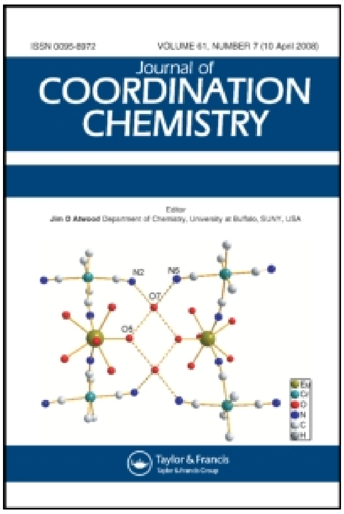

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Syntheses and Crystal Structures of Two Thiolato-Organophosphino Cobalt(II) Complexes, $(Et_4N)[Co(SC_6H_5)_3(PPh_3)]$ and $[Co(S\text{-}m\text{-}C_6H_4CH_3)_2(Ph_2PCH_2CH_2P(Ph)CH_2CH_2PPh_2)]$

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SYNTHESES AND CRYSTAL STRUCTURES OF TWO THIOLATO-ORGANOPHOSPHINO COBALT(II) COMPLEXES, $(Et_4N)[Co(SC_6H_5)_3(PPh_3)]$ AND $[Co(S\text{-}m\text{-}C_6H_4CH_3)_2(Ph_2PCH_2CH_2P(Ph)CH_2CH_2PPh_2)]$

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$(Et_4N)[Co(SC_6H_5)_3(PPh_3)]$ (1) and the neutral complex $[Co(S\text{-}m\text{-}C_6H_4CH_3)_2(Ph_2PCH_2CH_2P(Ph)\text{-}CH_2CH_2PPh_2)]$ (2) have been prepared by reaction of $CoCl_2$, NaSR (R = C_6H_5, $m\text{-}C_6H_4CH_3$) and an organophosphine PPh_3, dppep) in methanol. Red crystals of compound 1 are triclinic, space group $P\bar{1}$ with cell dimensions $a = 11.284(5)$, $b = 11.987(5)$, $c = 15.929(5)$ Å, $\alpha = 91.33(3)$, $\beta = 96.51(2)$, $\gamma = 105.42(4)°$, $Z = 2$, $Dc = 1.255$ g cm^{-3}, $R = 0.063$ for 1905 observed reflections. The $CoPS_3$ core possesses a distorted trigonal pyramidal geometry. Average distances (Co–S) are 2.262 Å and (Co–P) 2.366(2) Å. Black crystals of compound 2 are monoclinic, space group $P2_1/c$ with cell dimensions $a = 11.024(3)$, $b = 28.061(2)$, $c = 14.895(2)$ Å, $\beta = 104.59(1)°$, $Z = 4$, $Dc = 1.263$ g cm^{-3}, $R = 0.071$ for 2021 reflections. The CoP_3S_2 core of 2 forms a trigonal bipyramid with average (Co–S) distances of 2.247 Å and (Co–P) of 2.241 Å.

Keywords: Cobalt, phosphine, thiolate, complexes, crystal structure

INTRODUCTION

Transition metal thiolato-complexes have been widely investigated because of their chemical properties and their potential for serving as biological models.[1-2] Organophosphines have played an important role in the development of the stereochemistry of transition metal complexes. A number of studies on complexes of transition metals containing both thiolate and organophosphine ligands have been reported.[3-4] In order to examine the nature of their coordination with transition metals, we have initiated a systematic investigation of this type of complex.[5-6] Herein we report the syntheses and structural characterization of two thiolato-organophosphino cobalt(II) complexes, $(Et_4N)[Co(SC_6H_5)_3(PPh_3)]$ (1) and $[Co(S\text{-}m\text{-}C_6H_4CH_3)_2\text{-}dppep]$ (2), (dppep = bis (2-diphenylphosphinoethyl)phenylphosphine).

EXPERIMENTAL

All operations were carried out under a purified dinitrogen atmosphere using conventional Schlenk techniques. Solvents were dried over molecular sieves and

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degassed with dry nitrogen before use. Cobalt chloride, dppep, triphenylphosphine, thiophenol, and thiocresol were commercially available (Aldrich Chemical Co.). IR spectra were recorded on a Perkin-Elmer 577 spectrophotometer in KBr pellets, and ^1H NMR spectra on a Varian FT-80A spectrometer at room temperature with DMSO-d_6 as solvent and TMS as internal standard.

