Synthesis and reactivity of a novel hydridocobalt(III) complex containing trimethylphosphine and thiophenolato ligands

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Abstract

The novel hydridocobalt(III) complex [*mer*-Co(H)(SPh)$_2$(PMe$_3$)$_3$] (**1**) was prepared by reaction of thiophenol with [Co(PMe$_3$)$_3$Cl], [Co(PMe$_3$)$_4$] and [Co(PMe$_3$)$_4$Me]. A dinuclear cobalt dithiophenolato complex [Co(PMe$_3$)$_2$(SPh)]$_2$ (**2**) was obtained from the reaction of thiophenol with [Co(PMe$_3$)$_4$Me]. Reaction of **1** with iodomethane afforded complex [Co(PMe$_3$)$_3$(I)$_2$] (**3**). Reaction of complex **2** with carbon monoxide gave a mononuclear dicarbonyl cobalt(I) complex [Co(PMe$_3$)$_3$(CO)$_2$(SPh)] (**4**). The crystal structures of **1**–**4** were determined by X-ray diffraction. Formation mechanism of **1** is discussed.
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Keywords: Hydridocobalt(III) complex; Trimethylphosphine; Thiophenol; Crystal structure

1. Introduction

Hydrido compounds of transition metals play an important role in synthetic and industrial processes. According to a widely accepted mechanism for the hydroformylation process given by Heck and Breslow, a hydridocobalt compound is regarded as a necessary precatalyst [1]. So far very few examples of hydridocobalt(III) complexes are known.

Metal thiolato complexes are known as ubiquitous biological electron-transfer mediators [2,3], yet complexes containing both phosphine and thiolato ligands have received relatively little attention and only a few reports are found in this area [4]. Interest in mono- and polynuclear transition-metal thiolates has undergone a remarkable increase in recent years [5]. Metal thiolate complexes are involved in fundamental catalytic (e.g. hydrodesulfurization [6]) and biological (e.g. iron–sulfur proteins [7]) processes. In particular, the study of sulfur–metal centers,

associated with several important features such as redox behavior, unusual geometries, stabilization of uncommon metal oxidation states, electron deficiency or abundance, can contribute to the understanding of structure, bonding and function of biologically important sulfur–metal sites [7]. Polyphosphine–transition-metal complexes with bis-sulfido coligands usually display good electron-transfer capability [8,9]. Recently, homogeneous nickel catalysts for the selective transfer of a single arylthio group in the catalytic hydrothiolation of alkynes were developed [10].

One of the difficulties in studying thiolate coordination chemistry is that RS$^-$ donors have a strong tendency to bridge metal ions acting as bidentate soft bases. If not controlled by coligands this can lead to the formation of aggregates or polymers of varying size which can be hard to study [11]. Control has been exerted by the use of bulky substituents and/or by the use of thiolate bearing electron-withdrawing groups. Bridging of thiolates is more easily controlled with aromatic RS$^-$ donors such as thiophenolates.

The main purpose of this study is to investigate the reactivity of the trimethylphosphine supported hydrido cobalt

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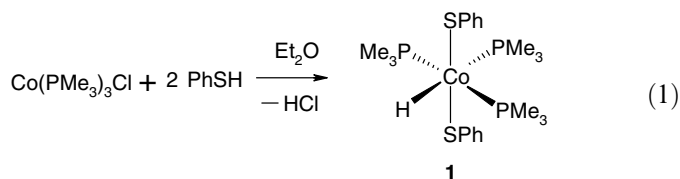*E-mail address:* xli63@sdu.edu.cn (X. Li).

complex to thiophenol. At the same time some chemical properties of the thiophenolato hydrido cobalt complexes were studied. In this paper we report on recent studies of the chemistry of hydridocobalt(III) complexes. In this account reactions of thiophenol with [Co(PMe₃)₃Cl], [Co(PMe₃)₄], and [Co(PMe₃)₄Me] are described. [*mer*-Co(H)(SPh)₂(PMe₃)₃] (**1**) could be obtained from each of the starting materials. A dinuclear complex [Co(P-Me₃)₂(SPh)]₂ (**2**) was produced from the reaction of thiophenol with [Co(PMe₃)₄Me]. Reaction of **1** with iodomethane has been studied in detail. The reaction of the dinuclear complex **2** with carbon monoxide afforded the mononuclear dicarbonyl cobalt(I) complex **4**. The crystal structures of complexes **1**–**4** were determined by X-ray crystallography. The formation mechanism of **1** is proposed.

2. Results and discussion

2.1. Preparation of 1

2.1.1. Reaction of [Co(PMe₃)₃Cl] with thiophenol

[Co(PMe₃)₃Cl] reacts with thiophenol giving the novel hydriocobalt(III) complex **1** according to Eq. (1) **1** forms yellow brown crystals from diethyl ether which decompose above 80 °C. In the IR spectra there is a conspicuous ν(Co–H) absorption at 1977 cm⁻¹. The ¹H NMR spectrum indicates a pattern of PMe₃ signals expected for complex **1**: a virtual triplet for two *trans*-PMe₃ groups and a doublet for the single PMe₃ ligand. A doublet of triplets appears in the CoH region at −9.2 ppm with $^2J(\text{P}cis,\text{H}) = 111.9$ Hz and $^2J(\text{P}trans,\text{H}) = 69.6$ Hz (Fig. 1). ³¹P NMR data clearly show two singlets (1:2) for three coordinated trimethylphosphine groups, one at −6.86 ppm for the singular PMe₃ and the other at 1.72 ppm for the two *trans*-PMe₃ ligands.

