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Synthesis, structure and possible formation pathway of a novel cobalt carbonyl compound with new type B–O bond, $Co(CO)_3(PPh_3)_2BEt_3$, and mixed metal Co–Fe–S cluster with possible nonlinear optical property, $[Et_4N][CoFe_2(CO)_8S(PPh_3)]$

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Abstract

Reaction of $Co(CNS)_2$ with $Fe_2S_2(CO)_6$, $LiBEt_3H$ and PPh_3 in THF–MeCN resulting in a novel cobalt carbonyl complex, $Co(CO)_3(PPh_3)_2BEt_3$ (**1**) and mixed-metal Co–Fe–S cluster compound, $[Et_4N][Fe_2Co(CO)_8S(PPh_3)]$ (**2**). The structures of **1** and **2** were determined from X-ray three dimension data. Structure studies reveal that **1** is a new cobalt carbonyl complex containing a novel B–O bond of 1.601(5) Å in which the oxygen atom is from metal carbonyl and the B atom is from BEt_3 and **2** contained a triangular pyramid mixed-metal Co–Fe–S core $[CoFe_2S]^-$ with Co–S of 2.189, Fe–S of 2.208, Co–Fe of 2.56 and Fe–Fe of 2.58 Å. Theoretical calculation on **1** and **2** shows that B–O bonding energy of complex **1** is lower than that of normal covalent bonding and **2** possesses a calculated nonlinear optical first molecular hyperpolarizability component of 28.5×10^{-30} esu. The possible formation pathway of **1** and **2** was discussed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Co–B compound; Co–Fe–S compound; Synthesis and structure; Theoretical chemical calculation

1. Introduction

Diirondisulfide hexacarbonyl has been a versatile and attractive reagent for formation of mixed metallic polynuclear cluster compounds, and the chemistry of this reagent and the compounds from the reaction involving this reagent has interested chemists since the dianion of this reagent, $[Fe_2S_2(CO)_6]^{2-}$ was synthesized [1]. As a part of our investigation on metal–sulfur cluster complexes containing low- and mixed-valence metal atoms, we have reported several metal–sulfur cluster complexes with different configuration and coordination mode of $[Fe_2S_2(CO)_6]$-units from the reaction of diirondisulfide hexacarbonyl dianion with different metal complexes, $[Cu_5Fe_6S_6(CO)_{18}(PPh_3)_2]^-$ [2] $[MFe_2S_2(CO)_8(S_2CNEt_2)]^-$ (M = Mo, W) [3] and $[Fe_6S_6(CO)_{12}]^{2-}$ [4] Herein, we report a new cobalt carbonyl compound with novel B–O bond, $Co(CO)_3(PPh_3)_2BEt_3$ (**1**), and new Co–Fe–S cluster compound possessing possible nonlinear optical property, $[Et_4N][CoFe_2(CO)_8S(PPh_3)]$ (**2**), from the reaction of diirondisulfide hexacarbonyl dianion with $Co(SCN)_2$ and PPh_3. Preliminary theoretical calculation and the reaction pathway were also discussed.

2. Results and discussion

2.1. The structure of $Co(CO)_3BEt_3(PPh_3)_2$ (1) and novel B–O bonding

The selected bond distances and bond angles of **1** are given in Table 1 and the molecular structure of **1** is depicted in Fig. 1. As shown in Fig. 1, **1** is a neutral molecule with Co atom in zero oxidation state. The Co

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Table 1
Selected bond distances (Å) and angles (°) for $Co(PPh_3)_2(CO)_3BEt_3$ (**1**)

