Electronic Supplementary Information for Dalton Transactions

Supporting Information for:

Four- and Five-membered Cobaltacycles by Regioselective Cyclometalation of Benzylsulfide Derivatives via Co(V) intermediates

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Experimental Section

General Considerations. All air-sensitive and volatile materials were handled using standard vacuum techniques[1] and kept under argon. Air-sensitive samples were provided in capillaries sealed under vacuum and were analyzed by H. Kolbe Microanalytical Laboratory, Mülheim/Ruhr, Germany. The melting and decomposition points were measured on a Büchi 510 Melting point apparatus and are uncorrected. Air-sensitives substances were sealed in capillaries under 1 bar of Argon. Chemicals (Merck/Schuchardt) were used as purchased.

Literature methods were applied for the preparation of PMe_3[2] and $[CoMe(PMe_3)_4]$[3]. IR spectra were obtained from as Nujol mulls between KBr plates using a Bruker FRA 106 spectrophotometer and were recorded in the range 4000 – 400 cm^{-1}. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded with a Bruker DRX 500 spectrometer, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ resonances were obtained with broad-band proton decoupling. Magnetic suscepitbility data were obtained by the Faraday method using a Cahn D 200 torsion balance (Bruker) at 1.5 Tesla. X-ray diffraction data were collected on a Bruker Platform (Bruker-AXS SMART APEX). Structures were solved by Direct and Patterson methods using SHELXTL program library.[4]

Supporting Information for X-ray data are Available: Tables of crystallographic data collection and refinement parameters, position and thermal parameters, and bond distances and angles for complex **1** and **2** (PDF, CIF). This material have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-619513 for (**1**) and CCDC-619514 for (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ ccdc.cam.ac.uk).

Preparation of *mer*-Methyl-(phenyl-2-thiolato-*C*,*S*)tris(trimethylphosphine)cobalt(III) (1): Benzylphenylsulfide (301 mg, 1.50 mmol) in 50 mL of diethylether was combined at - 70 °C with $[CoMe(PMe_3)_4]$ (570 mg, 1.50 mmol) in 50 mL of diethylether. After warm up and further stirring for 30 min at 20 °C all volatiles were removed from the mixture in vacuo, and the solid residue was extracted with 80 mL of pentane. From the solution 25 mg, orange thin crystal plates were obtained at 4 °C which proved suitable for X-ray diffraction. Upon cooling to - 27 °C a second fraction of **1** was collected and combined with the first. Yield 105 mg

(17%); m.p. 106–108 °C. ^{1}H-NMR for **1** (500 MHz, [D$_8$]THF, 300 K) : δ = - 0.80 (dt, $^{3}J_{P,H}$ = 9.3 Hz, $^{3}J_{P,H}$ = 8.5 Hz 3H, Co–CH$_3$); 1.16 (t', $|^{2}J_{P,H} + {}^{4}J_{P,H}|$ = 6.3 Hz, 18H, PCH$_3$); 1.34 (d, $^{2}J_{P,H}$ = 6.6 Hz, 9H, PCH$_3$); 6.03 (d, $^{3}J_{H,H}$ = 6.9 Hz, 1H, Ar–H); 6.54 (t, $^{3}J_{H,H}$ = 6.6 Hz, 1H, Ar–H); 6.65 (t, $^{3}J_{H,H}$ = 6.0 Hz, 1H, Ar–H); 6.89 (s(br), 1H, Ar–H). - ^{13}C NMR (125 MHz, [D$_8$]THF, 300 K, ppm): δ = - 8.5 (m, Co-CH$_3$); 15.2 (dt', $|^{1}J_{P,C} + {}^{3}J_{P,C}|$ = 13.5 Hz, $^{3}J_{P,C}$ = 3.1 Hz, PCH$_3$); 17.2 (td', $|^{1}J_{P,C} + {}^{3}J_{P,C}|$ = 18.7 Hz, $^{3}J_{P,C}$ = 2.9 Hz, PCH$_3$); 118.8 (s, CH); 122.4 (s, CH); 123.9 (d, $^{3}J_{P,C}$ = 8.3 Hz, CH); 136.1 (s, CH); 152.7 (s, C-S); 178.7 (m, Co-C).- ^{31}P NMR (202 MHz, [D$_8$]THF, 300 K, ppm): δ = 17.8 (m(br), 2P, PCH$_3$); 27.93 (m(br), 1P, PCH$_3$). - *Anal* calc. for C$_{16}$H$_{34}$CoP$_3$S, (410.3): calcd. C 46.83, H 8.35, P 22.64; found C 47.06, H 7.67, P 22.80.

