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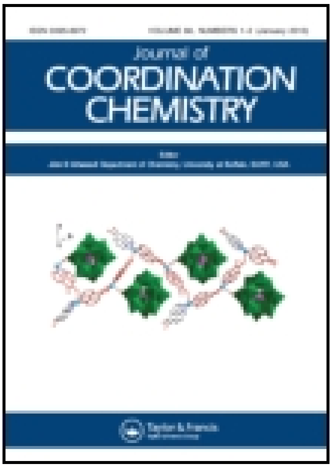

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Publication details, including instructions for authors and subscription information:
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Reactions of the μ_3-sulfido dicobalt-iron cluster (μ_3-S)$FeCo_2(CO)_9$ with triphenylphosphine or 1,4-bis(diphenylphosphino)butane

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Accepted author version posted online: 03 Jan 2014.Published online: 22 Jan 2014.

To cite this article: Xu-Feng Liu, Meng-Yan Chen & Hao-Qi Gao (2014) Reactions of the μ_3-sulfido dicobalt-iron cluster (μ_3-S)$FeCo_2(CO)_9$ with triphenylphosphine or 1,4-bis(diphenylphosphino)butane, Journal of Coordination Chemistry, 67:1, 57-63, DOI: 10.1080/00958972.2013.879123

To link to this article: http://dx.doi.org/10.1080/00958972.2013.879123

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Journal of Coordination Chemistry, 2014
Vol. 67, No. 1, 57–63, http://dx.doi.org/10.1080/00958972.2013.879123

Reactions of the μ_3-sulfido dicobalt-iron cluster (μ_3-S)FeCo$_2$(CO)$_9$ with triphenylphosphine or 1,4-bis(diphenylphosphino)butane

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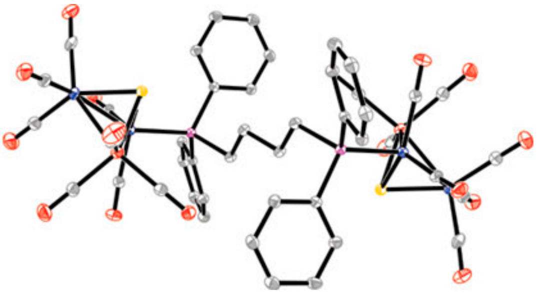
(*Received 3 October 2013; accepted 5 December 2013*)



Reaction of (μ_3-S)FeCo$_2$(CO)$_9$ (**A**) with PPh$_3$ at room temperature in CH$_2$Cl$_2$ gave μ_3-sulfido dicobalt-iron clusters (μ_3-S)FeCo$_2$(CO)$_8$(PPh$_3$) (**1**) and (μ_3-S)FeCo$_2$(CO)$_7$(PPh$_3$)$_2$ (**2**) in 37 and 54% yields, whereas reaction of **A** with 1,4-bis(diphenylphosphino)butane (Ph$_2$PCH$_2$CH$_2$CH$_2$CH$_2$PPh$_2$, dppb) afforded [(μ_3-S)FeCo$_2$(CO)$_8$]$_2$(Ph$_2$PCH$_2$CH$_2$CH$_2$CH$_2$PPh$_2$) (**3**) in 49% yield. Complexes **1–3** were characterized by elemental analysis, spectroscopy, and for **1** and **3** by X-ray crystallography.

Keywords: Dicobalt-iron; Carbonyl substitution; Phosphine ligand; Synthesis; Crystal structure

1. Introduction

Mixed-metal clusters have received attention due to their potential applications in catalytic reactions [1, 2]. Previous studies have shown that carbonyls bound to cobalt centers of (μ_3-S)FeCo$_2$(CO)$_9$ are more easily substituted by two electron donors than the carbonyls bound to iron [3–5]. Reactions of **A** with monophosphine or diphosphine ligands afforded phosphine-substituted derivatives, such as (μ_3-S)FeCo$_2$(CO)$_8$[P(OCH$_2$Ph)$_3$] [6] and (μ_3-S)FeCo$_2$(CO)$_7$(bpcd) (bpcd = 4,5-bis(diphenylphosphino)-4-cyclopenten-1,3-dione) [7]. We have recently reported [8, 9] the reactions of **A** with *N*-substituted bis(diphenylphosphanyl)

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*Corresponding author. Email: nkxfliu@126.com amine $Ph_2PN(R)PPh_2$ ($R = CH_2CH_2CH_3$, CH_2Ph), $Ph_2PCH_2PPh_2$, $Ph_2PCH_2CH_2PPh_2$, or *cis*-$Ph_2PCH{=}CHPPh_2$ and these derivatives were characterized by spectroscopy and X-ray diffraction analysis. As continuation of our studies on mixed-metal dicobalt-iron clusters, we carried out the reactions of **A** with PPh_3 or dppb and synthesized three clusters. In this article, we will describe the synthesis and structural characterization of dicobalt-iron clusters containing monophosphine or diphosphine ligands.