Bond distances			
Co–P(1)	2.2087(13)	O(3)–B	1.601(5)
Co–P(2)	2.2095(13)	O(1)–C(1)	1.136(4)
Co–C(1)	1.773(4)	O(2)–C(2)	1.147(4)
Co–C(2)	1.766(4)	O(3)–C(3)	1.157(4)
Co–C(3)	1.891(3)	B–C(4)	1.622(6)
P(1)–C(11)	1.827(3)	B–C(6)	1.620(5)
P(1)–C(21)	1.827(3)	B–C(8)	1.621(5)
P(1)–C(31)	1.829(3)	C(4)–C(5)	1.546(6)
P(2)–C(41)	1.822(3)	C(6)–C(7)	1.536(6)
P(2)–C(51)	1.820(3)	C(8)–C(9)	1.511(6)
P(2)–C(61)	1.827(3)		
Bond angles			
P(1)–Co–P(2)	175.82(4)	O(3)–B–C(6)	106.2(3)
P(1)–Co–C(1)	90.52(11)	O(3)–B–C(8)	105.4(3)
P(1)–Co–C(2)	90.92(11)	C(4)–B–C(6)	113.4(3)
P(1)–Co–C(3)	88.69(9)	C(4)–B–C(8)	113.5(3)
P(2)–Co–C(1)	90.54(11)	C(6)–B–C(8)	111.7(3)
P(2)–Co–C(2)	92.02(11)	Co–C(3)–O(3)	179.2(3)
P(2)–Co–C(3)	87.28(9)	Co–C(2)–O(2)	177.6(4)
C(1)–Co–C(2)	120.62(17)	Co–C(1)–O(1)	178.4(4)
C(1)–Co–C(3)	119.94(16)	B–C(4)–C(5)	113.1(3)
C(2)–Co–C(3)	119.44(15)	B–C((6)–C(7)	116.2(3)
Co–P(1)–C(11)	114.72(11)	B–C(8)–C(9)	116.2(4)
Co–P(1)–C(21)	114.97(12)	P(1)–C(11)–C(12)	120.5(3)
Co–P(1)–C(31)	112.95(11)	P(1)–C(11)–C(16)	121.3(3)
C(11)–P(1)–C(21)	105.24(15)	P(1)–C(21)–C(22)	121.6(3)
C(11)–P(1)–C(31)	104.59(16)	P(1)–C21)–C(26)	123.3(3)
C(21)–P(1)–C(31)	103.14(16)	P((1)–C31)–C(32)	121.0(3)
Co–P(2)–C(41)	114.05(11)	P(1)–C31)–C(36)	121.8(3)
Co–P(2)–C(51)	114.31(11)	P(2)–C(41)–C(42)	122.1(3)
Co–P(2)–C(61)	115.25(11)	P(2)–C(41)–C(46)	120.2(2)
C(41)–P(2)–C(51)	105.05(15)	P(2)–C51)–C(52)	118.0(3)
C(41)–P(2)–C(61)	104.32(16)	P(2)–C(51)–C(56)	123.4(3)
C(51)–P(2)–C(61)	102.52(15)	P(2)–C(61)–C(62)	120.0(3)
B–O(3)–C(3)	178.0(3)	P(2)–C(61)–C(66)	121.6(3)
O(1)–B–C(4)	105.9(3)		

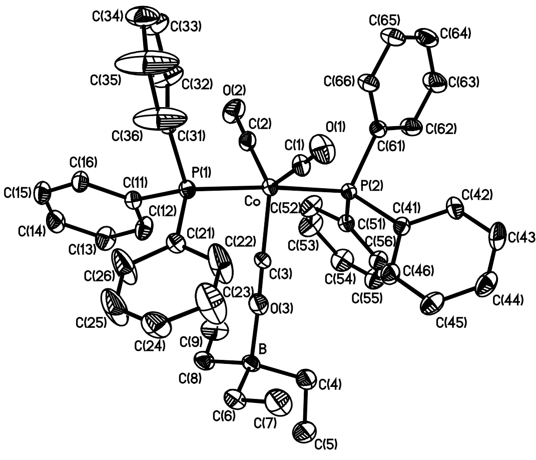


Fig. 1. Structure of complex $Co(PPh_3)_2(CO)_3BEt_3$ (**1**).