GC-MS Detection: From the reaction of **1** with stoichiometric amounts benzylphenylsulfide, the volatiles were removed in vacuo after 3 h and collected in a 100 mL flask. The collected volatiles were investigated by using a sample of 1.0 µL. GCMS (EI) spectra were recorded using a Hewlett-Packard HP 5890 series II instrument with a DB-5 capillary column (30 × 0.25 mm × 0.25 µm, Agilent) and a Finnigan MAT-95 mass detector (Thermo) set to scan from 40 to 450 m/z at a rate of 1.5 scans/s. The oven temperature program was as follows: initial temperature 40 °C, ramp at 20 °C/min to 250 °C, hold for 10 min. GC-MS peak assignments: toluene at retention time 5.7 min, molecular peak (EI) at m/z 92; at retention time 19.1 min, molecular peak (EI) at m/z 180 (unknown byproduct).

Preparation of *mer*-Methyl-(naphthyl-8-thiolato-*C*,*S*)tris(trimethylphosphine)cobalt(III) (2): Benzylnaphthylsulfide (456 mg, 1.82 mmol) in 50 mL of THF was combined at - 70 °C with [CoMe(PMe$_3$)$_4$] (690 mg, 1.82 mmol) in 50 mL of THF. After warm up and further

stirring for 16 h at 20 °C all volatiles were removed from the mixture in vacuo, and the solid residue was extracted with 80 mL of diethylether. From the solution orange rhombic crystals were obtained at -27 °C which proved suitable for X-ray diffraction. Yield 621 mg (74%); m.p. 141–143 °C. ^{1}H-NMR for **2** (500 MHz, [D$_8$]THF, 300 K): δ = - 0.38 (dt, $^{3}J_{P,H}$ = 8.8 Hz, $^{3}J_{P,H}$ = 7.6 Hz, 3H, Co–CH$_3$); 0.80 (t', $|^{2}J_{P,H} + {}^{4}J_{P,H}|$ = 7.1 Hz, 18H, PCH$_3$); 1.45 (d, $^{2}J_{P,H}$ = 6.7 Hz, 9H, PCH$_3$); 6.84 (t, $^{3}J_{H,H}$ = 7.5 Hz, 1H, Ar–H); 6.98 (tt, $^{3}J_{H,H}$ = 8.0 Hz, $^{3}J_{H,H}$ = 7.8 Hz, 2H, Ar–H); 7.12 (td, $^{3}J_{H,H}$ = 7.7 Hz, $^{4}J_{H,H}$ = 1.5 Hz, 1H, Ar–H); 7.16 (dd, $^{3}J_{H,H}$ = 7.2 Hz, $^{4}J_{H,H}$ = 0.7 Hz, 1H, Ar–H); 7.20 (dt, $^{3}J_{H,H}$ = 7.2 Hz, $^{4}J_{P,H}$ = 3.5 Hz, 1H, Ar–H).- ^{13}C NMR (125 MHz, [D$_8$]THF, 300 K, ppm): δ = - 9.1 (m, Co-CH$_3$); 16.9 (dt', $|^{1}J_{P,C} + {}^{3}J_{P,C}|$ = 13.7 Hz, $^{3}J_{P,C}$ = 2.5 Hz, PCH$_3$); 19.3 (d, $^{1}J_{P,C}$ = 18.7 Hz, PCH$_3$); 120.9 (s, CH); 123.2 (t, $^{5}J_{P,C}$ = 3.8 Hz, CH); 123.6 (s, CH); 126.0 (s, CH); 126.1 (d, $^{3}J_{P,C}$ = 10.0 Hz, CH); 132.9 (t, $^{4}J_{P,C}$ = 5.0 Hz, CH); 136.4 (s, C); 153.8 (s, C); 159.3 (d, $^{3}J_{P,C}$ = 8.8 Hz, C); 172.7 (m, Co-C).- ^{31}P NMR (202 MHz, [D$_8$]THF, 300 K, ppm): δ : - 4.5 (m(br), 1P, PCH$_3$); 4.3 (m(br), 2P, PCH$_3$). - ^{31}P NMR (202 MHz, [D$_8$]THF, 203 K, ppm): δ = 9.1 (t, $^{2}J_{P,P}$ = 37.6, 1P, PCH$_3$), 15.5 (d, $^{2}J_{P,P}$ = 37.6 Hz, 2P, PCH$_3$). - *Anal* calc. for C$_{20}$H$_{36}$CoP$_3$S, (460.4): calcd. C 52.17, H 7.88, P 20.18; found C 52.10, H 8.28, P 20.15.