2. Experimental

2.1. *Materials and methods*

All reactions were performed using standard Schlenk and vacuum line techniques under N_2. CH_2Cl_2 was distilled over CaH_2 under N_2. PPh_3, dppb and other materials were available commercially and used as received. **A** [10] was prepared according to literature procedures. IR spectra were recorded on a Nicolet MAGNA 560 FT-IR spectrometer. NMR spectra were obtained on a Bruker Avance 500 MHz spectrometer. Elemental analyses were performed by a Perkin-Elmer 240C analyzer.

2.2. *Synthesis of (μ_3-S)FeCo$_2$(CO)$_8$(PPh$_3$) (1) and (μ_3-S)FeCo$_2$(CO)$_7$(PPh$_3$)$_2$ (2)*

A solution of **A** (0.092 g, 0.2 mmol) and PPh_3 (0.105 g, 0.4 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature overnight. The solvent was reduced *in vacuo* and the residue was subjected to TLC separation using petroleum ether as eluent. The first main brown band afforded 0.052 g (37%) of **1** as a black solid. The second brown band afforded 0.101 g (54%) of **2** as a black solid. **1**: Anal. Calcd for $C_{26}H_{15}Co_2FeO_8PS$ (%): C, 45.12; H, 2.18. Found (%): C, 44.84; H, 2.02. IR (KBr disk, cm^{-1}): $\nu_{C\equiv O}$ 2076 (vs), 2012 (vs), 1966 (vs), 1943 (vs). ^1H NMR (500 MHz, $CDCl_3$): 7.46 (s, 15H, Ph*H*) ppm. $^{31}P\{^1H\}$ NMR (200 MHz, $CDCl_3$, 85% H_3PO_4): 48.49 (s) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): 206.01 (s, C≡O), 134.18 (d, $J_{P\text{-}C} = 43.0$ Hz, *i*-Ph*C*), 133.27 (d, $J_{P\text{-}C} = 10.7$ Hz, *o*-Ph*C*), 130.68 (s, *p*-Ph*C*), 128.64 (d, $J_{P\text{-}C} = 10.0$ Hz, *m*-Ph*C*) ppm. **2**: Anal. Calcd for $C_{43}H_{30}Co_2FeO_7P_2S$ (%): C, 55.75; H, 3.26. Found (%): C, 55.98; H, 3.13. IR (KBr disk, cm^{-1}): $\nu_{C\equiv O}$ 2041 (vs), 1997 (vs), 1966 (vs). ^1H NMR (500 MHz, $CDCl_3$): 7.49–7.29 (m, 30H, Ph*H*) ppm. $^{31}P\{^1H\}$ NMR (200 MHz, $CDCl_3$, 85% H_3PO_4): 46.94 (s) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): 210.99 (s, C≡O), 135.92 (d, $J_{P\text{-}C} = 40.2$ Hz, *i*-Ph*C*), 133.44 (d, $J_{P\text{-}C} = 10.5$ Hz, *o*-Ph*C*), 130.10 (s, *p*-Ph*C*), 128.31 (d, $J_{P\text{-}C} = 9.2$ Hz, *m*-Ph*C*) ppm.

