

Reactions of cationic iron P-coordinated (diphenylphosphino) alkynes with dicobalt octacarbonyl

Elmostafa Louattani ^a, Joan Suades ^{a,*}, Angel Alvarez-Larena ^b, Joan F. Piniella ^b,
Gabriel Germain ^c

^a *Departament de Química, Edifici C, Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain*

^b *Departament de Geologia, Edifici C, Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain*

^c *Unité de Chimie Physique Moléculaire et de Cristallographie, Université de Louvain, B-1348 Louvain la Neuve, Belgium*

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Abstract

Reaction of the P-coordinated transition metal complexes $[(Fp)Ph_2PC\equiv CR][BF_4]$ ($R = H, CH_3, Ph, p\text{-tolyl}$; $Fp = CpFe(CO)_2$) with cobalt octacarbonyl at room temperature affords the cationic heterometallic complexes $[(Fp)Ph_2PC\equiv CR\{Co_2(CO)_6\}][BF_4]$ (**1–4**) in high yields. A single-crystal X-ray structural analysis of **3** showed that the hexacarbonyldicobalt fragment is π -bonded to the alkynyl group of the P-coordinated (diphenylphosphino)alkyne without significant interaction between the iron and cobalt fragments. Spectroscopic data for **1–4** and structural data for **3** suggest that the positive charge is mainly located on the iron fragment.

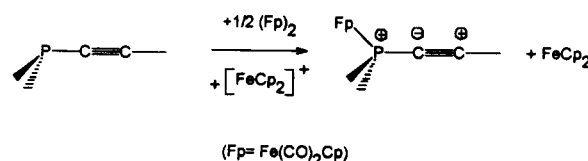
Keywords: Phosphinoalkyne; Carbonyl; Iron; Cobalt; Cyclopentadienyl

1. Introduction

The acetylenic phosphines $Ph_2PC\equiv CR$ have been extensively used as ligands in transition metal chemistry [1]. The reaction between these ligands and polynuclear metal complexes under mild conditions usually involves breaking of the phosphorus–alkynyl bond to yield η^2 -acetylide phosphido-bridged clusters [2], but other interesting rearrangements have also been observed [3].

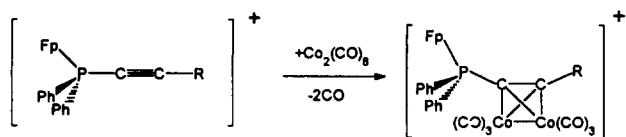
The P-coordinated transition metal complexes $[PPh_4][Fe_3(CO)_9(\mu_3-CCH_3)(Ph_2PC\equiv CR)]$ [**4**] and $[(Fp)Ph_2PC\equiv CR][BF_4]$ [**5**] were made in order to study the effects on the alkyne function of phosphorus coordination to metal atoms. The uncoordinated alkyne in the cationic complexes $[(Fp)Ph_2PC\equiv CR][BF_4]$ was studied by NMR and IR spectroscopy and by Natural Population Analysis (NPA) and Natural Bond Orbital Analysis (NBO). We observed a significant increase in the polarization of the $C\equiv C$ triple bond in cationic complexes, and this is attributed to the cationic charge induced by the coordinated phosphorus atom (Scheme 1) [5].

This paper is concerned with the formation of adducts between the cationic complexes and cobalt octacarbonyl through the uncoordinated alkyne. Although the synthesis of heteropolymetallic complexes is an interesting subject in itself [6], and the bifunctional character of phosphinoalkynes has been utilized in this respect [7], we undertook the synthesis of the cationic heterometallic complexes $[(Fp)Ph_2PC\equiv CR\{Co_2(CO)_6\}][BF_4]$ because it seemed likely that there would be delocalization of the cationic charge from the iron atom to the cobalt fragment $\{Co_2(CO)_6(\mu-C_2)\}$ in these complexes. Moreover, we had in mind the fact that the cationic cobalt complex $[Co_2(CO)_2(\mu-RC_2R)(\mu-dppm)_2]^+$ had been prepared from the neutral complex by oxidation with ferrocenium cation or by electrochemical techniques and that notable structural differences had been ob-



Scheme 1.