$$\text{Co(PMe}_3)_3\text{Cl} + 2\ \text{PhSH} \xrightarrow[-\text{HCl}]{\text{Et}_2\text{O}} \begin{array}{c} \text{SPh} \\ | \\ \text{Me}_3\text{P}_{\prime\prime\prime\prime\prime}\text{Co}_{\prime\prime\prime\prime\prime}\text{PMe}_3 \\ | \\ \text{H} \quad \text{PMe}_3 \\ | \\ \text{SPh} \\ \mathbf{1} \end{array} \tag{1}$$

The molecular structure of **1** (Fig. 2) shows a hexa-coordinate cobalt atom surrounded by three P-donor atoms in a meridional configuration. Two thiophenolato donors S1, S2 are arranged in opposite positions. The angle S2–Co1–S1 of 177.38(4)° (Table 1) indicates the position of the hydrogen atom. Owing to the *trans*-influence of the hydrido ligand the distance Co1–P3 (2.2726(19) Å) is larger than Co1–P1 (2.2263(18) Å) and Co1–P2 (2.2266(19) Å).

To understand this mechanism the additional experiments were carried out (Scheme 1). Lithium thiphenolate obtained from the reaction of thiophenol with *n*-butyllithium reacted with [Co(PMe₃)₃Cl] directly giving rise to dinuclear complex **2** without any evidence of formation of the tetra-coordinate cobalt(I) intermediate (route a). This result proves the low stability of this 16-valence-electron cobalt(I) intermediate. The dinuclear complex **2** with the interaction of thiophenol delivered complex **1** (route b). Complex **1** could also be prepared through one-pot reaction of lithium thiophenolate with [Co(PMe₃)₃Cl] in the presence of thiophenol (route c).

2.1.2. Reaction of [Co(PMe₃)₄] with thiophenol

The reaction of [Co(PMe₃)₄] with thiophenol also yields complex **1** according to Eq. (2).
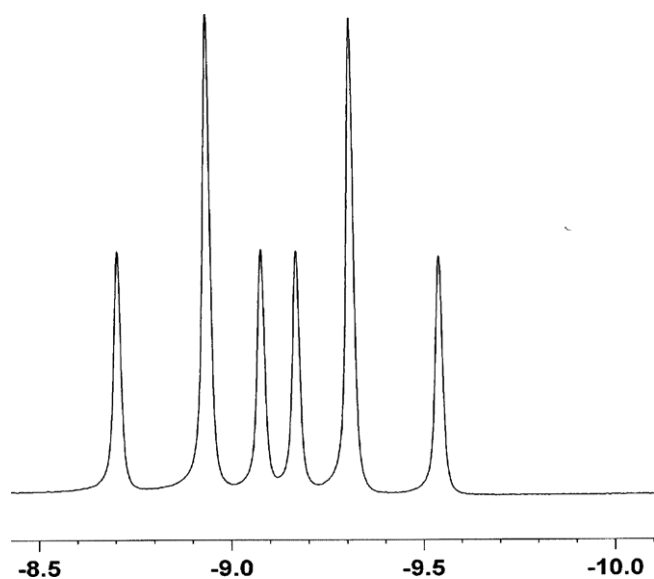

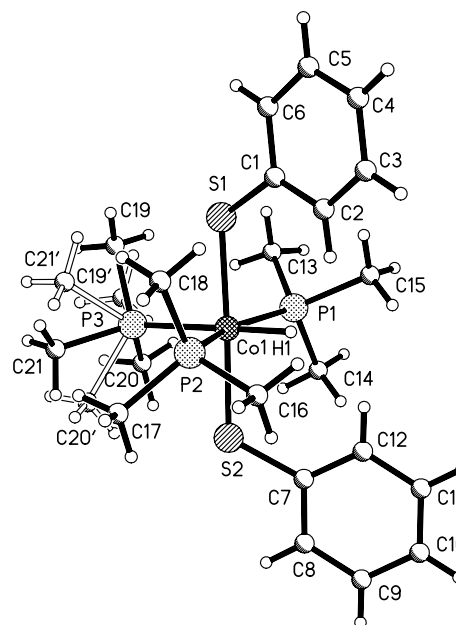Fig. 1. The NMR spectrum of the hydrido ligand of **1**.

Fig. 2. Molecular structure of **1**.