2.3. *Synthesis of [(μ_3-S)FeCo$_2$(CO)$_8$]$_2$(Ph$_2$PCH$_2$CH$_2$CH$_2$CH$_2$PPh$_2$) (3)*

A solution of **A** (0.092 g, 0.2 mmol) and dppb (0.043 g, 0.1 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature overnight. The solvent was reduced *in vacuo* and the residue was subjected to TLC separation using CH_2Cl_2/petroleum ether (v/v = 1 : 5) as eluent. The main brown band afforded 0.063 g (49%) of **3** as a black solid. Anal. Calcd for $C_{44}H_{28}Co_4Fe_2O_{16}P_2S_2$ (%): C, 41.09; H, 2.19. Found (%): C, 41.37; H, 2.36. IR (KBr disk, cm^{-1}): $\nu_{C\equiv O}$ 2042 (vs), 1997 (vs), 1965 (vs), 1937 (vs). ^1H NMR (500 MHz, $CDCl_3$): 7.52–7.29 (m, 20H, Ph*H*), 2.28–2.27 (m, 4H, $2PCH_2$), 1.45–1.37 (m, 4H, $2CH_2$) ppm. $^{31}P\{^1H\}$ NMR (200 MHz, $CDCl_3$, 85% H_3PO_4): 43.33 (s) ppm. $^{13}C\{^1H\}$ NMR (125 MHz,

$CDCl_3$): 206.12 (C≡O), 134.99 (d, $J_{P\text{-}C} = 4.2$ Hz, *i*-Ph*C*), 134.66 (d, $J_{P\text{-}C} = 4.6$ Hz, *i*-Ph*C*), 134.33 (d, $J_{P\text{-}C} = 6.7$ Hz, *i*-Ph*C*), 134.00 (d, $J_{P\text{-}C} = 7.6$ Hz, *i*-Ph*C*), 132.22 (d, $J_{P\text{-}C} = 7.7$ Hz, *o*-Ph*C*), 131.62 (d, $J_{P\text{-}C} = 8.1$ Hz, *o*-Ph*C*), 130.80, 130.64 (2s, *p*-Ph*C*), 128.80 (t, $J_{P\text{-}C} = 9.4$ Hz, *m*-Ph*C*), 32.40 (d, $J_{P\text{-}C} = 24.7$ Hz, P*C*H_2), 25.48 (d, $J_{P\text{-}C} = 14.5$ Hz, *C*H_2) ppm.

2.4. *X-ray structure determination*

Single crystals of **1** and **3** suitable for X-ray diffraction analysis were grown by slow evaporation of CH_2Cl_2/hexane solutions of **1** and **3** at 4 °C. A single crystal of **1** or **3** was mounted on a Rigaku MM-007 CCD diffractometer. Data were collected at 113 K by using a graphite monochromator with Mo Kα radiation ($\lambda = 0.71073$ Å) in the ω-ϕ scanning mode. Data collection, reduction, and absorption correction were performed by *CRYSTALCLEAR* [11]. The structure was solved by direct methods using SHELXS-97 [12] and refined by full-matrix least-squares (SHELXL-97) [13] on F^2. Hydrogens were located using the geometric method. Details of crystal data, data collections, and structure refinement are summarized in table 1.

Table 1. Crystal data and structure refinements details for **1** and **3**.

Complex	**1**	**3**
Empirical formula	$C_{26}H_{15}Co_2FeO_8PS$	$C_{44}H_{28}Co_4Fe_2O_{16}P_2S_2$
Formula weight	692.12	1286.14
Temperature (K)	113(2)	113(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	*P2(1)/n*	*P–1*
a (Å)	10.700(5)	10.109(5)
b (Å)	16.701(8)	11.300(6)
c (Å)	16.192(8)	11.573(6)
α (°)	90	81.05(3)
β (°)	104.855(8)	75.67(2)
γ (°)	90	79.31(2)
V (Å^3)	2797(2)	1250.3(11)
Z	4	1
D_{Calcd} (g cm^{-3})	1.644	1.708
μ (mm^{-1})	1.862	2.075
F(000)	1384	642
Crystal size (mm^3)	0.20 × 0.18 × 0.16	0.20 × 0.18 × 0.12
θ_{min}, θ_{max} (°)	1.78, 27.88	1.83, 27.86
Reflections collected/unique	28643/6653	12895/5838
R_{int}	0.0698	0.0847
hkl range	$-14 \le h \le 14$	$-13 \le h \le 13$
	$-21 \le k \le 21$	$-14 \le k \le 14$
	$-21 \le l \le 21$	$-14 \le l \le 15$
Completeness to θ_{max} (%)	99.8	98.1
Data/restraints/parameters	6653/0/352	5838/0/316
Goodness of fit on F^2	1.019	1.063
$R1/wR2$ ($I > 2\sigma(I)$)	0.0366/0.0664	0.0566/0.1509
$R1/wR2$ (all data)	0.0488/0.0697	0.0609/0.1546
Largest diff. peak and hole (e Å^{-3})	0.418/−0.573	1.417/−1.433

3. Results and discussion

3.1. *Synthesis and characterization*

The PPh_3-monosubstituted cluster **1** and the PPh_3-disubstituted cluster **2** could be prepared in 37 and 54% yields by treatment of **A** with 2 equivalents of PPh_3 in CH_2Cl_2 at room temperature (scheme 1). However, reaction of **A** with dppb resulted in the formation of **3** containing bridging diphosphine ligand in 49% yield (scheme 2).