* Corresponding author.



Scheme 2.

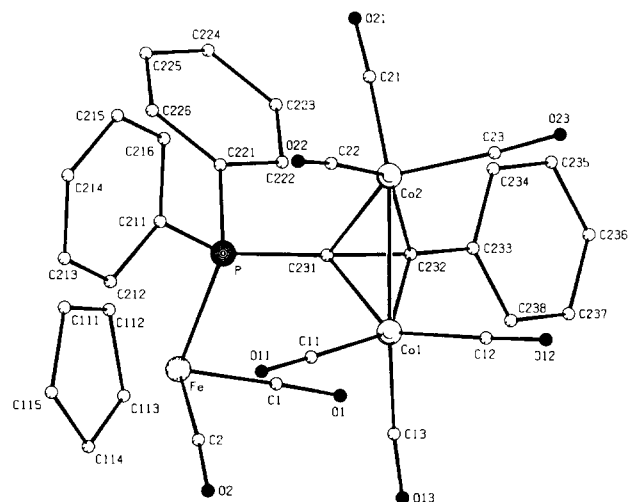
served between the two complexes [8]. Thus a study of the cationic heterometallic complexes $[(\text{Fp})\text{Ph}_2\text{PC}\equiv\text{CR}\{\text{Co}_2(\text{CO})_6\}][\text{BF}_4]$ seemed of interest, and we undertook this by use of spectroscopic methods and X-ray diffraction studies.

2. Results and discussion

2.1. Synthesis and characterization

Reaction of the cationic complexes $[(\text{Fp})\text{Ph}_2\text{PC}\equiv\text{CR}][\text{BF}_4]$ with $[\text{Co}_2(\text{CO})_8]$ at room temperature in dichloromethane afforded the expected cationic heterometallic complexes 1–4 ($\text{R} = \text{H}$ (1), CH_3 (2), Ph (3), Tol (4) ($\text{Tol} = p\text{-MeC}_6\text{H}_4$)) in high yield (Scheme 2).

The products were isolated as brown crystals and characterized by the usual analytical and spectroscopic techniques. In the IR spectrum all complexes showed a set of bands at $2100\text{--}2000\text{ cm}^{-1}$, with a marked similarity to the pattern of $\nu(\text{CO})$ bands of the $\text{Co}_2(\text{CO})_6$ fragment [9], overlapping the two $\nu(\text{CO})$ bands of the fragment $[\text{CpFe}(\text{CO})_2]^+$ [5,10]. The intense band near 2200 cm^{-1} , assigned to the $\nu(\text{C}\equiv\text{C})$ band of the uncoordinated alkyne in the $[(\text{Fp})\text{Ph}_2\text{PC}\equiv\text{CR}]^+$ compounds, was absent, suggesting that the coordination of the triple bond had occurred. The ^{31}P NMR resonances of the phosphorus atom in complexes 1–4 are all shifted 26–30 ppm downfield with respect to those of the corresponding alkyne complex $[(\text{Fp})\text{Ph}_2\text{PC}\equiv\text{CR}]^+$ [5]. This shift can be attributed to the loss of the π alkynyl $\text{C}\equiv\text{C}$ bond, since the relatively high field shifts observed in alkynyl and cyano derivatives of phosphorus have been related to the electron ring current of the π bonds [11]. Carbonyl groups bonded to cobalt and iron atoms give separate signals in the ^{13}C NMR spectra for complexes 1–4 at 211–213 ppm ($\text{Fe}\text{--CO}$) and 198–199 ppm ($\text{Co}\text{--CO}$). The assignment of these signals was made on the basis of the broad shape of ^{59}Co resonances due to quadrupolar coupling with the ^{59}Co nucleus [12], and of the $|^2J_{\text{P-C}}|$ values (22–30 Hz) of FeCO resonances, which are similar to those reported for the cationic alkyne complexes $[(\text{Fp})\text{Ph}_2\text{PC}\equiv\text{CR}]^+$ [5]. The ^{13}C NMR spectra of complexes 1–4 also show two doublets, with different P–C couplings which are assigned to the two carbon atoms of the bridging PC_2 entity, since the chemical shift falls within the range found for alkyne adducts $[\text{Co}_2(\text{CO})_6(\mu\text{-RC}_2\text{R}')] (70\text{--}110\text{ ppm})$

Fig. 1. View of the $[(\text{Fp})\text{Ph}_2\text{C}\equiv\text{CR}\{\text{Co}_2(\text{CO})_6\}]^+$ cation.