Table 1
The selected bond distances and angles of complexes **1**–**4**

Complex	Bond distances (Å)	Bond angle (°)
1	Co1–P1 2.2264(17)	P1–Co1–P2 159.41(5)
	Co1–P2 2.2265(19)	P1–Co1–P3 100.35(6)
	Co1–P3 2.2701(19)	P2–Co1–P3 100.24(5)
	Co1–S2 2.274(2)	P1–Co1–S2 94.79(4)
	Co1–S1 2.2749(19)	P2–Co1–S2 85.57(4)
	Co1–H1 1.45(2)	P3–Co1–S2 88.85(5)
		P1–Co1–S1 85.62(4)
		P2–Co1–S1 94.94(4)
		P3-Co1–S1 88.58(5)
		S2–Co1–S1 177.43(4)
2	Co1–P1 2.2077(5)	P1–Co1–P2 100.37(2)
	Co1–P2 2.2082(6)	P1–Co1–S1 114.00(2)
	Co1–S1 2.2399(5)	P2–Co1–S1 103.30(2)
	Co1–S1A 2.2412(6)	P1–Co1–S1A 102.87(2)
	Co1–Co1A 2.3997(5)	P2–Co1–S1A 120.47(2)
	S1–C1 1.7863(19)	S1–Co1–S1A 115.245(16)
	S1–Co1A 2.2412(6)	P1–Co1–Co1A 125.99(2)
	P1–C9 1.826(2)	P2–Co1–Co1A 133.49(2)
	P1–C8 1.829(2)	S1–Co1–Co1A 57.648(17)
	P1–C7 1.834(2)	S1A–Co1–Co1A 57.596(15)
	P2–C12 1.821(2)	C1–S1–Co1 112.47(6)
	P2–C10 1.823(2)	C1–S1–Co1A 119.19(7)
	P2–C11 1.839(3)	Co1–S1–Co1A 64.757(16)
3	Co1–P2 2.227(3)	P2–Co1–P1 94.70(11)
	Co1–P1 2.248(2)	P2–Co1–P3 95.33(9)
	Co1–P3 2.263(2)	P1–Co1–P3 169.81(11)
	Co1–I1 2.6109(11)	P2–Co1–I1 117.01(8)
	Co1–I2 2.6285(12)	P1–Co1–I1 88.99(7)
		P3–Co1–I1 110.38(8)
		P1–Co1–I2 87.13(7)
		P3–Co1–I2 87.69(7)
		I1–Co1–I2 132.61(5)
4	Co1–C14 1.747(3)	C14–Co1–C13 118.88(16)
	Co1–C13 1.757(3)	C14–Co1–P2 89.05(12)
	Co1–P2 2.1972(9)	C13–Co1–P2 92.10(12)
	Co1–P1 2.1978(10)	C13–Co1–P1 4.77(4)
	Co1–S1 2.3207(10)	C14–Co1–S1 126.86(11)
		C13–Co1–S1 6.69(3)
		P1–Co1–S1 88.55(3)

$$\text{Co(PMe}_3)_4 + \text{PhSH} \xrightarrow{\text{Et}_2\text{O}} \mathbf{1} \tag{2}$$
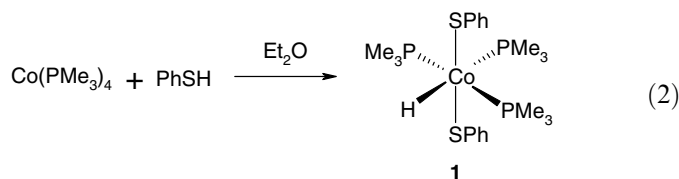
2.1.3. Reaction of [Co(PMe₃)₄Me] with thiophenol

Reaction of [Co(PMe₃)₄Me] with thiophenol also gave the hydrio cobalt(III) complex **1**. In addition, a novel sulfur-bridged dicobalt(I) complex **2** was obtained (Eq. (3)).

$$4\,\text{PhSH} + 3\,\text{Co(PMe}_3)_4\text{Me} \xrightarrow[- 5\,\text{PMe}_3]{- 3\,\text{CH}_4} \mathbf{1} + \mathbf{2} \tag{3}$$
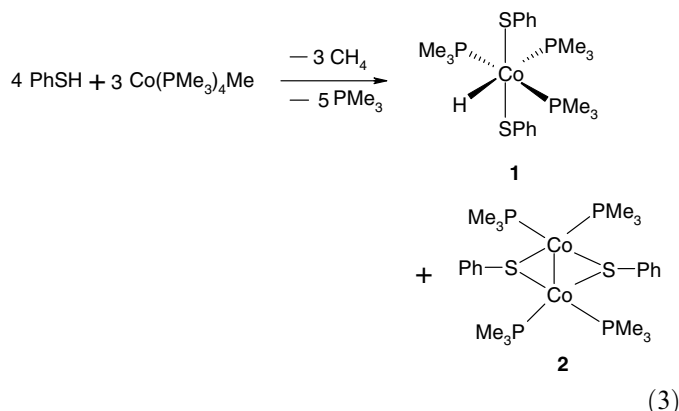
Complex **2** forms dark red crystals suitable for X-ray diffraction which decomposes above 68 °C and under ambient conditions are stable in the air for several minutes. ¹H NMR of complex **2** shows broad resonances with large paramagnetic shifts. The molecular structure of **2** (Fig. 3) belongs to C_{2h} symmetry. Four atoms (Co1, S1A, S1, Co1A) lie almost in one plane. Both cobalt(I) centers show a tetrahedral configuration. The two bridging thiophenolato ligands are arranged in opposite directions with respect to the plane Co1–S1A–S1–Co1A. In contrast, the tetrahedral core Co₂(μ-S)₂ in [Co₂(dppm)(SPh)₄] is non-planar [12]. Pushed by the bulky (diphenylphosphanyl)ethane