Preparation of $(Et_4N)[Co(SC_6H_5)_3(PPh_3)]$ *(1)*

A solution of $NaSC_6H_5$ (0.8 g, 6 mmol) in methanol (20 cm^3) was added to a stirred mixture of $CoCl_2$ (0.26 g, 2 mmol) PPh_3 (0.26 g, 2 mmol) and Et_4NBr (0.4 g, 2 mmol) in methanol (50 cm^3). The reaction solution was stirred for 12 hours at room temperature and filtered. The volume of filtrate was reduced under vacuum. Deep red crystals of **1** were obtained at 4°C after several days. Recrystallization can be effected from a mixture of toluene/hexane to yield crystals suitable for X-ray crystallographic analysis, with a yield of 72%.

Preparation of $[Co(S\text{-m-}C_6H_4CH_3)_2dppep]$ *(2)*

To a stirred solution of $CoCl_2$ (0.26 g, 2 mmol) in methanol (50 cm^3), dppep (1.06 g, 2 mmol) was added, followed by Na(S-*m*-$C_6H_4CH_3$) (0.58 g, 4 mmol) in methanol (20 cm^3) at room temperature. The reaction was completed overnight with stirring and the resulting mixture was concentrated and filtered. Black crystals suitable for X-ray analysis were obtained after allowing the filtrate to stand at 4°C for several days. The total yield of compound **2** was 61%.

TABLE I
Summary of crystal data and data collection parameters.

Compound	1	2
Formula	$C_{44}CoH_{50}NPS_3$	$C_{48}CoH_{47}P_3S_2$
F.W.	778.99	839.86
Space group	$P\bar{1}$	$P2_1/c$
a, Å	11.284(5)	11.024(3)
b, Å	11.987(5)	28.061(2)
c, Å	15.929(5)	14.895(2)
α, deg	91.33(3)	
β, deg	96.51(2)	104.59(1)
γ, deg	105.42(4)	
V, Å^3	2060.56	4459.04
Z	2	4
D_c, g cm^{-3}	1.255	1.263
Radiation	MoKα	MoKα
μ, cm^{-1}	6.285	6.030
F(000)	822	1756
Crystal dimensions, mm	0.50 × 0.40 × 0.40	0.20 × 0.20 × 0.40
Scan width, deg	0.60 + 0.350 tan θ	1.00 + 0.350 tan θ
2θ range, deg	2–44.0	2–50.0
No. of reflections refined	1905	2021
Largest shift/esd	0.20	0.88
R	0.063	0.071
R_w	0.072	0.096

TABLE II

Atomic coordinates and thermal parameters for **1**.