atom is located at the center of triangle in the trigonal bipyramid consisting of two phosphor atoms from the phosphine ligands and three carbon atoms from carbonyls resulting in five coordination of cobalt atom. Co–C bond distances of 1.773(4), 1.766(4) and 1.891(3) Å in **1** are similar to that of $SCo_3(CO)_9$ (1.75 and 1.78 Å) [5]. It is worth pointing out that **1** contains a novel B–O bonding, of which the oxygen atom comes from a carbonyl ligand of metal carbonyl. In our knowledge, there are four kinds of B–O bonding: (i) B links with the oxygen atom from organic alkoxide, OR ligand, (ii) B connects with the oxygen atom only resulting in borate, (iii) B as in B_3O_3 links to the oxygen atom from triosmium oxymethylidyne [6] and (iv) B coordinates to the oxygen atom from organic carbonyl forming an adduct [7]. Compound **1** is the first compound with bonding of B to the oxygen atom from metal carbonyl. B–O bond distance of **1** (1.601(5) Å) is obviously larger than that of $Na_3B_3O_6$ (1.433 and 1.280 Å), $K_3B_3O_6$ (1.398 and 1.331 Å), $Ba_3(B_3O_6)_2$ (1.397 and 1.332 Å) [8], LiB_3O_5 (1.469 and 1.336 Å) [9], CsB_2O_5 (1.48 and 1.38 Å) [10] and boron-containing organic compounds, for example, $(2,4,6\text{-}C_6H_2(CH_3)_3)_2BOCH_3$ (1.352(5) Å) [11] and that of the (iii) type of compound $(\mu\text{-}H)_3Os_3(CO)_9(\mu_3\text{-}C)(O_3B_3O_3)$ (1.39(6)–1.25(6) Å) [6]. These imply that the B–O bonding observed in **1** possesses a different bonding nature from the (i) to (iii) kinds of B–O bond. Noteworthy, B–O bonding of **1** seems to be similar to that of the (iv) type adducts formed between $B(C_6F_5)_3$ and various organic carbonyl compounds because in both of them, the B atoms are coordinated by oxygen atom from carbonyl and the B–O bond distances of them are comparable, for example, the B–O bond lengths of $PhC(X)O\text{–}B(C_6F_5)_3$ (X = H, Me, OEt, NPr_2) are in 1.52(1)–1.610(8) Å [7]. However, there are obvious differences between them: (a) in **1**, the oxygen atom coordinating to B is from metal carbonyl and in the (iv) type adducts, the oxygen atom is from organic carbonyl; (b) in **1**, the B–O–C angle is 178.0(3)° (almost linear coordination geometry) and in the (iv) type adducts, the B–O–C angles are in 126.7(5)–138.2(4)°. Thus, different carbonyl (triple bond in compound **1** and double bond in the (iv) type adducts) and different coordination geometries (linear coordination geometry in compound **1** and bending geometries in the (iv) type adducts) addition to the cobalt atom with 19 electrons in **1** lead to somewhat different B–O bonding nature. Also, it should be pointed out that linking of BEt_3 to the carbonyl of cobalt(0) in **1** enlarges the corresponding Co–C(3) bond distance (1.891(3) Å) and somehow stabilized the cobalt(0)-complex, $[Co(CO)_3(PPh_3)_2]$, which is unstable because of its cobalt atom possessing 19 electrons running counter to 18-electron configuration. In order to understand the B–O bonding nature and confirm the structure of complex **1**, a theoretical calculation has been done. Using density function theory (ADF) [12a,12b] and GAUSSIAN 98w program [12c] to calculate molecule $Co(CO)_3(PPh_3)_2\cdot BEt_3$ (**1**), the results of ADF with the double theta basis sets indicate that the bonding energy between $Co(CO)_3(PPh_3)_2$ and BEt_3 groups is 13.1 kcal mol^{-1}, which is lower than the normal covalence bonding. This result is in agreement with the slightly long B–O bond (1.601 Å). In order to demonstrate that the molecular energy vary with distance between the two groups, the Scan function of GAUSSIAN 98w with LANL2DZ basis sets was carried out (as shown in Fig. 2). It was found that the energy minimized point was near 1.65 Å, which is quite in agreement with X-ray result (1.601 Å of B–O distance in **1**). The highest occupied molecular orbital (HOMO) is non-bonding orbital occupied by the unpaired electron, and its main component is contributed from $Co(CO)_3(PPh_3)_2$. It is interesting to note that if we performed a geometry optimized at the part of $Co(CO)_3(PPh_3)_2$, the band angle of P–Co–P of the equilibrium structure would lead to 180°, while this angle in compound **1** is 176.8°. The P–Co–P bonds slightly bending to the group BEt_3 is reasonable because there is interaction between the HOMO of $Co(CO)_3(PPh_3)_2$ and BEt_3, whose energies were near to each other. The interaction causes the energy gap of HOMO and LUMO to increase from 0.15 a.u. of the group $Co(CO)_3(PPh_3)_2$ to 0.34 a.u. of compound **1.** The variety of the energy gap indicates that the addition group BEt_3 leads to stabilization of the molecule.