Scheme 1. Investigation of mechanism for Eq. (1).
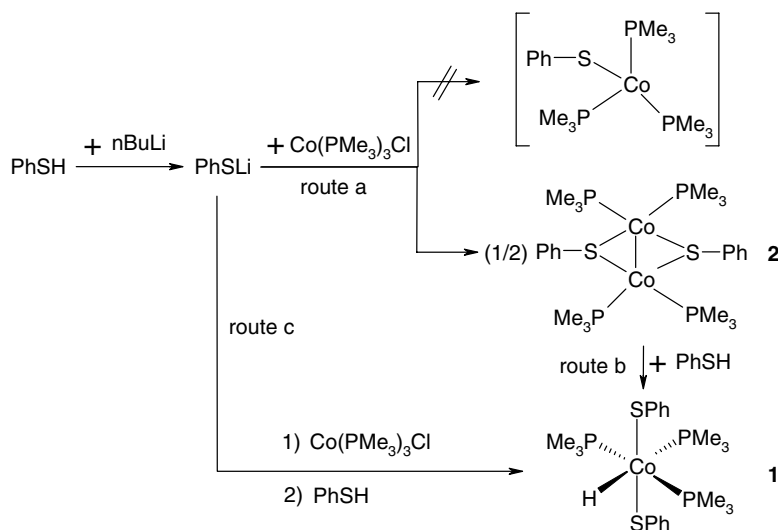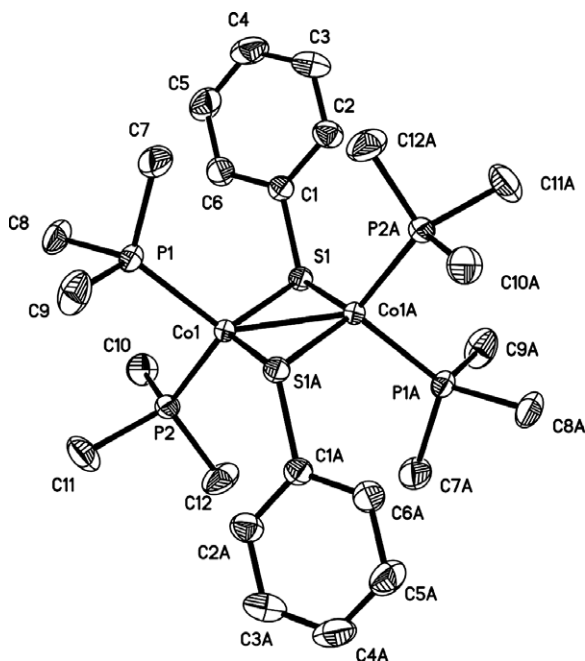
Fig. 3. Molecular structure of **2**.
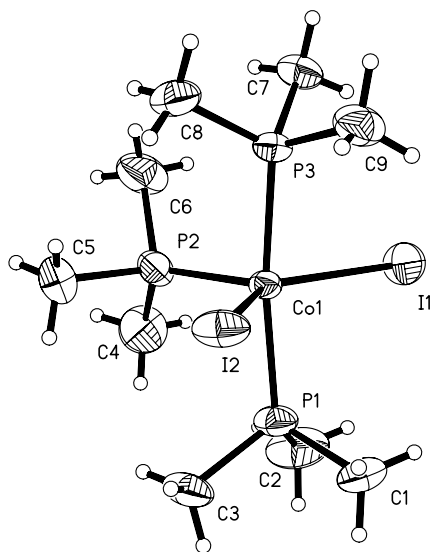
Fig. 4. Molecular structure of **3**.

ligand the bridging SPh-groups orient to the same side of the Co_2S_2-plane. The Co1–Co1A distance (2.3997(5) Å) in **2** is shorter than that in $[Co_2(dppm)(SPh)_4]$ (2.6 Å).

2.2. Reaction of hydrido cobalt(III) complex 1 with iodomethane

The hydrido cobalt(III) complex **1** reacts with iodome-thane giving the tris(trimethylphosphine)diiodocobalt(II) complex **3** according to Eq. (4). Complex **3** can be obtained through the substitution reaction of tris(trimethylphos-phine)dichlorocobalt(II) compound with sodium iodide

quantitatively [13]. The evolution of ethane could be veri-fied with gas chromatography.

(4)
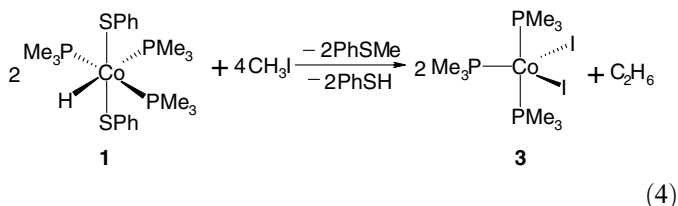
The molecular structure of **3** (Fig. 4) shows that there are three molecules in an unsymmetric unit. Bond lengths and angles in the three molecules are approximately the same. The cobalt atom lies in the center of a trigonal bipyr-amid in which two iodine atoms and one P atom form an equatorial plane, P1 and P3 are arranged in axial positions with an angle P1–Co1–P3 (169.81(11)°).

2.3. Reaction of 2 with carbon monoxide

In a pentane solution under 1 bar of CO at 20 °C, com-plex **2** slowly transforms a dicarbonyl complex **4**. The yel-low crystals of complex **4** are quite air-stable and thermally decompose above 117 °C.