[13]. The resonances of the Ph, Cp and R groups are observed in the ^1H and ^{13}C NMR spectra of complexes 1–4, all with normal chemical shifts.

The complex $[(\text{Fp})\text{Ph}_2\text{PC}\equiv\text{C}^t\text{Bu}][\text{BF}_4]$ was also treated with cobalt octacarbonyl under the same conditions, but no reaction was observed and the reagents were always recovered. This behaviour may be attributed to steric hindrance by the bulky *t*-butyl group.

2.2. Crystal structure of $[(\text{Fp})\text{Ph}_2\text{C}\equiv\text{CR}\{\text{Co}_2(\text{CO})_6\}][\text{BF}_4]$

The crystal contains discrete cations. The $[\text{BF}_4]^-$ anion is highly disordered and was not resolved, but the highest residual density peaks attributed to $[\text{BF}_4]^-$ are a long way from the cation. A view of the cation, with the labelling scheme, is shown in Fig. 1. Selected intramolecular bond lengths and angles are presented in Table 1.

As indicated by the spectroscopic data, the cation consists of a hexacarbonyldicobalt fragment π -bonded to the alkynyl group of the P-coordinated (diphenylphosphino)alkyne. The iron fragment $\{\text{FpPPH}_2\}$ is too far removed from the cobalt fragment $\{\text{Co}_2\text{C}_2\}$ for there to be substantial bonding interaction (the shortest dis-

Table 1
Selected bond lengths (Å) in 3 with e.s.d.s in parentheses

Fe–C1	1.77(2)	Co1–C232	1.97(1)
Fe–C2	1.75(1)	Co2–C231	1.99(1)
Fe–P	2.232(3)	Co2–C232	1.96(1)
P–C211	1.822(6)	Co1–C11	1.83(1)
P–C221	1.814(6)	Co1–C12	1.81(2)
P–C231	1.77(1)	Co1–C13	1.78(2)
C231–C232	1.37(2)	Co2–C21	1.80(2)
C232–C233	1.46(1)	Co2–C22	1.82(1)
Co1–Co2	2.456(2)	Co2–C23	1.80(2)
Co1–C231	1.97(1)		

Table 2
Comparison of X-ray structure determinations on cationic complexes with the {FpPPh₂} fragment (e.s.d.s in parentheses)

Complex	Bond lengths (Å)			Bond angles (°)					Ref.	
	Fe–P	Fe–C(Cp) ^a	Fe–C(O)	C–O	P–C(Ph)	α(C)–Fe–C(O)	(O)C–Fe–P	(Ph)–C–P–C(Ph)		Fe–P–C(Ph)
[(Fp)Ph ₂ PC≡CPh(CO) ₆][BF ₄] ⁽³⁾	2.232(3)	2.097(9)	1.75(1)	1.14(2)	1.814(6)	94.7(9)	92.3(4)	106.3(3)	115.2(3)	This work
			1.77(2)	1.15(1)	1.822(6)		96.2(4)		108.2(3)	
[(Fp)PPh ₃][NC ₂ CC(CN)C(CN) ₂]	2.240(1)	2.094(7)	1.778(5)	1.129(7)	1.817(5) ^a	96.4(3)	90.7(2)	104.8(3) ^a	113.8(2) ^a	[15a]
			1.774(7)	1.138(9)			91.9(2)	178.4(7)		
[(Fp)PPh ₃][Cl·3H ₂ O]	2.242(1)	2.093(5)	1.767(4)	1.138(5)	1.824(3) ^a	94.9(2)	90.7(1)	104.3(1) ^a	114.3(1) ^a	[10]
			1.775(4)	1.140(5)			91.5(1)	177.2(4)		
[(Fp)Ph ₂ PCH ₂ SiMe ₃][BF ₄]	2.235(1)	2.078(6)	1.755(6)	1.149(7)	1.816(4)	94.7(2)	92.7(2)	104.3(2)	110.8(1)	[15b]
			1.769(6)	1.136(7)	1.816(4)		94.7(2)	176.8(4)		114.9(1)
[(Fp)Ph ₂ PC≡CPh][BF ₄]	2.207(1)	2.084(4)	1.785(3)	1.138(4)	1.825(3)	95.2(1)	92.1(1)	104.1(1)	116.3(1)	[5]
			1.785(4)	1.130(4)	1.815(3)		92.5(1)			114.7(1)

