates at 168.7 ppm as multiplet and the coordinated C=O group resonates at 167.9 ppm as a singlet. A view of the molecular geometry of 4 is shown in Figure 2 which confirms the geometry predicted from spectroscopic and analytical data. The unit cell contains two discrete molecules. The coordination geometry around the cobalt atom can be rationalized as a distorted trigonal

bipyramid with three phosphorus atoms of the trimethylphosphine ligands occupying axial and equatorial positions; C1-Co1-P2 163.89(14) $^\circ$ , O1-Co1-P1 135.02(10) $^\circ$ , and O1-Co1-P3 112.87(10) $^\circ$ . The cobalt sphere is completed by the ortho-metalated ketone, which acts with a bite angle of 82.26(16) $^\circ$ . The sum of the inner angles of the five membered metallacycle is 539.28 $^\circ$  and in the trigonal plane (formed by O1, P1, P3 and Co1) we have a sum of 359.95 $^\circ$ . The main axis lies along C1-Co1-P2 = 163.89(14) $^\circ$ . The plane of the phenyl ring which is not *ortho*-metalated forms an angle with that of the fluorinated phenyl ring about 40 $^\circ$ .



**Fig 5:** Molecular structure of complex 4. Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ]: Co1-O1 1.903(3), Co1-C1 1.934(4), Co1-P1 2.2038(14), Co1-P3 2.21958(13), Co1-P2 2.2294(13), C7-O1 1.297(5), C6-C7 1.419(6), C7-C8 1.472(6); O1-Co1-C1 82.28(16), C1-Co1-P2 163.89(14), C1-Co1-P1 94.71(14), O1-Co1-P3 112.87(10), C1-Co1-P3 91.35(13), P1-Co1-P3 112.06(5), P1-Co1-P2 96.14(5), P3-Co1-P2 95.56(5), O1-Co1-P2 81.62(9), O1-Co1-P1 135.02(10), C7-O1-Co1 117.9(3).

The distance Co1-P2 = 2.2294(13)  $\text{\AA}$  is longer than the equatorial bonds Co1-P1 = 2.2038(14)  $\text{\AA}$  and Co1-P3 = 2.1958(13)  $\text{\AA}$ . Due to the coordination and chelation, the bond C6-C7 = 1.419(6)  $\text{\AA}$  is shorter than the C7-C8 = 1.472(6)  $\text{\AA}$ . Thermodynamic and kinetic factors affect the selectivity of the activation in partially fluorinated systems [23]. A simple way to picture the whole process arises from bonding energy arguments. Intramolecular activation of the C-F bond has been carried out with Pt(II) and W(0) complexes and it has been demonstrated that the C-F bond is cleaved selectively in the presence of weaker C-H bonds if the ligands are designed with steric constraints; otherwise C-H attack is preferred. The kinetic analysis of these reactions supports a conventional oxidative addition mechanism [24-29]. Assuming that Co-C bonding energy is similar in all cases (the bond formed by C-H or C-F activation), the difference between both C-H and C-F activation processes can be traced to the relative bond energies C-F, C-H, H<sub>3</sub>C-F and H<sub>3</sub>C-H in complex 4. Thus, while the C-F activation process would be disfavoured because of the higher energy required to break a C-F bond, this should be largely compensated by the H<sub>3</sub>C-F formation energy. But on the other side C-F bond of H<sub>3</sub>C-F is weaker

than C-H bond of CH<sub>4</sub> to compensate the energy difference. Caulton stated that the coordination site strongly influence thermodynamics [30]. If coordination to the oxygen brings the metal close to the fluorinated aromatic ring, C-F activation is preferred. So this will be the one which needs less activation energy in the transition state. This is a case where the traditionally defined bond dissociation energies may be of little use for determining reaction thermodynamics. A similar situation has been reported by Su and Chu who found that the oxidative addition of the C-F bond in CH<sub>3</sub>-F to 3-coordinated 14-electron complexes M(X) (PH<sub>3</sub>)<sub>2</sub> (M = Rh, Ir; X = CH<sub>3</sub>, H, Cl) is thermodynamically favourable [31]. However, the C-F bond of CH<sub>3</sub>F is exceptionally weak compared with an aromatic C-H bond. If the concerted oxidative addition to a C-F bond is kinetically unfavourable, the reductive elimination of R-F is even more unfavorable because of microscopic reversibility. Compound 1 which is formed by C-H activation have the same structural characteristics with C-F bond activated 4. All two compounds show the same deviation from the ideal trigonal bipyramidal geometry. The five-membered metallacycle is very close to the ideal value in all two compounds.

**Table 1:** Crystal data for compound 1.

Empirical formula	C <sub>22</sub> H <sub>36</sub> Co O P <sub>3</sub>
Formula weight	468.35
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	Pna2(1)
Unit cell dimensions	a = 16.4913(9) Å α = 90° b = 9.5041(5) Å β = 90° c = 15.8471(9) Å γ = 90°
Volume	2483.8(2) Å <sup>3</sup>
Z	4
Density (calculated)	1.252 Mg/m <sup>3</sup>
Absorption coefficient	0.893 mm <sup>-1</sup>
F (000)	992
Crystal size	0.50 x 0.45 x 0.40 mm <sup>3</sup>
Theta range for data collection	2.47 to 28.30°
Index ranges	-21 ≤ h ≤ 21, -12 ≤ k ≤ 12, -19 ≤ l ≤ 21
Reflections collected	23133
Independent reflections	5960 [R (int) = 0.0234]
Completeness to 2theta = 26.37°	99.8%
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	5960 / 1 / 254
Goodness-of-fit on F <sup>2</sup>	1.051
Final R indices [I > 2σ(I)]	R1 = 0.0295, wR2 = 0.0702
R indices (all data)	R1 = 0.0339, wR2 = 0.0727
Largest diff. peak and hole	0.256 and -0.266 e. Å <sup>-3</sup>

**Table 2:** Crystal data for compound 4.

Empirical formula	C <sub>22</sub> H <sub>32</sub> Co O P <sub>3</sub>
Formula weight	540.32
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	P -1
Unit cell dimensions	a = 12.7954(16) Å α = 90.220(11)° b = 13.2517(16) Å β = 89.935(12)° c = 14.830(2) Å γ = 95.992(10)°
Volume	2.5008(6) Å <sup>3</sup>
Z	4
Density (calculated)	1.435 Mg/m <sup>3</sup>
Absorption coefficient	0.920 mm <sup>-1</sup>
F (000)	1120
Crystal size	0.2 x 0.3 x 0.28 mm <sup>3</sup>
Theta range for data collection	1.55 to 26.86°
Index ranges	-16 ≤ h ≤ 16, -16 ≤ k ≤ 16, -18 ≤ l ≤ 18
Reflections collected	35118
Independent reflections	10617 [R (int) = 0.1728]
Completeness to 2theta = 26.37°	98.5%
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	10617 / 0 / 559
Goodness-of-fit on F <sup>2</sup>	0.973
Final R indices [I > 2σ(I)]	R1 = 0.0604, wR2 = 0.1135
R indices (all data)	R1 = 0.1142, wR2 = 0.1280
Largest diff. peak and hole	0.542 and -0.582 e. Å <sup>-3</sup>

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