Atom	x/a	y/b	z/c	B(Å^2)
Co	0.0821(2)	0.2913(2)	0.2449(1)	3.67(5)
S1	0.0545(3)	0.1534(3)	0.1399(2)	4.4(1)
S2	0.1640(3)	0.4768(3)	0.2124(3)	4.7(1)
S3	0.1056(3)	0.2401(3)	0.3802(2)	4.5(1)
P	−0.1249(3)	0.3015(3)	0.2414(2)	3.5(1)
C11	0.188(1)	0.163(1)	0.0928(8)	4.8(3)
C12	0.301(1)	0.261(1)	0.1083(9)	5.1(4)
C13	0.397(1)	0.259(1)	0.063(1)	6.1(5)
C14	0.392(1)	0.176(1)	0.0024(9)	6.4(5)
C15	0.284(2)	0.086(2)	0.012(1)	7.1(5)
C16	0.187(1)	0.085(1)	0.0334(9)	5.6(4)
C21	0.324(1)	0.526(1)	0.2501(9)	4.7(4)
C22	0.371(1)	0.500(1)	0.328(1)	5.9(5)
C23	0.493(2)	0.543(2)	0.359(1)	8.7(6)
C24	0.574(1)	0.613(2)	0.314(1)	8.4(6)
C25	0.532(1)	0.636(1)	0.235(1)	6.5(5)
C26	0.408(1)	0.596(1)	0.2016(9)	5.7(5)
C31	0.243(1)	0.200(1)	0.3971(8)	3.5(3)
C32	0.315(1)	0.188(1)	0.3355(8)	4.3(4)
C33	0.422(1)	0.151(1)	0.354(1)	5.5(4)
C34	0.457(1)	0.127(1)	0.434(1)	6.2(5)
C35	0.387(1)	0.142(2)	0.4966(9)	7.0(5)
C36	0.283(1)	0.179(1)	0.479(1)	6.2(5)
C41	−0.242(1)	0.165(1)	0.2299(8)	3.7(3)*
C42	−0.351(1)	0.147(1)	0.1745(9)	4.9(4)*
C43	−0.442(1)	0.037(1)	0.1695(9)	5.2(4)*
C44	−0.424(1)	−0.048(1)	0.219(1)	5.9(4)*
C45	−0.316(1)	−0.032(1)	0.274(1)	6.0(4)*
C46	−0.226(1)	0.075(1)	0.2781(9)	5.0(4)*
C51	−0.175(1)	0.385(1)	0.1570(8)	3.6(3)*
C52	−0.257(1)	0.449(1)	0.1640(9)	4.7(3)*
C53	−0.291(1)	0.510(1)	0.0962(9)	5.3(4)*
C54	−0.241(1)	0.506(1)	0.024(1)	6.1(4)*
C55	−0.156(1)	0.447(1)	0.016(1)	5.6(4)*
C56	−0.122(1)	0.383(1)	0.0815(9)	4.9(4)*
C61	−0.156(1)	0.371(1)	0.3328(8)	3.6(3)*
C62	−0.076(1)	0.476(1)	0.3643(9)	4.4(3)*
C63	−0.101(1)	0.537(1)	0.432(1)	5.5(4)*
C64	−0.203(1)	0.497(1)	0.470(1)	5.8(4)*
C65	−0.281(1)	0.393(1)	0.443(1)	6.1(4)*
C66	−0.261(1)	0.330(1)	0.3728(9)	5.5(4)*
N	0.102(1)	0.830(1)	0.2651(7)	4.6(3)*
C711	0.176(1)	0.889(1)	0.200(1)	5.9(4)*
C712	0.205(2)	0.808(2)	0.136(1)	8.7(5)*
C721	0.077(2)	0.921(1)	0.321(1)	7.1(5)*
C722	−0.003(2)	0.885(2)	0.388(1)	9.2(6)*
C731	−0.021(1)	0.749(1)	0.225(1)	6.5(4)*
C732	−0.097(2)	0.810(2)	0.167(1)	10.4(6)*
C741	0.165(2)	0.754(2)	0.319(1)	7.5(5)*
C742	0.291(2)	0.814(2)	0.364(1)	9.0(5)*

Starred atoms were refined isotropically.

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3) \times [a^2 \times \beta(1,1) + b^2 \times \beta(2,2) + c^2 \times \beta(3,3) + ab(\cos\gamma) \times \beta(1,2) + ac(\cos\beta) \times \beta(1,3) + bc(\cos\alpha) \times \beta(2,3)]$.

Intensity data collection and structure analysis

Single crystals were coated with epoxy resin and mounted on glass fibres. Diffraction data for **1** and **2** were collected at room temperature on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). After data reduction (including correction for fluctuation of monitored reflections, LP factors and empirical absorption), the remaining unique reflections with $I > 3\sigma(I)$ were used for subsequent structure solution and refinement. Calculations were performed on a VAX 11/785 computer with the SDP program package. Crystal data and data collection parameters are summarized in Table I. The structures were solved by direct and Fourier methods. All non-hydrogen atoms were refined by full-matrix least-squares techniques.

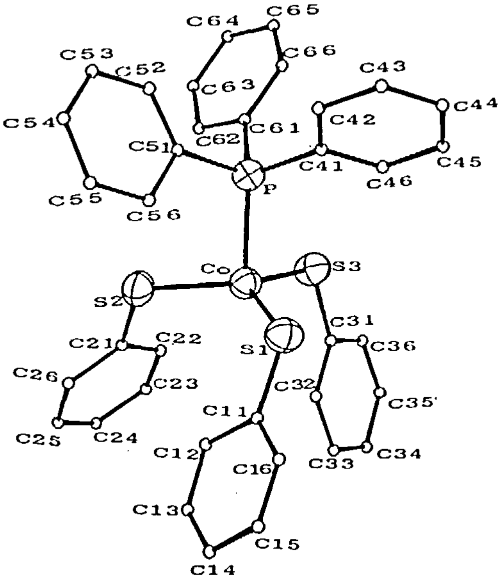

FIGURE 1 Molecular structure and numbering scheme for the $[Co(SC_6H_5)_3(PPh_3)]^-$ anion.