Complexes **1–3** have been characterized by elemental analysis and spectroscopy. The IR spectra of **1–3** showed three to four absorptions from 2076 to 1937 cm^{-1} for terminal carbonyls and the $\nu_{C\equiv O}$ band lie at much lower frequencies relative to those of **A** (2106, 2067, 2054, 2041, 2029, and 1973 cm^{-1}) [10], due to carbonyl substitution with the stronger electron-donating phosphine ligands [14]. The $^{31}P\{^1H\}$ NMR spectra of **1–3** each displayed a singlet in the region of 43–49 ppm. The $^{13}C\{^1H\}$ NMR spectra of **1** and **2** exhibited a singlet at 206 and 211 ppm for their terminal carbonyls and three doublets and a singlet for their phenyl carbons, whereas the $^{13}C\{^1H\}$ NMR spectra of **3** exhibited four doublets at 134.99, 134.66, 134.33, and 134.00 ppm for *i*-Ph carbons, two doublets at 132.22 and 131.62 ppm for *o*-Ph carbons, two singlets at 130.80 and 130.64 ppm for *p*-Ph carbons, and a triplet at 128.80 ppm for *m*-Ph carbons (figure 1).

3.2. *X-ray crystal structures of 1 and 3*

The molecular structures of **1** and **3** were determined by single-crystal X-ray diffraction analysis. ORTEP views of **1** and **3** are shown in figures 2 and 3, and selected bond lengths and angles are given in table 2. Complex **1** crystallizes in monoclinic space group *P2(1)/n*. As shown in figure 2, **1** consists of a dicobalt-iron triangle cluster capped by a μ_3-S with eight terminal carbonyls and one PPh_3 ligand. The phosphorus of PPh_3 attached to Co1 is located in the apical position of the square-pyramidal geometry of Co1, which is in accord

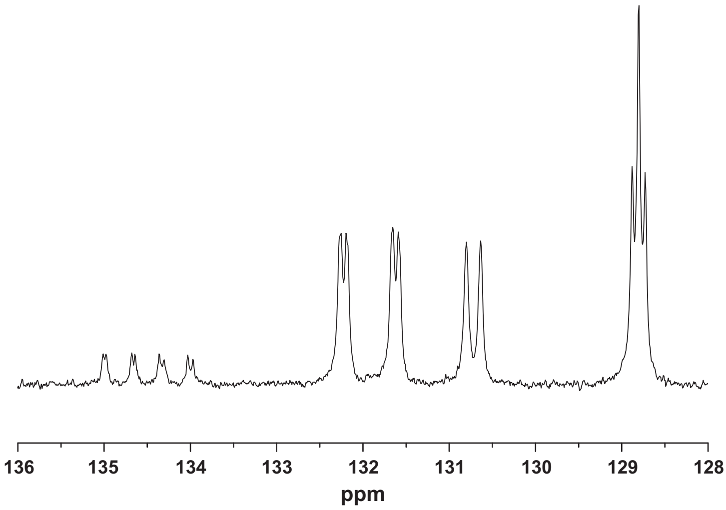


Figure 1. The $^{13}C\{^1H\}$ NMR spectra of **3** (136–128 ppm).