(5)
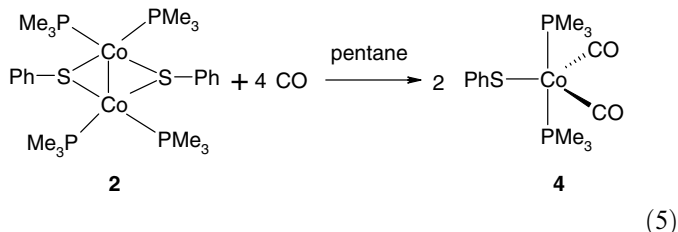
The IR spectrum of **4** contains two strong absorptions of terminal carbonyl ligands: 1969 cm^{-1} (νCO) and 1886 cm^{-1} (νCO). The molecular structure (Fig. 5) con-
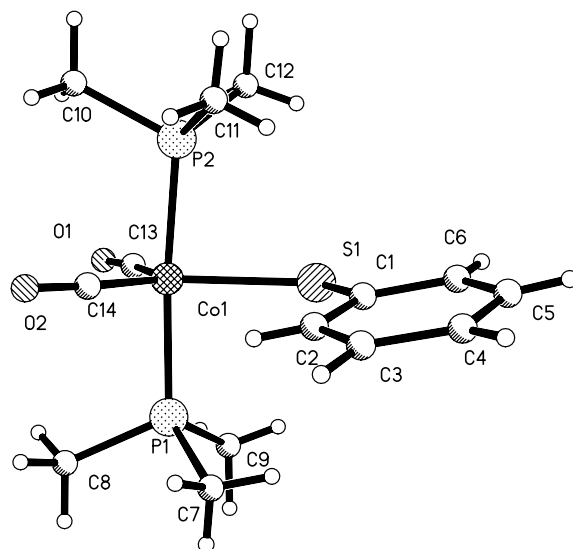
Fig. 5. Molecular structure of **4**.

firms the presence of two trimethylphosphine ligands in axial positions with an angle P2–Co1–P1 of 174.77(4)° in a trigonal bipyramidal coordination geometry.

3. Conclusion

Three different trimethylphosphine cobalt complexes react with thiophenol under the similar experimental conditions yielding the same hydridocobalt(III) complex **1**. By reaction with iodomethane all Co–S bonds of **1** are cleaved forming a known iodocobalt compound. The dinuclear cobalt complex **2** is a by-product in one of the syntheses and with carbon monoxide is transformed to a mononuclear dicarbonyl cobalt(I) complex **4**. Likely formation mechanism of complex **1** can be suggested.

4. Experimental

4.1. General procedures and materials

Standard vacuum techniques were used in manipulations of volatile and air sensitive materials. [Co(PMe$_3$)$_3$Cl] [14], [Co(PMe$_3$)$_4$] and [Co(PMe$_3$)$_4$Me] [15] were prepared by published procedures. Thiophenol was used as purchased. Infrared spectra (4000–400 cm^{-1}), as obtained from Nujol mulls between KBr discs, were recorded on NICOLET 5700. ^{1}H, ^{13}C and ^{31}P NMR (300, 75 and 121 MHz, respectively) spectra were recorded on Bruker AVANCE 300 spectrometer. ^{13}C and ^{31}P NMR resonances were obtained with broad-band proton decoupling. Elemental analyses were carried out on Elementar Vario EL III. Melting points were measured in capillaries sealed under argon and are uncorrected.

4.1.1. Synthesis of [mer-Co(H)(SPh)$_2$(PMe$_3$)$_3$] (1)

Method a: A sample of [Co(PMe$_3$)$_3$Cl] (1.53 g, 4.7 mmol) in 40 mL of diethyl ether at −80 °C was combined with a solution of thiophenol (1.02 g, 9.2 mmol) in 20 mL of diethyl ether. The resulting mixture was warmed up to 20 °C and stirred for 3 h to give a yellow brown solution. A slight turbidity was filtered off and at −21 °C the solution afforded yellow brown crystals of **1** suitable for X-ray diffraction (0.42 g, 36%). *Method b*: A sample of [Co(PMe$_3$)$_4$] (1.70 g, 4.7 mmol) in 40 mL of pentane at −80 °C was combined with a solution of thiophenol (0.51 g, 4.6 mmol) in 30 mL of pentane. The resulting mixture was warmed up to 20 °C to give a dark brown solution. A slight turbidity was filtered off and the solution at 4 °C afforded yellow brown crystals of **1**. After concentration the mother liquor at 4 °C afforded yellow brown crystals (0.32 g, 27%). *Method c (one-pot reaction, route c, Scheme 1)*: A sample of thiophenol (0.33 g, 2.98 mmol) in 20 mL of diethyl ether at −80 °C was combined with a solution of *n*-butyllithium (2.5 mol/L, 1.20 mL) of hexane. After 1 h a sample of [Co(PMe$_3$)$_3$Cl] (0.97 g, 2.98 mmol) and thiophenol (0.33 g, 2.98 mmol) were successively added to the resulting mixture. The color of the solution changed from red to brown yellow. After 2 h the reaction mixture was filtered off and the filtrate at −20 °C afforded yellow brown crystals of **1** (0.94 g, 62%). *Method d (route b, Scheme 1)*: A sample of thiophenol (0.31 g, 2.80 mmol) in 20 mL of diethyl ether at −80 °C was combined with a solution of *n*-butyllithium (2.5 mol/L, 1.10 mL) of hexane. After 1 h a sample of [Co(PMe$_3$)$_3$Cl] (0.90 g, 2.80 mmol) was added to the resulting mixture. After 18 h a sample of thiophenol (0.31 g, 2.8 mmol) was added to the reaction solution. The filtrate at −20 °C afforded yellow brown crystals of **1** (0.75 g, 53%). *Method e*: A sample of [Co(PMe$_3$)$_4$]