References

1 W. Strohmeier, *Chem. Ber.* **1955**, *88*, 1218–1233.

2 W. Wolfsberger, H. Schmidbaur, *Syn. React. Inorg. Metal-Org. Chem.* **1974**, *4*, 149.

3 Klein, H.-F.; Karsch, H. H. *Chem. Ber.* **1975**, *108*, 944–955.

4 G. M. Sheldrick. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Crystallographic Section

Table 1. Crystal data and structure refinement for **1**.

Identification code	**1**	
Empirical formula	C16 H34 Co P3 S	
Formula weight	410.33	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pcab	
Unit cell dimensions	a = 12.3187(11) Å	α= 90.000(8)°.
	b = 12.7608(12) Å	β= 90.000(8)°.
	c = 26.990(3) Å	γ = 90.000(7)°.
Volume	4242.7(7) $Å^3$	
Z	8	
Density (calculated)	1.285 Mg/m^3	
Absorption coefficient	1.127 mm^{-1}	
F(000)	1744	
Crystal size	0.32 x 0.25 x 0.10 mm^3	
Theta range for data collection	4.25 to 26.37°.	
Index ranges	-14<=h<=15, -15<=k<=15, -33<=l<=33	
Reflections collected	37218	
Independent reflections	4321 [R(int) = 0.0743]	
Completeness to theta = 26.37°	99.6 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4321 / 0 / 190	
Goodness-of-fit on F^2	1.111	
Final R indices [I>2sigma(I)]	R1 = 0.0466, wR2 = 0.1231	
R indices (all data)	R1 = 0.0665, wR2 = 0.1344	
Largest diff. peak and hole	0.879 and -0.302 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **1**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	1888(3)	259(3)	9005(1)	46(1)
C(2)	1252(3)	-255(2)	8648(1)	44(1)
C(3)	136(3)	-320(3)	8680(1)	55(1)
C(4)	-380(3)	155(3)	9088(2)	66(1)
C(5)	228(3)	683(3)	9430(2)	70(1)
C(6)	1356(3)	732(3)	9397(1)	60(1)
C(7)	4266(3)	736(3)	9296(1)	59(1)
C(8)	4677(3)	-1898(3)	9468(2)	74(1)
C(9)	2643(4)	-2516(3)	9098(2)	111(2)
C(10)	2818(5)	-1092(5)	9890(2)	126(2)
C(11)	4843(3)	-1932(3)	8161(2)	68(1)
C(12)	4659(4)	-104(3)	7623(1)	71(1)
C(13)	6138(3)	-192(3)	8421(2)	81(1)
C(14)	2417(3)	1783(3)	7891(1)	70(1)
C(15)	2657(3)	2610(3)	8845(2)	72(1)
C(16)	4492(3)	2301(3)	8277(2)	67(1)
P(1)	3383(1)	-1339(1)	9277(1)	56(1)
P(2)	3243(1)	1609(1)	8443(1)	44(1)
P(3)	4743(1)	-528(1)	8272(1)	46(1)
S(1)	2135(1)	-774(1)	8195(1)	48(1)
Co(1)	3377(1)	12(1)	8758(1)	35(1)

Table 3. Bond lengths [Å] and angles [°] for **1**.