RESULTS AND DISCUSSION

Positional and thermal parameters for all non-hydrogen atoms in **1** and **2** are summarized in Tables II and III, respectively. Selected distances and bond angles are listed in Tables IV and V, respectively. Perspective views of the molecular structures of **1** and **2** are shown in Figures 1 and 2, respectively. The cobalt atom in **1** is coordinated by one phosphorus atom of the triphenylphosphine and three sulfur atoms of the thiolate ligands. The CoS_3P core is much different from the CoS_4 core in $[Co(SC_6H_5)_4]^{2-}$ (**3**) which has a distorted tetrahedral structure.[7] The CoS_3P core possesses pseudo-C_{3v} symmetry as may be seen in Figure 1, and can be considered in terms of trigonal pyramidal geometry with three sulfur atoms in the basal plane and one phosphorus atom occupying the apical position. The Co atom lies above the trigonal plane with three nearly equivalent Co–S bonds (2.260–2.266 Å). As the triphenylphosphine ligand replaces one of the thiophenolate ligands in **3**, the remaining thiophenolate ligands are compressed along the pseudo-3-fold axis. All phenyl groups of the three thiolate ligands are in same orientation owing to steric crowding of the triphenylphosphine ligand. This compression is indicated by the fact that the S–Co–S angles range from 116.5(1)° to 120.1(2)°, much larger than the tetrahedral value of 109.28°, while the average S–Co–P angles range from 96.81(9)–98.98(9)°. The influence of stereochemistry due to ligand substitution of one of the four thiolates was also found in $[Co(SC_{10}H_{13})_3(CH_3CN)]^-$, in which, unlike compound **1**, the rings of the three thiolate ligands have different orientation.[8] The average Co–S distance in **1** (2.262 Å) appears to be significantly shorter than in $[Co(SC_6H_5)_4]^{2-}$ (2.328 Å), and a little shorter than in $[Co(SC_{10}H_{13})_3(CH_3CN)]^-$ (2.28(1) Å). The Co–P bond length is 2.366(2) Å, longer than the corresponding distances (2.180–2.242 Å) found in other Co–PPh_3–S compounds.[9]

TABLE III
Atomic coordinates and thermal parameters for **2**.

Atom	*x/a*	*y/b*	*z/c*	*B*(Å²)
Co	0.1258(3)	0.1728(1)	0.6864(2)	3.21(6)
S1	0.1763(7)	0.0960(2)	0.7047(4)	4.9(2)
S2	0.1181(6)	0.1907(2)	0.8334(4)	4.8(2)
P1	0.2915(6)	0.2227(2)	0.6984(4)	3.7(1)
P2	0.1345(5)	0.1619(2)	0.5408(4)	3.4(1)
P3	−0.0452(6)	0.2150(2)	0.6215(4)	3.5(1)
C1	0.329(2)	0.2262(9)	0.584(1)	4.6(6)
C2	0.293(2)	0.1794(8)	0.531(1)	4.2(6)
C3	0.031(2)	0.2029(8)	0.461(1)	3.9(6)
C4	−0.019(2)	0.2423(8)	0.515(2)	4.3(6)
C11	0.236(2)	0.0702(8)	0.815(1)	4.4(6)
C12	0.198(3)	0.024(1)	0.825(2)	7.5(8)
C13	0.250(3)	0.002(1)	0.905(2)	8(1)
C14	0.338(3)	0.021(1)	0.978(2)	7.5(9)
C15	0.378(3)	0.0653(9)	0.965(2)	6.4(8)
C16	0.331(2)	0.0901(9)	0.882(2)	5.3(7)
C17	0.481(4)	0.090(1)	1.043(3)	14(2)
C21	0.061(2)	0.1445(8)	0.891(2)	4.3(6)
C22	0.111(3)	0.138(1)	0.987(1)	6.8(8)
C23	0.069(3)	0.103(1)	1.033(2)	8.3(9)
C24	−0.026(3)	0.074(1)	0.978(2)	9.6(9)
C25	−0.072(3)	0.081(1)	0.881(2)	8.9(9)
C26	−0.030(2)	0.1164(9)	0.843(2)	6.1(7)
C27	−0.181(3)	0.037(2)	0.829(2)	13(1)
C31	0.295(2)	0.2846(8)	0.730(1)	3.8(6)
C32	0.191(2)	0.3053(8)	0.755(1)	4.6(6)
C33	0.190(2)	0.352(1)	0.777(2)	5.8(7)
C34	0.295(3)	0.3814(9)	0.777(2)	5.6(7)
C35	0.398(2)	0.362(1)	0.749(2)	6.4(8)
C36	0.397(2)	0.3148(8)	0.726(2)	5.7(7)
C41	0.440(2)	0.2008(8)	0.777(1)	4.2(6)
C42	0.458(2)	0.2100(9)	0.867(2)	5.5(7)