2.2. The structure and calculated optical nonlinearity of $[Et_4N][CoFe_2(CO)_8S(PPh_3)]$ (2)

The selected bond distances and bond angles of **2** are listed in Table 2 and the anion of **2** is depicted in Fig. 3. Compound **2** consisted of a cation Et_4N^+ and an anion $[CoFe_2(CO)_8S(PPh_3)]^-$. As shown in Fig. 3, the anion, $[CoFe_2(CO)_8S(PPh_3)]^-$, contained a $[CoFe_2S]^-$ core, which possessed a slightly distorted triangular pyramid geometry, the apical was occupied by a sulfur atom and the base was $CoFe_2$ triangle. Around the core there were six carbonyl ligands coordinating to the iron atoms and two carbonyls and one PPh_3 ligand connecting with the Co atom leading to four-coordination of cobalt and each iron atoms. This is the first structure determination of the anion compound containing triangular pyramid core $CoFe_2S$, although the preparation [13] of $[CoFe_2(CO)_9S]^-$ and $[CoFe_2(CO)_9SNO]$ and the structure of the later [14] have been reported more than 10

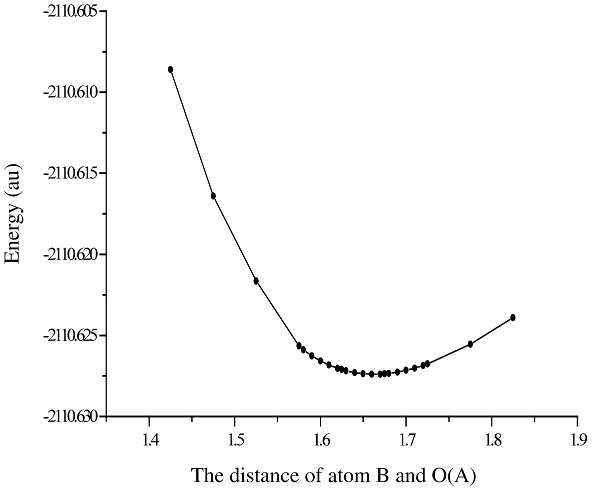


Fig. 2. The molecular energy varied with the B–O bond length for **1**.

Table 2
Selected bond distances (Å) and angles (°) for $[Et_4N][CoFe_2(CO)_8S(PPh_3)]$ (**2**)

Bond distances			
Co–Fe(2)	2.5511(7)	Fe(2)–C(5)	1.779(4)
Co–Fe(1)	2.5626(7)	Fe(2)–C(4)	1.813(5)
Co–S	2.1885(10)	P–C(11)	1.838(3)
Co–P	2.1868(10)	P–C(21)	1.824(3)
Co–C(7)	1.739(4)	P–C(31)	1.831(4)
Co–C(8)	1.772(4)	O(1)–C(1)	1.140(7)
Fe(1)–Fe(2)	2.5841(8)	O(2)–C(2)	1.135(5)
Fe(1)–S	2.2197(10)	O(3)–C(3)	1.135(5)
Fe(1)–C(3)	1.769(4)	O(4)–C(4)	1.130(5)
Fe(1)–C(1)	1.773(4)	O(5)–C(5)	1.139(5)
Fe(1)–C(2)	1.777(4)	O(6)–C(6)	1.124(5)
F(2)–S	2.1959(10)	O(7)–C(7)	1.153(5)
F(2)–C(6)	1.772(4)	O(8)–C(8)	1.143(5)
Bond angles			
Fe(1)–Co–Fe(2)	60.71(2)	Co–Fe(2)–C(4)	102.49(13)
Fe(1)–Co–S	50.02(3)	Fe(1)–Fe(2)–S	54.61(3)
Fe(1)–Co–P	132.50(3)	Fe(1)–Fe(2)–C(6)	94.30(14)
Fe(1)–Co–C(7)	72.16(12)	Fe(1)–Fe(2)–C(5)	100.65(14)
Fe(1)–Co–C(8)	130.68(13)	Fe(1)–Fe(2)–C(4)	154.55(15)
Fe(2)–Co–S	54.55(3)	S–Fe(2)–C(6)	104.96(14)
Fe(2)–Co–P	144.06(3)	S–Fe(2)–C(5)	148.93(13)
Fe(2)–Co–C(7)	116.60(12)	S–Fe(2)–C(4)	100.64(15)
Fe(2)–Co–C(8)	78.47(13)	C(6)–Fe(2)–C(5)	94.5(2)
S–Co–P	102.13(4)	C(6)–Fe(2)–C(4)	98.58(19)
S–Co–C(7)	123.45(12)	C(5)–Fe(2)–C(4)	100.1(2)
S–Co–C(8)	121.27(12)	Co–S–Fe(2)	71.16(3)
P–Co–C(7)	98.94(12)	Co–S–Fe(1)	71.09(3)
P–Co–C(8)	96.75(13)	Fe(1)S–Fe(2)	71.64(3)
C(7)–Co–C(8)	107.27(17)	Co–P–C(11)	116.37(12)
Co–Fe(1)–Fe(2)	59.43(2)	Co–P–C(21)	112.45(12)
Co–Fe(1)–S	53.89(3)	Co–P–C(31)	117.22(11)
Co–Fe(1)–C(1)	103.86(13)	C(11)–P–C(21)	101.53(16)
Co–Fe(1)–C(2)	102.44(12)	C(11)–P–C(31)	103.28(16)
Co–Fe(1)–C(3)	148.48(15)	C(21)–P–C(31)	104.10(17)
Fe(2)–Fe(1)–S	53.75(3)	Co–C(7)–O(7)	168.9(3)
Fe(2)–Fe(1)–C(3)	97.91(14)	Co–C(8)–O(8)	173.9(4)
Fe(2)–Fe(1)–C(1)	91.88(214	Fe(1)–C(1)–O(1)	177.9(4)
Fe(2)–Fe(1)–C(2)	160.80(12)	Fe(1)–C(2)–O(2)	178.2(4)
S–Fe(1)–C(3)	95.56(15)	Fe(1)–C(3)–O(3)	177.8(4)
S–Fe(1)–C(1)	144.52(14)	Fe(2)–C(4)–O(4)	178.8(4)
S–Fe(1)–C(2)	111.72(13)	Fe(2)–C(5)–O(5)	179.1(4)
C(3)–Fe(1)–C(1)	98.1(2)	Fe(2)–C(6)–O(6)	177.6(4)
C(3)–Fe(1)–C(2)	95.96(18)	P–C(11)–C(12)	119.6(3)
C(1)–Fe(1)–C(2)	99.25(19)	P–C(11)–C(16)	121.9(3)
Co–Fe(1)–Fe(2)	59.43(2)	P–C(21)–C(22)	122.3(3)
Co–Fe(2)–S	54.28(3)	P–C(21)–C(26)	120.0(3)
Co–Fe(2)–C(6)	152.73(14)	P–C(31)–C(32)	118.0(3)
Co–Fe(2)–C(5)	98.63(14)	P–C(31)–C(36)	124.0(3)