Table 2
Crystallographic data for **1–4**

Complex	1[a]	2	3	4
Formula	C$_{21}$H$_{38}$CoP$_3$S$_2$	C$_{24}$H$_{46}$Co$_2$P$_4$S$_2$	C$_9$H$_{27}$CoI$_2$P$_3$	C$_{14}$H$_{23}$CoO$_2$P$_2$S
Molecular weight	506.47	640.46	540.95	376.25
Crystal size (mm)	0.22 × 0.20 × 0.14	0.24 × 0.20 × 0.14	0.30 × 0.25 × 0.15	0.21 × 0.20 × 0.13
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P$\bar{1}$	P2(1)/c	P2(1)/c	P2(1)
a (Å)	9.780(7)	10.0645(11)	14.3055(6)	7.0213(14)
b (Å)	12.173(9)	11.5078(12)	28.0578(11)	12.896(3)
c (Å)	12.777(9)	14.6232(16)	14.9298(6)	9.999(2)
α (°)	79.888(11)	90	90	90
β (°)	67.586(10)	104.232(2)	101.625(3)	92.89(3)
γ (°)	66.455(11)	90	90	90
V (Å^3)	1288.7 (15)	1641.7 (3)	5869.6 (4)	904.2 (3)
Z	2	4	12	2
D_c (g cm^{-3})	1.303	1.296	1.836	1.382
μ (mm^{-1})	1.019	1.344	4.257	1.239
θ_{max} (°)	25.00	26.35	27.53	27.05
Reflections measured	6684	9070	29809	4854
Unique reflections	4519	3349	13389	3358
R_1 ($I > 2\sigma(I)$)	0.0412	0.0238	0.0459	0.0357
wR_2 (all data)	0.1023	0.0675	0.1200	0.1072

[a] The position of the hydrido hydrogen atom on cobalt atom was extracted from difference Fourier synthesis and refined.

Table 3

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for complex **1–4** U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U(eq)
Complex 1				
Co(1)	3253(1)	7500(1)	7500(1)	34(1)
P(1)	4458(1)	7749(1)	5655(1)	42(1)
P(2)	2863(1)	7249(1)	9347(1)	42(1)
P(3)	932(1)	7500(1)	7500(1)	65(1)
S(1)	2166(1)	9537(1)	7534(1)	43(1)
S(2)	4237(1)	5464(1)	7465(1)	43(1)
C(1)	3126(4)	10267(3)	7911(3)	40(1)
C(2)	4514(5)	9717(4)	8155(3)	53(1)
C(3)	5128(5)	10385(5)	8492(4)	68(1)
C(4)	4390(7)	11597(5)	8573(4)	78(2)
C(5)	3038(6)	12150(4)	8317(4)	71(1)
C(6)	2403(5)	11498(4)	7999(3)	54(1)
C(7)	6310(4)	4732(3)	7085(3)	41(1)
C(8)	6898(5)	3507(4)	7005(3)	51(1)
C(9)	8508(6)	2856(4)	6682(4)	70(1)
C(10)	9556(5)	3410(5)	6422(4)	76(2)
C(11)	9008(5)	4617(5)	6507(4)	69(1)
C(12)	7387(4)	5285(4)	6851(3)	53(1)
C(13)	3319(5)	8759(4)	4792(3)	57(1)
C(14)	5569(5)	6451(4)	4765(3)	60(1)
C(15)	5955(4)	8391(4)	5377(3)	53(1)
C(16)	4718(4)	6616(4)	9623(3)	54(1)
C(17)	1879(4)	6238(4)	10200(3)	57(1)
C(18)	1792(5)	8550(4)	10232(3)	61(1)
C(19)	−332(10)	8957(8)	6977(9)	88(3)
C(20)	1266(10)	6616(8)	6294(7)	71(3)
C(21)	−519(11)	7098(11)	8588(8)	109(4)
C(19′)	183(13)	7900(11)	6410(8)	107(4)
C(20′)	599(11)	6046(7)	8027(9)	87(3)
C(21′)	−826(8)	8368(8)	8709(7)	69(3)
Complex 2				
Co(1)	4743(1)	4082(1)	305(1)	30(1)
S(1)	5555(1)	5591(1)	1243(1)	35(1)
P(1)	6090(1)	2540(1)	549(1)	40(1)
P(2)	3027(1)	3448(1)	864(1)	40(1)
C(1)	7245(2)	5337(2)	1955(1)	38(1)
C(2)	8358(2)	5985(2)	1852(2)	52(1)
C(3)	9661(2)	5776(3)	2433(2)	70(1)
C(4)	9854(3)	4937(3)	3112(2)	74(1)
C(5)	8748(3)	4311(2)	3237(2)	72(1)
C(6)	7456(2)	4510(2)	2661(2)	56(1)
C(7)	7904(2)	2797(2)	596(2)	71(1)
C(8)	6269(3)	1586(2)	1572(2)	63(1)
C(9)	5656(3)	1479(2)	−406(2)	77(1)
C(10)	3396(2)	3338(2)	2146(2)	62(1)
C(11)	2196(3)	2038(2)	514(2)	77(1)
C(12)	1547(3)	4411(3)	663(2)	77(1)
Complex 3				
C(1)	3777(6)	851(3)	4337(7)	99(3)
C(2)	2980(9)	790(3)	2470(7)	127(4)
C(3)	1804(6)	698(3)	3751(6)	91(3)
C(4)	1000(7)	1449(3)	1630(7)	115(3)
C(5)	205(6)	1852(3)	3047(7)	103(3)
C(6)	983(7)	2427(3)	1830(7)	116(4)
C(7)	2908(6)	3072(3)	2981(6)	82(2)
C(8)	1632(6)	2932(3)	4203(6)	84(2)
C(9)	3631(6)	2814(3)	4786(6)	95(3)
C(11)	5295(6)	1792(4)	6124(7)	116(4)
C(12)	6086(5)	1641(3)	7982(5)	81(2)
C(15)	8755(9)	1815(5)	4819(9)	179(7)