^a Mean value.

tances between the two fragments are $O2-C13 = 3.10(2)$ Å; $O2-O13 = 3.15(2)$ Å). The Co_2C_2 core adopts a pseudo-tetrahedral geometry with the C–C bond of the alkyne at an angle of $90.8(6)^\circ$ with respect to the Co–Co bond. Structural studies of the neutral complex $[Co_2(CO)_2(\mu-PhC_2Ph)(\mu-dppm)_2]$ and the corresponding cationic complex $[Co_2(CO)_2(\mu-PhC_2Ph)(\mu-dppm)_2]^+$ showed significant differences between the two compounds after oxidation. The most notable was the twist position of the alkyne C–C bond relative to the Co–Co bond (12.0° with respect to the perpendicular orientation in the cationic complex; 0.7° in the neutral complex) [8]. Comparison of the geometry of the Co_2C_2 core in these complexes and **3** reveals minor differences from the neutral complex, whereas the differences in the base of the cationic complex are substantial. This suggests that the positive charge mainly lies on the $\{FpPPh_2\}$ group rather than in the hexacarbonyldicobalt fragment. This view is consistent with the observed geometry of the $\{FpPPh_2\}$ fragment in **3**. For comparison, selected data from the X-ray structure determinations of cationic complexes containing the $\{FpPPh_2\}$ fragment are given in Table 2.

The data reveal a remarkable similarity between the geometry of the $\{FpPPh_2\}$ fragment in complexes **3**, $[(Fp)PPh_3]^+$ and $[(Fp)PPh_2CH_2SiMe_3]^+$. This shows that the charge distribution must be very similar in all of these complexes, and it is also consistent with the geometry observed in the Co_2C_2 core in **3**. Some notable differences are revealed by Table 2 on comparison of the data for the $\{FpPPh_2\}$ fragment in complexes **3** and $[(Fp)Ph_2PC\equiv CPh]^+$. The effects of coordination of the alkyne to the hexacarbonyldicobalt group can be seen in the structure of the $\{Ph_2PFp\}$ fragment, the most significant being the increase in the Fe–P distance, which may be related to the loss of the polarized $\pi-C\equiv C$ group bonded to the phosphorus atom [5].

2.3. ^{13}C chemical shifts for the acetylenic carbon atoms

The ^{13}C NMR spectra of the P-coordinated transition metal complexes $[(Fp)Ph_2PC\equiv CR][BF_4]$ show the two characteristic signals assigned to acetylenic carbon atoms (Table 3). The resonances of C1 and C2 are shifted upfield and downfield, respectively, with respect

to those for the free diphenylphosphinoalkynes, and this has been related to the $\pi C\equiv C$ bond polarization in the cationic complexes [5].

Previous ^{13}C NMR studies of the acetylenic complexes $[Co_2(CO)_6(RC_2R')]$ [13a] have shown that in the cobalt complexes each acetylenic carbon atom is less sensitive to the nature of the substituent on the other acetylenic carbon atom than it is in the free alkyne. This feature is clearly seen from Table 3 by comparing the ^{13}C NMR chemical shifts for the complexes $[(Fp)Ph_2PC\equiv CR][BF_4]$ and **1–4**. The $\pi C\equiv C$ bond polarization observed in complexes $[(Fp)Ph_2PC\equiv CR][BF_4]$ nearly vanishes after the coordination of the alkyne to the $\{Co_2(CO)_6\}$ fragment, and thus for complexes **1–4** the ^{13}C NMR chemical shifts of the acetylenic carbon atoms are essentially affected only by substituents directly bonded to it.