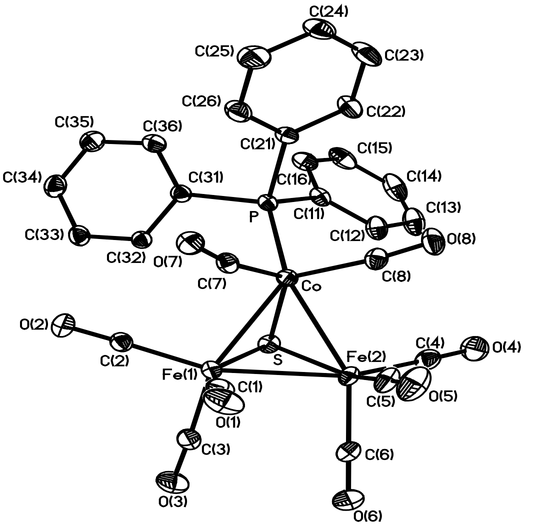


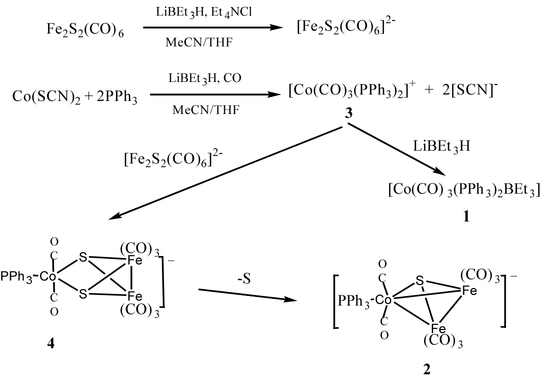
Fig. 3. Structure of the anion of the complex, $[Et_4N][Co-Fe_2(CO)_8S(PPh_3)]$ (**2**).