Table 3 (*continued*)

	x	y	z	U(eq)
C(16)	8971(7)	594(3)	5646(6)	89(3)
C(17)	10132(5)	1297(3)	6700(7)	104(3)
C(18)	9242(6)	568(3)	7558(6)	92(3)
C(19)	6430(7)	171(3)	3588(5)	99(3)
C(20)	5843(6)	−606(3)	2390(7)	104(3)
C(21)	7756(7)	−542(4)	3305(7)	118(4)
C(22)	4873(6)	427(4)	1365(8)	134(4)
C(23)	6134(9)	1210(4)	1958(8)	148(5)
C(24)	5608(7)	963(4)	116(7)	123(4)
C(25)	8149(7)	1211(3)	544(6)	97(3)
C(26)	7465(6)	457(3)	−724(5)	89(3)
C(27)	9233(6)	365(4)	553(7)	106(3)
Co(1)	2609(1)	1868(1)	3569(1)	46(1)
Co(2)	7699(1)	1448(1)	6653(1)	43(1)
Co(3)	7297(1)	227(1)	1541(1)	42(1)
I(1)	4189(1)	1956(1)	2964(1)	107(1)
I(2)	2261(1)	1750(1)	5218(1)	79(1)
I(3)	6659(1)	662(1)	6432(1)	74(1)
I(4)	8679(1)	1844(1)	8160(1)	76(1)
I(5)	7455(1)	−593(1)	740(1)	85(1)
I(6)	8640(1)	624(1)	2806(1)	88(1)
P(1)	2765(2)	1071(1)	3511(2)	69(1)
P(2)	1250(1)	1892(1)	2538(2)	67(1)
P(3)	2668(1)	2661(1)	3847(1)	56(1)
P(4)	7745(2)	1840(1)	5366(1)	63(1)
P(5)	6402(1)	1835(1)	6922(1)	62(1)
P(6)	8984(1)	995(1)	6610(1)	57(1)
P(7)	7993(1)	566(1)	489(1)	60(1)
P(8)	6017(1)	691(1)	1235(2)	72(1)
P(9)	6810(1)	−169(1)	2683(1)	64(1)
C(10)	6486(7)	2483(3)	7115(7)	100(3)
C(13)	7331(8)	2434(3)	5169(8)	135(3)
C(14)	6971(8)	1563(4)	4389(8)	135(3)
Complex 4				
Co(1)	1868(1)	2030(1)	7537(1)	25(1)
P(2)	1041(1)	3652(1)	7163(1)	29(1)
P(1)	2727(1)	395(1)	7714(1)	30(1)
C(1)	2673(4)	1925(2)	4162(3)	29(1)
C(2)	4627(4)	2018(3)	4496(3)	31(1)
C(3)	5946(4)	2102(3)	3515(3)	34(1)
C(4)	5367(5)	2140(3)	2162(4)	38(1)
C(5)	3422(6)	2089(3)	1819(3)	40(1)
C(6)	2087(5)	1981(3)	2799(3)	35(1)
C(7)	4583(6)	−32(3)	6636(5)	43(1)
C(8)	3683(6)	21(3)	9373(4)	44(1)
C(9)	791(6)	−524(3)	7394(5)	43(1)
C(10)	1229(8)	4461(4)	8656(5)	51(1)
C(11)	2495(5)	4341(3)	6002(5)	40(1)
C(12)	−1374(5)	3883(3)	6524(4)	40(1)
C(13)	84(5)	1837(3)	8682(4)	37(1)
C(14)	4113(4)	2459(3)	8135(3)	31(1)
S(1)	892(1)	1714(1)	5323(1)	31(1)
O(1)	−924(4)	1710(3)	9557(4)	62(1)
O(2)	5517(4)	2761(2)	8649(3)	45(1)

(1.68 g, 4.4 mmol) in 30 mL of diethyl ether at −80 °C was combined with a solution of thiophenol (0.5 g, 4.5 mmol) in 20 mL of diethyl ether under vigorous stirring to give a red brown mixture which was kept stirring for 15 h at 20 °C. All volatile materials were removed in vacuo. The residue was extracted with 50 mL of pentane. Crystallisation at 4 °C afforded yellow brown crystals of **1** suitable for X-ray diffraction (0.28 g, 13%). M.p.: 80 – 80.4 °C,