3. Experimental section

3.1. General

All reactions were performed under dinitrogen by standard Schlenk tube techniques. Infrared spectra were recorded with a Perkin-Elmer 1710 FT spectrometer using dichloromethane solutions or KBr pellets. The NMR spectra were recorded by the Servei de Resonància Magnètica Nuclear de la Universitat Autònoma de Barcelona on a Bruker AM400 instrument. The ^{31}P chemical shifts are reported in ppm upfield from external 85% H_3PO_4 . The 1H and ^{13}C chemical shifts are expressed in ppm upfield from TMS.

Compounds $[(Fp)Ph_2PC\equiv CR][BF_4]$ ($R = H, CH_3, Ph, Tol$) were prepared by published procedures [5]. Microanalysis were performed in Servei d'Anàlisi Química de la Universitat Autònoma de Barcelona.

The X-ray diffraction studies were carried out by the Servei de Difracció de Raigs X de la Universitat Autònoma de Barcelona.

3.2. Synthesis of **1–4** ($R = H$ (**1**), CH_3 (**2**), Ph (**3**), Tol (**4**))

In a typical procedure a solution of $[Co_2(CO)_8]$ (0.26 g, 0.76 mmol) in dichloromethane (20 cm³) was added

Table 3

^{13}C Chemical shifts (δ , ppm) for the acetylenic carbon atoms (in parentheses, values for the corresponding free phosphinoalkynes $Ph_2PC^1\equiv C^2R$)

	$Ph_2PC^1\equiv C^2R$		$[(Fp)Ph_2PC^1\equiv C^2R]^+$		$[(Fp)Ph_2PC^1\equiv C^2R\{Co_2(CO)_6\}]^+$	
	C ¹	C ²	C ¹	C ²	C ¹	C ²
H	92.0	98.8	76.1	107.0	81.0	89.4
CH ₃	75.4	107.2	70.9	117.9	82.5	107.7
Ph	86.5	109.4	80.3	115.7	84.7	107.7
Tol	85.3	108.9	80.0	116.5	84.3	107.9

with stirring to $[(\text{Fp})\text{Ph}_2\text{PC}\equiv\text{CR}][\text{BF}_4]$ (0.76 mmol) in dichloromethane (20 cm³). The mixture was stirred at room temperature for 18 h, then filtered and the filtrate evaporated to dryness. The residue was recrystallized from CH_2Cl_2 –diethyl ether at -20°C . The brown crystals were collected, washed with diethyl ether and dried in vacuo.

Yield of **1**, 77%. Anal. Calc. for $\text{C}_{27}\text{H}_{16}\text{BCo}_2\text{F}_4\text{FeO}_8\text{P}$: C, 42.68; H, 2.12. Found: C, 42.53; H, 2.35%. IR (ν_{CO} , CH_2Cl_2): 2098, 2064, 2035, 2020, 1988 cm⁻¹. ^1H NMR ($(\text{CD}_3)_2\text{CO}$): 5.43 (s, Cp), 5.76

(s, $\equiv\text{CH}$), 7.8 (m, Ph) ppm. ^{31}P NMR ($(\text{CD}_3)_2\text{CO}$): 68.5 ppm. ^{13}C NMR ($(\text{CD}_3)_2\text{CO}$; except phenyl resonances): 213.0 (d, $J = 22.0$ Hz, Fe–CO), 198.7 (broad, Co–CO), 90.1 (s, Cp), 89.4 (d, $J = 6.7$ Hz, $\equiv\text{CH}$), 81.0 (d, $J = 20$ Hz, $\text{PC}\equiv$) ppm.