C(1)-C(6)	1.382(5)
C(1)-C(2)	1.405(5)
C(1)-Co(1)	1.977(3)
C(2)-C(3)	1.380(5)
C(2)-S(1)	1.765(3)
C(3)-C(4)	1.409(6)
C(3)-H(3)	0.9300
C(4)-C(5)	1.367(6)
C(4)-H(4)	0.9300
C(5)-C(6)	1.393(5)
C(5)-H(5)	0.9300
C(6)-H(6)	0.9300
C(7)-Co(1)	2.040(3)
C(7)-H(7A)	0.9600
C(7)-H(7B)	0.9600
C(7)-H(7C)	0.9600
C(8)-P(1)	1.822(4)
C(8)-H(8A)	0.9600
C(8)-H(8B)	0.9600
C(8)-H(8C)	0.9600
C(9)-P(1)	1.822(4)
C(9)-H(9A)	0.9600
C(9)-H(9B)	0.9600
C(9)-H(9C)	0.9600
C(10)-P(1)	1.823(4)
C(10)-H(10A)	0.9600
C(10)-H(10B)	0.9600
C(10)-H(10C)	0.9600
C(11)-P(3)	1.822(4)
C(11)-H(11A)	0.9600
C(11)-H(11B)	0.9600
C(11)-H(11C)	0.9600
C(12)-P(3)	1.835(4)
C(12)-H(12A)	0.9600
C(12)-H(12B)	0.9600
C(12)-H(12C)	0.9600
C(13)-P(3)	1.816(4)

C(13)-H(13A)	0.9600
C(13)-H(13B)	0.9600
C(13)-H(13C)	0.9600
C(14)-P(2)	1.818(4)
C(14)-H(14A)	0.9600
C(14)-H(14B)	0.9600
C(14)-H(14C)	0.9600
C(15)-P(2)	1.824(4)
C(15)-H(15A)	0.9600
C(15)-H(15B)	0.9600
C(15)-H(15C)	0.9600
C(16)-P(2)	1.829(4)
C(16)-H(16A)	0.9600
C(16)-H(16B)	0.9600
C(16)-H(16C)	0.9600
P(1)-Co(1)	2.2205(10)
P(2)-Co(1)	2.2147(9)
P(3)-Co(1)	2.2437(9)
S(1)-Co(1)	2.3781(9)

C(6)-C(1)-C(2)	117.7(3)
C(6)-C(1)-Co(1)	140.1(3)
C(2)-C(1)-Co(1)	102.2(2)
C(3)-C(2)-C(1)	122.8(3)
C(3)-C(2)-S(1)	129.4(3)
C(1)-C(2)-S(1)	107.8(3)
C(2)-C(3)-C(4)	118.1(4)
C(2)-C(3)-H(3)	121.0
C(4)-C(3)-H(3)	121.0
C(5)-C(4)-C(3)	119.6(4)
C(5)-C(4)-H(4)	120.2
C(3)-C(4)-H(4)	120.2
C(4)-C(5)-C(6)	121.7(4)
C(4)-C(5)-H(5)	119.2
C(6)-C(5)-H(5)	119.2
C(1)-C(6)-C(5)	120.1(4)
C(1)-C(6)-H(6)	119.9
C(5)-C(6)-H(6)	119.9
Co(1)-C(7)-H(7A)	109.5

Co(1)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
Co(1)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
P(1)-C(8)-H(8A)	109.5
P(1)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
P(1)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
P(1)-C(9)-H(9A)	109.5
P(1)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
P(1)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
P(1)-C(10)-H(10A)	109.5
P(1)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
P(1)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
P(3)-C(11)-H(11A)	109.5
P(3)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
P(3)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
P(3)-C(12)-H(12A)	109.5
P(3)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
P(3)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
P(3)-C(13)-H(13A)	109.5
P(3)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
P(3)-C(13)-H(13C)	109.5