years ago. The average bond lengths of M–M (2.57(2)), M–S (2.20(2)), M–C_{ax} (1.76(2)), M–C_{eq} (1.78(2)), C–O (1.14(1) Å) and bond angles of M–S–M (71.3(3)), M–M–S (54(2)), C_{eq}–M–C_{eq} (97(2)), C_{eq}–M–C_{ax} (100(5)°) in the anion of **2** [15] are comparable with that in the neutral compound, $[CoFe_2(CO)_8NO]$ (M–M, 2.56(2); M–S, 2.16(3); M–C_{ax}, 1.79(2); M–C_{eq}, 1.78(3); C–O, 1.13(2) Å and M–S–M, 72.5(2); M–M–S, 54(1); C_{eq}–M–C_{eq}, 99(7); C_{eq}–M–C_{ax}, 101(7)°). The fact that Co–μ_3-S bond length of 2.189 Å in **2** is very similar to that in Co(I)-complex, $[SCo_3(CO)_7]_2S_2$, [16] indicated that the oxidation state of cobalt atom in **2** is +1, thus, the oxidation states of the two iron atoms in **2** should be zero in terms of the principle of electric charge balance. In fact, the Fe–Fe bond distance of 2.5841(8) Å in **2** is approximate to the one in Fe^0-complex, $Fe_3(CO)_9S^{2-}$ (Fe–Fe, 2.58 Å). The $SFe_2(CO)_6$ unit of **2** could be considered as an incomplete $Fe_2S_2(CO)_6^{2-}$ unit with losing one of the sulfur atoms and reduction of each Fe^{+1} to Fe^0 because the configuration of the two $Fe(CO)_3$ fragments including the Fe–Fe bond distance (2.5841(8) Å) in **2** is very similar to those in starting material $[Fe_2S_2(CO)_6]^{2-}$ (Fe–Fe, 2.54 Å) [1,17]. The skeleton electron number of **2** is 48 and three metal–metal bonds (one Fe–Fe and two Fe–Co bonds) were observed in **2**. This showed that the structure of **2** complied with the $2(9N-L)$ (N = number of metal and L = number of metal–metal bonds) rule [18].

By using density functional theory (DFT) method, the frequency-dependent first hyperpolarizabilities of the molecular cluster, $[Et_4N][CoFe_2(CO)_8S(PPh_3)]$ (**2**), was determined with the widely used local density approximation (LDA) and the asymptotically correct Van Leeuwen–Baerends (LB94) potential. The triple basis set was used and the frozen-core is up to 3p for Fe and Co, 2p for P and 1s for C and O. If we let the x-axis lie in the direction of Co to bisection point of the two Fe atoms, the calculated β_{xxx} component is about 28.5×10^{-30} esu ($\lambda = 1.064$ µm), which is about 100 times larger than the average β value of a urea molecule [19]. The rest β components of the cluster are all less than 7.0×10^{-30} esu, and it is found that the largest component of dipole moment is also X direction with $\mu_x = -11.4$ Debye, while μ_y and μ_z has only 1.4 and -4.1 Debye, respectively. These results indicate that this molecular cluster might have great potential to be second-harmonic generation material, which has its application in optical communication device.

2.3. *The synthetic reaction and possible formation pathway of products*

As is described above, it can be found evidently that (i) the product **1** contains a Co^0 atom with five coordination geometry and product **2** possesses a Co^+ ion with distorted tetrahedral coordination geometry; (ii) Co atoms in both product **1** and **2** have carbonyl ligands, (iii) product **2** contains a $[Fe_2S(CO)_6]^{2-}$ unit which could be considered as an incomplete $Fe_2S_2(CO)_6^{2-}$ unit with losing one of its two sulfur atoms and low valence iron atoms, Fe^0, and (iii) according to the reaction of $Co_2(CO)_8$ with PPh_3 [20] and the IR data of its products $[Co(CO)_3(PPh_3)_2]$-$[Co(CO)_4]$ (2002, 1883 cm^{-1}), $[Co(CO)_3(PPh_3)_2][BPh_4]$ (2004 cm^{-1}) and $[Co(CO)_3(PPh_3)_2][Cr(SCN)_4(NH_3)_2]$ (2014, 1944 cm^{-1}) [21], the 1986 and 1930 cm^{-1} absorption of **3** implied that compound **3** possessed a trigonal bipyramid configuration like $[Co(CO)_3$-$(PPh_3)_2]^+$. Thus, it is evident that the synthetic reaction involves the substitution of carbonyl and phosphine for SCN-ligands, reduction of cobalt ion Co^{2+} and iron ions Fe^I, desulfurization process and participation of $Fe_2S_2(CO)_6^{2-}$ as a building block come from the reaction of $[Fe_2S_2(CO)_6]$ with $LiBEt_3H$ [1]. Taking the reactants, reaction condition used and phenomenon observed during the reaction process together into



Scheme 1.

account, the synthetic reaction and reaction pathway could be proposed as in Scheme 1.