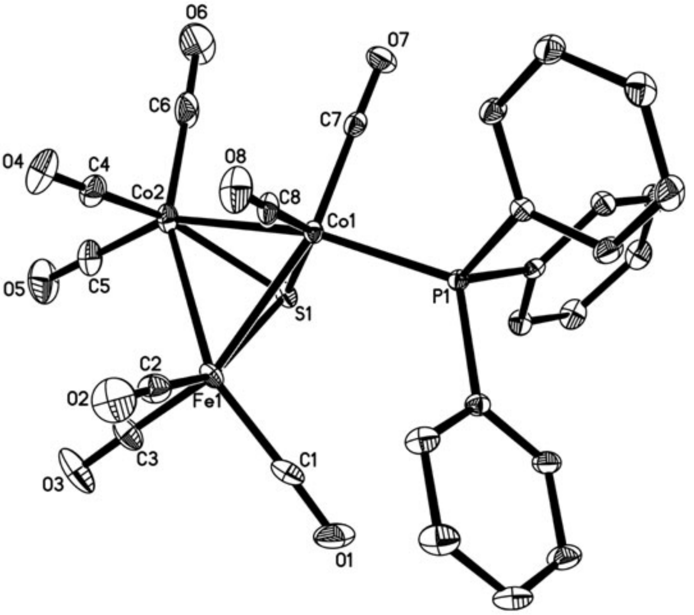


Figure 2. ORTEP view of **1** with 30% probability ellipsoids.

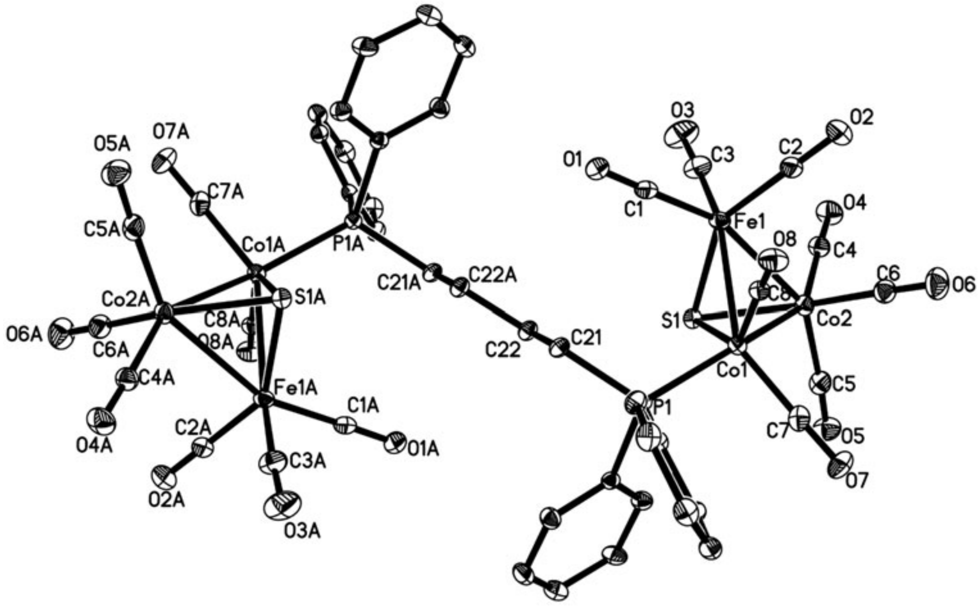
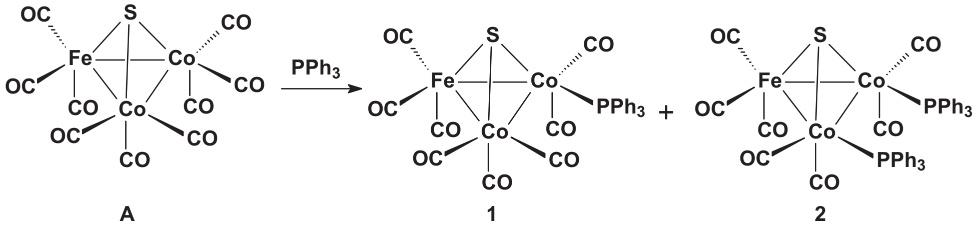
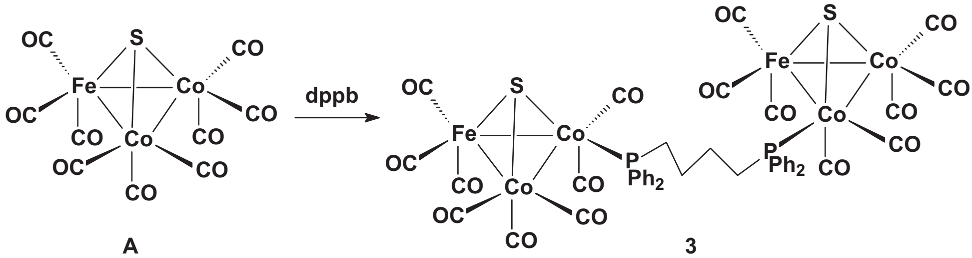


Figure 3. ORTEP view of **3** with 30% probability ellipsoids.