H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
P(2)-C(14)-H(14A)	109.5
P(2)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
P(2)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
P(2)-C(15)-H(15A)	109.5
P(2)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
P(2)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
P(2)-C(16)-H(16A)	109.5
P(2)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
P(2)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(8)-P(1)-C(9)	100.9(2)
C(8)-P(1)-C(10)	98.3(2)
C(9)-P(1)-C(10)	101.1(3)
C(8)-P(1)-Co(1)	119.06(14)
C(9)-P(1)-Co(1)	118.13(16)
C(10)-P(1)-Co(1)	115.90(17)
C(14)-P(2)-C(15)	100.43(19)
C(14)-P(2)-C(16)	102.20(19)
C(15)-P(2)-C(16)	98.09(19)
C(14)-P(2)-Co(1)	117.95(13)
C(15)-P(2)-Co(1)	116.39(14)
C(16)-P(2)-Co(1)	118.40(13)
C(13)-P(3)-C(11)	101.80(19)
C(13)-P(3)-C(12)	101.3(2)
C(11)-P(3)-C(12)	97.87(18)
C(13)-P(3)-Co(1)	120.47(16)
C(11)-P(3)-Co(1)	116.70(13)
C(12)-P(3)-Co(1)	115.20(13)
C(2)-S(1)-Co(1)	78.23(12)

C(1)-Co(1)-C(7)	100.73(15)
C(1)-Co(1)-P(2)	85.08(10)
C(7)-Co(1)-P(2)	84.08(10)
C(1)-Co(1)-P(1)	85.08(10)
C(7)-Co(1)-P(1)	84.34(11)
P(2)-Co(1)-P(1)	163.15(4)
C(1)-Co(1)-P(3)	160.46(10)
C(7)-Co(1)-P(3)	98.80(11)
P(2)-Co(1)-P(3)	96.49(4)
P(1)-Co(1)-P(3)	97.35(4)
C(1)-Co(1)-S(1)	71.69(10)
C(7)-Co(1)-S(1)	172.42(11)
P(2)-Co(1)-S(1)	95.42(3)
P(1)-Co(1)-S(1)	94.44(4)
P(3)-Co(1)-S(1)	88.78(3)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for **1**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	41(2)	50(2)	46(2)	2(2)	5(2)	3(1)
C(2)	47(2)	42(2)	43(2)	10(1)	3(2)	2(1)
C(3)	44(2)	50(2)	72(2)	16(2)	1(2)	-1(2)
C(4)	45(2)	59(2)	95(3)	20(2)	18(2)	7(2)
C(5)	68(3)	69(2)	72(3)	4(2)	29(2)	13(2)
C(6)	60(2)	66(2)	55(2)	-9(2)	10(2)	2(2)
C(7)	67(2)	61(2)	48(2)	-8(2)	-12(2)	0(2)
C(8)	73(3)	75(3)	73(3)	21(2)	-15(2)	12(2)
C(9)	85(3)	81(3)	166(5)	64(3)	-33(3)	-38(3)
C(10)	133(5)	171(6)	74(3)	66(3)	46(3)	68(4)
C(11)	75(3)	52(2)	78(3)	-13(2)	7(2)	7(2)
C(12)	87(3)	77(3)	48(2)	-3(2)	26(2)	10(2)
C(13)	43(2)	85(3)	114(4)	-16(3)	8(2)	-4(2)
C(14)	76(3)	68(2)	67(3)	16(2)	-18(2)	2(2)
C(15)	69(3)	47(2)	100(3)	-8(2)	6(2)	10(2)
C(16)	64(2)	53(2)	83(3)	10(2)	9(2)	-13(2)
P(1)	48(1)	63(1)	57(1)	25(1)	0(1)	0(1)
P(2)	43(1)	38(1)	51(1)	3(1)	-1(1)	-1(1)
P(3)	40(1)	46(1)	52(1)	-3(1)	6(1)	1(1)
S(1)	44(1)	52(1)	49(1)	-7(1)	-4(1)	-5(1)
Co(1)	34(1)	38(1)	32(1)	-1(1)	0(1)	-1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **1**.