TABLE III (*continued*)

Atom	x/a	y/b	z/c	B(Å^2)
C43	0.555(2)	0.194(1)	0.929(2)	6.1(7)
C44	0.646(2)	0.168(1)	0.898(2)	7.4(8)
C45	0.620(3)	0.157(1)	0.807(2)	8.0(9)
C46	0.524(2)	0.175(1)	0.745(2)	5.9(7)
C51	0.104(2)	0.1058(8)	0.480(1)	3.7(6)
C52	−0.015(2)	0.089(1)	0.442(2)	5.8(7)
C53	−0.021(3)	0.040(1)	0.397(2)	9.0(9)
C54	0.073(3)	0.015(1)	0.395(2)	9(1)
C55	0.185(3)	0.029(1)	0.434(2)	7.7(9)
C56	0.204(2)	0.073(1)	0.478(2)	5.9(7)
C61	−0.118(2)	0.2624(8)	0.673(1)	4.2(6)
C62	−0.116(2)	0.3095(8)	0.646(2)	5.8(7)
C63	−0.177(3)	0.3432(9)	0.682(2)	6.9(8)
C64	−0.241(2)	0.333(1)	0.745(2)	7.6(8)
C65	−0.243(3)	0.285(1)	0.774(2)	6.7(8)
C66	−0.180(2)	0.2491(9)	0.737(2)	5.4(7)
C71	−0.183(2)	0.1779(7)	0.577(1)	3.1(5)
C72	−0.293(2)	0.1978(8)	0.522(1)	4.9(6)
C73	−0.400(2)	0.171(1)	0.486(2)	6.6(8)
C74	−0.397(2)	0.124(1)	0.499(2)	6.8(8)
C75	−0.292(2)	0.1013(9)	0.554(2)	6.4(8)
C76	−0.183(2)	0.1305(9)	0.590(2)	5.2(6)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3) \times [a^2 \times \beta(1,1) + b^2 \times \beta(2,2) + c^2 \times \beta(3,3) + ab(\cos\gamma) \times \beta(1,2) + ac(\cos\beta) \times \beta(1,3) + bc(\cos\alpha) \times \beta(2,3)]$.

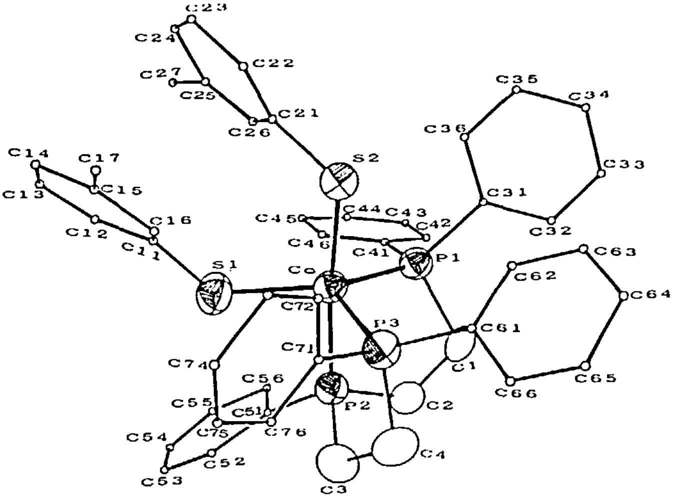

FIGURE 2 A perspective view of [Co(S-m-$C_6H_4CH_3$)$_2$dppep].

TABLE IV
Selected bond distances (Å) and angles (deg) for **1**.

Atoms	Distance	Atoms	Distance
Co–S1	2.260(3)	S2–C21	1.776(9)
Co–S2	2.266(3)	S3–C31	1.743(9)
Co–S3	2.260(2)	P–C41	1.800(8)
Co–P	2.366(2)	P–C51	1.821(8)
S1–C11	1.74(1)	P–C61	1.770(8)
Atoms	**Angle**	**Atoms**	**Angle**
S1–Co–S2	116.5(1)	Co–S1–C11	112.5(4)
S1–Co–S3	118.3(2)	Co–S2–C21	111.7(4)
S1–Co–P	98.98(9)	Co–S3–C31	108.0(4)
S2–Co–S3	120.1(2)	Co–P–C41	116.1(3)
S2–Co–P	96.81(9)	Co–P–C51	114.6(3)
S3–Co–P	96.88(9)	Co–P–C61	114.4(3)

TABLE V
Selected bond distances (Å) and angles (deg) for **2**.