Yield of **2**, 83%. Anal. Calc. for $\text{C}_{28}\text{H}_{18}\text{BCo}_2\text{F}_4\text{FeO}_8\text{P}$: C, 43.45; H, 2.34. Found: C, 43.44; H, 2.47%. IR (ν_{CO} , CH_2Cl_2): 2094, 2061, 2043, 2017, 1979 cm⁻¹. ^1H NMR ($(\text{CD}_3)_2\text{CO}$): 3.28 (s, CH_3), 5.43 (s, Cp), 7.8 (m, Ph) ppm. ^{31}P NMR ($(\text{CD}_3)_2\text{CO}$): 69.9 ppm. ^{13}C NMR ($(\text{CD}_3)_2\text{CO}$; except phenyl resonances): 213.0 (d,

Table 4

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **3**.

	x	y	z	U_{eq}^a
Fe	6201(1)	2537(1)	−267(1)	43(1)
C(1)	6318(6)	3088(7)	442(8)	58(4)
O(1)	6380(6)	3439(5)	907(6)	78(3)
C(2)	5637(7)	1962(6)	155(7)	55(3)
O(2)	5227(5)	1606(6)	409(6)	87(3)
C(111)	6454(4)	2486(4)	−1306(4)	56(3)
C(112)	6569(4)	3174(4)	−1072(5)	59(4)
C(113)	5915(5)	3432(4)	−818(5)	52(3)
C(114)	5397(4)	2904(5)	−894(5)	64(4)
C(115)	5730(4)	2319(4)	−1196(5)	55(3)
Co(1)	6888(1)	1342(1)	1561(1)	45(1)
C(11)	6477(8)	599(7)	1135(8)	64(4)
O(11)	6231(7)	150(5)	858(6)	97(4)
C(12)	7029(8)	1000(8)	2410(8)	65(4)
O(12)	7133(6)	791(6)	2931(6)	90(3)
C(13)	6095(7)	1816(7)	1729(7)	57(3)
O(13)	5609(6)	2143(6)	1873(6)	91(4)
Co(2)	8143(1)	1215(1)	1251(1)	48(1)
C(21)	8927(8)	1518(7)	822(8)	60(4)
O(21)	9391(6)	1730(6)	542(6)	87(3)
C(22)	8071(8)	331(7)	930(7)	61(4)
O(22)	7989(7)	−237(5)	772(6)	97(4)
C(23)	8551(8)	1079(8)	2067(9)	75(4)
O(23)	8841(9)	1016(11)	2566(7)	167(8)
P	7202(2)	1962(1)	−49(2)	37(1)
C(211)	7278(4)	1117(3)	−457(4)	40(3)
C(212)	6670(3)	769(4)	−663(4)	48(3)
C(213)	6722(4)	116(4)	−958(4)	57(3)
C(214)	7384(5)	−189(3)	−1047(4)	65(4)
C(215)	7992(4)	159(4)	−841(5)	71(4)
C(216)	7940(3)	812(4)	−547(4)	52(3)
C(221)	7940(3)	2477(3)	−359(3)	39(2)
C(222)	8129(4)	3058(4)	19(3)	43(3)
C(223)	8610(4)	3534(3)	−243(4)	57(3)
C(224)	8901(4)	3430(4)	−884(5)	67(4)
C(225)	8712(4)	2849(4)	−1262(3)	59(3)
C(226)	8232(4)	2373(3)	−999(3)	48(3)
C(231)	7402(6)	1796(5)	813(6)	40(3)
C(232)	7607(6)	2069(6)	1425(6)	42(3)
C(233)	7821(4)	2696(3)	1789(4)	42(3)
C(234)	8519(4)	2922(4)	1740(4)	67(4)
C(235)	8732(4)	3520(4)	2078(5)	75(4)
C(236)	8247(5)	3892(3)	2466(4)	59(4)
C(237)	7549(5)	3666(4)	2515(4)	64(4)
C(238)	7336(3)	3068(4)	2177(4)	54(3)

^a U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

$J = 24.2$ Hz, Fe–CO), 198.8 (broad, Co–CO), 107.7 (d, $J = 6.1$ Hz, $\equiv\text{CCH}_3$), 90.4 (s, Cp), 82.5 (d, $J = 21.4$ Hz, PC $\equiv$), 21.7 (s, CH₃) ppm.