Scheme 1. Preparation of **1** and **2**.



Scheme 2. Preparation of **3**.

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **3**.

1			
Fe(1)–S(1)	2.1647(10)	Co(1)–P(1)	2.2305(13)
Fe(1)–Co(2)	2.5626(9)	Co(1)–Co(2)	2.5458(12)
Fe(1)–Co(1)	2.5871(11)	Co(2)–S(1)	2.1903(11)
Co(1)–S(1)	2.1680(9)	P(1)–C(9)	1.838(2)
S(1)–Fe(1)–Co(2)	54.42(3)	P(1)–Co(1)–Co(2)	160.84(2)
S(1)–Fe(1)–Co(1)	53.40(2)	S(1)–Co(1)–Fe(1)	53.28(3)
Co(2)–Fe(1)–Co(1)	59.25(3)	P(1)–Co(1)–Fe(1)	108.62(2)
S(1)–Co(1)–P(1)	106.30(3)	Co(2)–Co(1)–Fe(1)	59.895(14)
S(1)–Co(1)–Co(2)	54.67(2)	S(1)–Co(2)–Co(1)	53.85(3)
3			
Co(1)–S(1)	2.1621(12)	Co(2)–S(1)	2.1819(12)
Co(1)–P(1)	2.2042(11)	Co(2)–Fe(1)	2.5508(13)
Co(1)–Co(2)	2.5289(12)	P(1)–C(9)	1.823(3)
Co(1)–Fe(1)	2.5510(14)	Fe(1)–S(1)	2.1843(12)
S(1)–Co(1)–P(1)	99.43(5)	S(1)–Co(2)–Fe(1)	54.30(3)
S(1)–Co(1)–Fe(1)	54.47(4)	S(1)–Fe(1)–Co(2)	54.21(3)
P(1)–Co(1)–Fe(1)	118.66(3)	S(1)–Co(2)–Co(1)	54.03(3)
S(1)–Co(1)–Co(2)	54.76(3)	Fe(1)–Co(2)–Co(1)	60.29(4)
Fe(1)–Co(1)–Co(2)	60.28(3)	S(1)–Fe(1)–Co(1)	53.66(3)

with previously reported (μ_3-S)$FeCo_2(CO)_8[P(OCH_2Ph)_3]$ [6]. The average M–M bond length (2.5652 Å) is slightly longer than that of **A** (2.557 Å) [15]. The average M–S bond length (2.1669 Å) is slightly longer than that of **A** (2.158 Å) [15].

Complex **3** crystallizes in triclinic space group P-1. As shown in figure 3, **3** consists of two dicobalt-iron triangle clusters capped by two μ_3-S ligands with 16 terminal carbonyls, and one bridging diphosphine ligand dppb. The molecule is centrosymmetric with the midpoint of C22C22A as the symmetry center, very similar to complexes containing a bridging dppb [16]. The main framework of **3** is composed of a zigzag chain Co1P1C21C22C22AC21AP1ACo1A. Each phosphorus of dppb is located in the apical position of the square-pyramidal geometry of cobalt, consistent with crystal structures of $[(\mu_3\text{-S})FeCo_2(CO)_8]_2(Ph_2PCH_2CH_2PPh_2)$ [9] and **1**. The average M–M bond length (2.5436 Å) is shorter than that of **1**, whereas the average M–S bond length (2.1761 Å) is longer than that of **1**.

4. Conclusion

Carbonyl substitution reactions of **A** with PPh_3 or dppb yielded μ_3-sulfido dicobalt-iron clusters **1–3**. Complexes **1–3** were structurally characterized by elemental analysis, NMR, and IR spectroscopy. In the molecular structures of **1** and **3**, the phosphorus of PPh_3 and dppb reside in an apical position of the square pyramidal coordination sphere of cobalt.

Supplementary material

CCDC 964076 (**1**) and 964077 (**3**) contain the supplementary crystallographic data for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Funding

This work was supported by the National Training Programs of Innovation and Entrepreneurship for Undergraduates [grant number 201311058010]; the Zhejiang Province Science and Technology Innovation Program [grant number 2013R422014]; the Ningbo Science and Technology Innovation Team [grant number 2011B82002].

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