Atoms	Distance	Atoms	Distance
Co–S1	2.225(7)	P1–C31	1.80(2)
Co–S2	2.269(7)	P1–C41	1.86(3)
Co–P1	2.273(7)	P2–C2	1.85(2)
Co–P2	2.216(7)	P2–C3	1.83(3)
Co–P3	2.232(6)	P2–C51	1.81(2)
S1–C11	1.77(2)	P3–C4	1.85(2)
S2–C21	1.76(2)	P3–C61	1.82(2)
P1–C1	1.86(2)	P3–C71	1.82(2)
Atoms	**Angle**	**Atoms**	**Angle**
S1–Co–S2	99.5(3)	Co–S1–C11	122.2(8)
S1–Co–P1	114.6(3)	Co–S2–C21	114.4(8)
S1–Co–P2	85.2(3)	Co–P1–C1	109.0(7)
S1–Co–P3	136.6(3)	Co–P1–C31	125.5(8)
S2–Co–P1	90.8(3)	Co–P1–C41	114.1(8)
S2–Co–P2	175.1(3)	Co–P2–C2	108.3(8)
S2–Co–P3	93.9(3)	Co–P2–C3	111.8(8)
P1–Co–P2	86.0(2)	Co–P2–C51	124.4(8)
P1–Co–P3	106.3(2)	Co–P3–C4	107.1(7)
P2–Co–P3	83.6(2)	Co–P3–C61	128.3(7)
		Co–P3–C71	113.1(7)

The cobalt atom in the neutral complex [Co(S-*m*-$C_6H_4CH_3)_2$dppep] is five-coordinated by two sulfur atoms from S-*m*-tolyl ligands and three phosphorus atoms from the dppep ligand. The structure is adequately represented by a distorted trigonal bipyramid with a CoP_3S_2 core. One sulfur (S1) and two phosphorus atoms

(P1, P3) are at the three corners of a triangular array, of which the cobalt atom lies in the centre; the remaining sulfur (S2) and phosphorus (P2) atoms are at the apical positions. The tridentate dppep ligand is chelatd to the cobalt atom with a mean Co–P distance of 2.241 Å, slightly shorter than that of 2.27(2) Å found in $[Co(dppe)_2Cl]^+$ for five-coordinated cobalt(II).[10] The average Co–S distance (2.241 Å) in **2**, is similar to that in **1** (2.262 Å) and is shorter than is found in $[Co(SC_6H_5)_4]^{2-}$ (2.32 Å). The observed variation in Co–S distances in both compounds is due to the organophosphine ligand affecting the sulfur atoms through the cobalt atom. The P–C and C–C distances appear normal for dppep complexes with average values of 1.83 Å and 1.39 Å, respectively.

The ^1H NMR spectrum of **1** (DMSO-d_6) showed a multiplet signal due to PPh_3 at 7.37 ppm, similar to that of the free ligand. The proton NMR spectrum also shows one broad peak at low field (17.1 ppm), is assigned to SC_6H_5, as compared with two broad peaks at 16.6 ppm and −22.7 ppm for the corresponding ligand in $(Et_4N)_2$-$[Co(SC_6H_5)_4]$,[11] thus confirming the paramagnetic character of **1**. Sharp triplets and quartets (3.31 and 1.22 ppm) due to Et_4N^+ in **1** are also observed. Infrared spectra (KBr pellet) of **1** exhibited characteristic bands for the SC_6H_5 group at 3000, 1575, 750 and 695 cm^{-1}, as well as bands for PPh_3 at 3050, 1435, 1100, 720 and 520 cm^{-1}. Two bands at 475 and 360 cm^{-1} were present in the Co–S stretching region.

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SUPPLEMENTARY MATERIAL

Complete lists of bond distances, bond angles, thermal parameters, and observed and calculated structure factors for **1** and **2** have been deposited with the editor and are available upon request.

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11. $(Et_4N)_2[Co(SC_6H_5)_4]$ was prepared in our lab; crystal data: a = 12.018, b = 14.845, c = 22.566 Å, β = 93.191°, V = 4020.16; ^{1}H NMR chemical shifts (DMSO-d_6): 16.62 (m, 8H, SC_6H_5), −22.79 (m, 4H, SC_6H_5), 3.58 (s, 16H, Et), 1.43 (s, 24H, Et).