	x	y	z	U(eq)
H(3)	-265	-669	8438	66
H(4)	-1129	111	9124	79
H(5)	-119	1018	9692	84
H(6)	1752	1085	9638	73
H(7A)	4922	349	9354	70
H(7B)	3850	766	9597	70
H(7C)	4443	1435	9192	70
H(8A)	5104	-1370	9630	88
H(8B)	5060	-2150	9182	88
H(8C)	4551	-2468	9693	88
H(9A)	2939	-2787	8794	133
H(9B)	1891	-2348	9050	133
H(9C)	2711	-3034	9354	133
H(10A)	2077	-868	9858	151
H(10B)	3232	-555	10052	151
H(10C)	2846	-1724	10083	151
H(11A)	4191	-2175	8003	82
H(11B)	4938	-2290	8470	82
H(11C)	5453	-2072	7949	82
H(12A)	4647	648	7609	85
H(12B)	4008	-377	7477	85
H(12C)	5278	-360	7445	85
H(13A)	6320	-473	8741	97
H(13B)	6216	556	8427	97
H(13C)	6614	-483	8175	97
H(14A)	1684	1573	7960	84
H(14B)	2704	1360	7627	84
H(14C)	2427	2506	7794	84
H(15A)	3091	2676	9139	86
H(15B)	1932	2411	8934	86
H(15C)	2642	3268	8673	86
H(16A)	4880	1904	8032	80
H(16B)	4937	2383	8566	80

H(16C)	4314	2978	8145	80

Perspective view of **1** with thermal ellipsoids at the 30 % probability level.

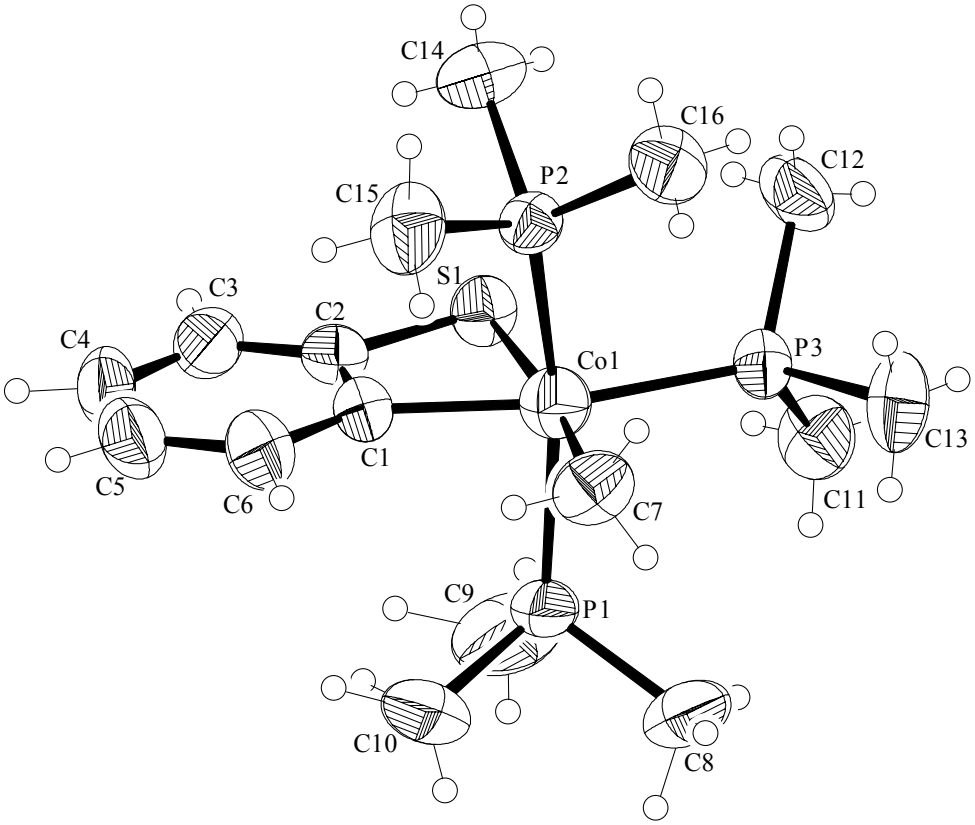

Figure 1. Molecular structure of **1**.