Anal. Calc. for $C_{21}H_{38}CoP_3S_2$, (506.47 g/mol): C, 49.80, H, 7.56; Found: C, 50.21, H, 7.25%. IR(nujol, cm^{-1}): 1975 s (Co-H), 1573 s (C=C).^{1}H NMR (300 MHz, C_6D_6, 297 K): δ 1.13 (d, ^2J(PH) = 7.2 Hz, 9H, PCH_3), 1.22 (t, $|^2J$(PH) + ^4J(PH)| = 7.2 Hz, 18 H, PCH_3), 6.91(t, ^3J = 14.4 Hz, 2 H, CH), 7.12 (t, ^3J = 16.2 Hz, 4 H, CH), 8.20 (d, ^3J = 7.2 Hz, 4 H, CH). −9.22 (dt, ^2J (P$_{trans}$H) = 111.9 Hz, ^2J (P$_{cis}$H) = 69.6 Hz, CoH); ^{13}C NMR (75 MHz, C_6D_6, 297 K): δ 14.88 (d, ^1J(PC) = 21 Hz, PCH_3), 17.86 (t, $|$ ^1J(PC) + ^3J(PC) $|$ = 29.2 Hz, PCH_3), 120.2, 129.6, 146.7, 146.8. ^{31}P NMR (121 MHz, C_6D_6, 297 K): δ −6.86 (s, 1P), 1.72 (s, 2P).

4.1.2. Synthesis of [Co(PMe₃)₂(SPh)]₂ (2)

Method a (route a, Scheme 1): A sample of thiophenol (0.16 g, 1.40 mmol) in 20 mL of diethyl ether at −80 °C was combined with a solution of *n*-butyllithium (2.5 mol/L, 0.60 mL) of hexane. After 1 h a sample of [Co(PMe₃)₃Cl] (0.58 g, 1.8 mmol) added to the resulting mixture. The reaction solution was warmed up to the room temperature to give a red solution. All of the volatiles were removed in vacuo. The residue was extracted with 30 mL of pentane. Crystallization at −20 °C afforded dark red crystals of **2** (0.30 g, 67%). *Method b:* A sample of [Co(PMe₃)₄Me] (1.68 g, 4.4 mmol) in 30 mL of diethyl ether at −80 °C was combined with a solution of thiophenol (0.5 g, 4.5 mmol) in 20 mL of diethyl ether under vigorous stirring to give a red brown mixture which was kept stirring for 15 h at 20 °C. All volatile materials were removed in vacuo. The residue was extracted with 50 mL of pentane. After complex **1** had been collected at 4 °C crystallization of the mother liquor at −21 °C afforded dark red crystals of **2** suitable for X-ray diffraction (0.26 g, 20%). M.p.: >68 °C (dec.). Anal. Calc. for $C_{24}H_{46}Co_2P_4S_2$, (640.46 g/mol): C, 45.00; H, 7.24. Found: C, 44.85; H. 7.29%. IR(nujol, cm^{-1}): 1570s (C=C).

4.2. Reaction of 1 with iodomethane

A sample of complex **1** (0.36 g, 0.7 mmol) in 20 mL of diethyl ether at −80 °C was combined with a solution of CH₃I (0.2 g, 1.4 mmol) in 10 mL of diethyl ether under vigorous stirring to give a violet solution which was kept stirring for 15 h at 20 °C. All volatile materials were removed in vacuo. The residue was extracted with 30 mL of pentane. Crystallisation at −21 °C afforded violet crystals of **3** suitable for X-ray diffraction (0.25 g, 75%).

4.3. Reaction of 2 with carbon monoxide

A sample of **2** (0.80 g, 1.64 mmol) in 50 mL of diethyl ether at room temperature was stirred under 1 bar of CO for 36 h, and the red brown solution slowly turned yellow. Upon filtration and cooling to 4 °C complex **4** was obtained as yellow crystals (0.61 g, 62%). M.p.: >117 °C (dec.). Anal. Calc. for $C_{14}H_{23}CoO_2P_2S$, (376.25 g/mol): C, 44.69; H, 6.16. Found: C, 44.50; H. 6.01%. IR (nujol,

cm^{-1}): 1969, 1886 (CO), 1572 (C=C).^{1}H NMR (300 MHz, CDCl₃, 297 K) δ 1.51 (d, ^2J(PH) = 4.2 Hz, 18H, PCH_3), 6.82 (t, ^3J = 14.4 Hz, 1H, CH), 7.00 (t, ^3J = 15.0 Hz, 2H, CH), 7.35 (d, ^3J = 9.9 Hz, 2 H, CH); ^{31}P NMR (121 MHz, CDCl₃, 297 K): δ −26.46.

4.4. X-ray structure determination

The crystal structure data for **1**–**4** are summarized in Table 2. Table 3 shows the atomic coordinates of complex **1**–**4**. X-ray data were collected on a Bruker Smart APEX CCD area detector diffractometer (graphite-monochromated Mo Kα radiation, $\lambda = 0.71073$ Å). The structures were solved by direct methods and refined with full-matrix least-squares on all F^2 (SHELXL-97) with non-hydrogen atoms anisotropic.

Appendix A. Supplementary material

CCDC 631271, 631272, 631273 and 631274 contain the supplementary crystallographic data for **1**, **2**, **3** and **4**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.06.031.

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