As shown in Scheme 1, $[Fe_2S_2(CO)_6$ reacts with $LiBEt_3H$ in the presence of Et_4NCl affording $[Fe_2S_2(CO)_6]^{2-}$ [1], $Co(SCN)_2$ reacts with PPh_3 in the presence of carbon monoxide (from dissociation of $[Fe_2S_2(CO)_6])^{2-}]$ and $LiBEt_3H$ resulting in Co^+–PPh_3–CO complex, $[Co(PPh_3)_2(CO)_3]^+$ (**3**), and this Co^+–PPh_3–CO complex **3** further reacts with $LiBEt_3H$ affording the Co^0-complex, $Co(PPh_3)_2(CO)_3BEt_3$ (**1**) as a side product in a very low yield. In terms of the expected reactivity of $[Fe_2S_2(CO)_6]^{2-}$ [1,2,22–24] the $[Co(PPh_3)_2(CO)_3]^+$ (**3**) would react with $[Fe_2S_2(CO)_6]^{2-}$ leading to a precursor product, $[CoFe_2S_2(CO)_8(PPh_3)]^-$ (**4**) which should be similar to the known Co–Fe–S compound, $(MeC_5H_4)_2Cr(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)_2Co(\mu_3\text{-}S)_2Fe_2(CO)_6$ [25], containing a '$CoFe_2S_2$' core and unstable because of the different oxidation state of Fe atoms and different ligands on Co atom. Thus, the unstable precursor product **4** further undergoes inner molecular redox leading to oxidation and lose of one brigding sulfur ion and reduction of the Fe^{+1} to Fe^0, and finally results in the stable product **2** which has a similar core framework to M_3S of Fe^0-compound, $[Fe_3S(CO)_9]^{2-}$ [26].

3. Experimental

3.1. Materials and methods

Acetonitrile was distilled with CaH_2, MeOH and isopropanol were dried by distillation with MgOMe. PPh_3 and $Fe(CO)_5$ were purchased from Fluka. $Co(SCN)_2$ and $LiBHEt_3$ in THF were purchased from Aldrich. $Fe_2S_2(CO)_6$ were prepared by reaction of $Fe(CO)_5$ with Na_2S_5 and KOH in MeOH [1,27].

All reaction and treatments were carried out under nitrogen atmosphere by using Schlenk technique and all the solvents and reagents were degassed before use.

IR spectra were recorded on Nicolet Magno 750 Fourier Transform IR Spectrometer and elemental analysis were performed on Carlo Erba Instrumentation Elemental Analyzer-MOD1106.

3.2. Synthesis of $Co(CO)_3(PPh_3)_2BEt_3$ (1) and $[Et_4N][CoFe_2(CO)_8S(PPh_3)]$ (2)

A mixture of 0.39 g (0.0015 mol) of PPh_3, 0.28 g (0.0017 mol) of Et_4NCl in 20 ml of MeCN was stirred at room temperature (r.t.) resulting in colorless solution, then, to the solution was added 0.13 g (0.0007 mol) of $Co(SCN)_2$ under stirring. The reaction mixture became blue solution (solution A). $Fe_2S_2(CO)_6$ (0.25 g, 0.0007 mol) in 30 ml MeCN was stirred at −78 °C giving orange solution and to this solution was dropped slowly 1.5 ml of $LiBHEt_3$–THF (it could be seen that the solution drops on the wall of the flask were green), and the blue solution A in turn, resulting in deep-red reaction mixture. The reaction mixture was stirred for more than 20 min and then, the cool bath was removed. After the temperature rose to r.t., the mixture was stirred continuously in r.t. for another 48 h. Filtering out the dark residue, the dark filtrate was cooled at 4 °C for several days. Black sparkling crystalline product (0.1 g) was obtained by filtration, washed with isopropanol and dried in vacuum (Yield: 17.4%). Anal. Calc. for $C_{34}H_{35}CoFe_2NO_8PS$: C, 49.8; H, 4.3; Co, 7.2; Fe, 13.7; N, 1.7. Found: C, 50.5; H, 4.4; Co, 6.9; Fe, 14.1; N, 1.9%. IR (KBr pellet) 2025s, 1967s, 1946s, 1905s and 1855s (ν_{CO}), X-ray crystallography study indicated that this product was $[Et_4N][CoFe_2(CO)_8S(PPh_3)]$ (**2**). The filtrate was concentrated by vacuum to volume of 15 ml, 20 ml of isopropanol was added and 0.02 g of yellow brown crystals were obtained by filtration and dried in vacuum. Anal. Calc. for $C_{45}H_{45}CoBO_3P_2$: C, 70.6; H, 5.9; Co, 7.7. Found: C, 69.8; H, 6.5; Co, 8.2%. IR (KBr pellet): 2000s, 1942s (ν_{CoC-O}), 1823w (ν_{C-OB}), 1263m (ν_{B-O}), and 885 (ν_{B-C}) cm^{-1}. X-ray crystal structure determination revealed that this yellow brown product was $Co(CO)_3(PPh_3)_2BEt_3$ (**1**). In fact, the atomic emission spectrum (AES) of **1** indicated the existence of boron. A small amount (about 0.01 g) of bright yellow product (**3**) was obtained from the filtrate, which was stayed at 4 °C for several days. Compound **3** was characterized only by AES and IR measurements because of its limited quantity and lack of crystal quality suitable for X-ray crystallography. IR (KBr) of **3**: 1986s, 1930s (ν_{CoC-O}) and AES measurement indicated the existence of cobalt and absence of boron.