Yield of **3**, 88%. Anal. Calc. for C₃₃H₂₀BCo₂F₄FeO₈P: C, 47.41; H, 2.41. Found: C, 47.34; H, 2.43%. IR (ν_{CO} , CH₂Cl₂): 2103, 2069, 2054, 2035, 2009 cm⁻¹. ¹H NMR ((CD₃)₂CO): 5.34 (s, Cp), 7.8 (m, Ph) ppm. ³¹P NMR ((CD₃)₂CO): 74.6 ppm. ¹³C NMR ((CD₃)₂CO; except phenyl resonances): 211.6 (d, $J = 30.0$ Hz, Fe–CO), 198.5 (broad, Co–CO), 107.7 (d, $J = 10.0$ Hz, $\equiv\text{CPh}$), 90.3 (s, Cp), 84.7 (d, $J = 23.7$ Hz, $\equiv\text{CP}$) ppm.

Yield of **4**, 92%. Anal. Calc. for C₃₄H₂₂BCo₂F₄FeO₈P: C, 48.04; H, 2.61. Found: C, 48.12; H, 2.54%. IR (ν_{CO} , CH₂Cl₂): 2098, 2063, 2035, 2020, 2004 cm⁻¹. ¹H NMR ((CD₃)₂CO): 2.42 (s, CH₃), 5.50 (s, Cp), 7.6 (m, Ph) ppm. ³¹P NMR ((CD₃)₂CO): 69.1 ppm. ¹³C NMR ((CD₃)₂CO; except phenyl resonances): 211.5 (d, $J = 23.7$ Hz, Fe–CO), 198.5 (broad, Co–CO), 107.9 (d, $J = 10.1$ Hz, $\equiv\text{CTol}$), 90.2 (s, Cp), 84.3 (d, $J = 24.3$ Hz, $\equiv\text{CP}$), 21.1 (s, CH₃) ppm.

3.3. X-ray structure determination and refinement of complex **3**

3.3.1. Crystal data

Poor-quality crystals of the complex **3** were obtained by crystallization from a methylene chloride–diethyl ether mixture. C₃₃H₂₀BCo₂F₄FeO₈P, $M = 835.98$. Orthorhombic, $a = 18.859(4)$, $b = 19.272(9)$, $c = 19.676(3)$ Å, $V = 7151(4)$ Å³ (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, $\lambda = 0.71069$ Å), space group P_{can} (No. 60), $Z = 8$, $D_x = 1.553$ g cm⁻³. Brown, air-stable crystals, $\mu(\text{Mo K}\alpha) = 14.30$ cm⁻¹.

3.3.2. Data collection and processing

The conditions used were a CAD4 diffractometer, $\omega/2\theta$ mode with ω scan width = $0.80 + 0.35 \tan \theta$, ω scan speed 1.3–5.5° min⁻¹, graphite-monochromated Mo K α radiation. Reflection ranges for the data collection were $1 < \theta < 25^\circ$ and $0 \leq h \leq 22$, $0 \leq k \leq 22$, $0 \leq l \leq 23$. 6170 unique reflections (Lp and empirical absorption correction from psi scans [16], minimum transmission = 0.879, maximum transmission = 0.999), 3071 with $I > 2\sigma(I)$.

3.3.3. Structure analysis and refinement

Direct methods (SHELXS-86 program) [17] and full-matrix least-squares refinement on F^2 for all reflections (SHELXL-93 program) [18] were applied.

Cyclopentadienyl and phenyl groups were refined as rigid groups. The BF₄ group is highly disordered and was not included in the refinement. The remaining non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions with

isotropic temperature factors fixed at 1.2 times U_{eq} for the corresponding carbon atoms. The weighting scheme was $w = 1/[\sigma^2(F_o^2) + (0.2075P)^2]$ where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$. Final $R(F)$ and $R_w(F^2)$ values were 0.0973 and 0.3050 for reflections with $I > 2\sigma(I)$. Atomic coordinates are listed in Table 4. Thermal parameters and a complete list of Bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

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