3.3. X-ray crystal structure determination

Crystal data and details of data collection and refinement procedures for **1** and **2** are summarized in Table 3. The structures were solved by conventional direct methods and refined by the full-matrix least-squares methods [28]. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were located at idealized positions and refined with fixed isotropic thermal parameters.

4. Summary

A novel Co–B carbonyl complex with new type B–O bonding, $Co(CO)_3(PPh_3)_2BEt_3$ (**1**), and a mixed-metal Co–Fe–S cluster compound with possible optical non-linearity, $[Et_4N][CoFe_2(CO)_8S(PPh_3)]$ (**2**), were obtained from the reaction of $Co(CNS)_2$ with $Fe_2S_2(CO)_6$, $LiBEt_3H$ and PPh_3 in THF–MeCN mixed solvents. X-

Table 3
Crystal data and details of data collection for **1** and **2**

Compounds	**1**	**2**
Empirical formula	$C_{45}H_{45}BCoO_3P_2$	$C_{34}H_{35}CoFe_2NO_8PS$
Formula weight	765.49	819.29
Crystal system	Monoclinic	Trigonal
Space group	$P2_1/c$ (No. 14)	$P3_1$
Unit cell dimensions		
a (Å)	11.245(3)	11.74(4)
b (Å)	14.267(5)	11.74(4)
c (Å)	26.076(5)	23.394(5)
α (°)		
β (°)	96.85(5)	
γ (°)	120	
V (Å^3)	4154(2)	2793
Z	4	3
D_{calc} (g cm^{-3})	1.224	1.461
$F(000)$	1604	1260
μ(Mo–K$_\alpha$) (cm^{-1})	5.28	13.56
Diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4
Temperature (K)	293(2)	293(2)
Radiation (Å)	Mo–K$_\alpha$ (0.71073 Å)	Mo–K$_\alpha$, 0.71073
Crystal size (mm^3)	0.40 × 0.30 × 0.25	0.40 × 0.32 × 0.28
θ Range (°)	2.38–24.98	2.00–25.98
Index ranges	$0 \leq h \leq 13$, $0 \leq k \leq 16$, $-30 \leq l \leq 30$	$0 \leq h \leq 12$, $0 \leq k \leq 12$, $-28 \leq l \leq 28$
Reflections collected/unique	7625/7235 [$R_{int} = 0.0680$]	3787/3644 [$R_{int} = 0.0807$]
Data/restraints/parameters	7235/0/469	3644/1/434
R_1, wR_2 [$I > 2\sigma(I)$]	0.0559, 0.1463	0.0267, 0.0578
R_1, wR_2 [all data]	0.0735, 0.1593	0.0301, 0.0584
Goodness-of-fit	1.023	1.007
Largest difference peak/hole (e Å^{-3})	0.539/−0.513	0.341/−0.304

ray crystal structure determination revealed that **1** contained a novel B–O bonding of which the oxygen atom came from a metal carbonyl ligand, and **2** possessed a triangular pyramid core $CoFe_2S$ with Co^+ and Fe^0 ions. Theoretical chemical calculation on **1** and **2** showed that B–O bonding energy of complex **1** was lower than that of normal covalence bonding and compound **2** possesses a calculated nonlinear optical first molecular hyperpolarizability component of 28.5×10^{-30}esu. A reaction pathway involving substitution of ligands, reduction of Co^{2+} and Fe^+ ions, participation of $[Fe_2S_2(CO)_6]^{2-}$ as a reactive building block and desulfurization process was proposed and discussed.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 178040 and 178041 for compounds **1** and **2**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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