Table 1. Crystal data and structure refinement for **2**.

Identification code	**2**:	
Empirical formula	C20 H36 Co P3 S	
Formula weight	460.39	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	*P*21/c	
Unit cell dimensions	a = 9.2185(14) Å	α= 90°.
	b = 9.4200(8) Å	β= 90.653(12)°.
	c = 26.563(4) Å	γ = 90°.
Volume	2306.6(5) $Å^3$	
Z	4	
Density (calculated)	1.326 Mg/m^3	
Absorption coefficient	1.045 mm^{-1}	
F(000)	976	
Crystal size	0.27 x 0.25 x 0.08 mm^3	
Theta range for data collection	1.53 to 26.82°.	
Index ranges	-11<=h<=11, -11<=k<=11, -33<=l<=33	
Reflections collected	22306	
Independent reflections	4882 [R(int) = 0.1325]	
Completeness to theta = 26.82°	98.7 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4882 / 0 / 370	
Goodness-of-fit on F^2	0.938	
Final R indices [I>2sigma(I)]	R1 = 0.0490, wR2 = 0.0998	
R indices (all data)	R1 = 0.0801, wR2 = 0.1086	
Largest diff. peak and hole	0.573 and -0.963 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **2**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	4547(5)	7961(4)	4581(1)	28(1)
C(2)	2485(4)	6120(4)	4017(1)	21(1)
C(3)	2307(4)	5505(4)	4489(1)	29(1)
C(4)	1308(5)	4402(4)	4573(1)	33(1)
C(5)	460(4)	3864(4)	4195(1)	29(1)
C(6)	593(4)	4420(4)	3699(1)	25(1)
C(7)	-272(4)	3901(4)	3291(1)	30(1)
C(8)	-179(4)	4525(4)	2822(1)	33(1)
C(9)	776(4)	5654(4)	2738(1)	26(1)
C(10)	1685(4)	6161(4)	3123(1)	22(1)
C(11)	1592(4)	5558(4)	3615(1)	21(1)
C(12)	5764(6)	5273(5)	3168(2)	42(1)
C(13)	5386(6)	4482(5)	4161(2)	45(1)
C(14)	7367(5)	6619(6)	3963(2)	42(1)
C(15)	6435(5)	10499(5)	3942(2)	39(1)
C(16)	6310(5)	9087(6)	2999(2)	41(1)
C(17)	4184(6)	11020(5)	3237(2)	41(1)
C(18)	722(5)	9799(5)	3622(2)	36(1)
C(19)	2488(5)	10746(5)	4451(2)	37(1)
C(20)	685(5)	8392(5)	4541(2)	35(1)
Co(1)	3799(1)	7730(1)	3855(1)	19(1)
P(1)	5528(1)	6096(1)	3785(1)	26(1)
P(2)	5156(1)	9534(1)	3534(1)	28(1)
P(3)	1990(1)	9126(1)	4099(1)	25(1)
S(1)	2951(1)	7514(1)	3038(1)	24(1)

Table 3. Bond lengths [Å] and angles [°] for **2**.

C(1)-Co(1)	2.051(3)
C(2)-C(3)	1.393(5)
C(2)-C(11)	1.441(4)
C(2)-Co(1)	1.991(4)
C(3)-C(4)	1.408(6)
C(4)-C(5)	1.363(5)
C(5)-C(6)	1.426(5)
C(6)-C(7)	1.424(5)
C(6)-C(11)	1.432(5)
C(7)-C(8)	1.381(5)
C(8)-C(9)	1.401(5)
C(9)-C(10)	1.399(5)
C(10)-C(11)	1.429(4)
C(10)-S(1)	1.745(4)
C(12)-P(1)	1.827(4)
C(13)-P(1)	1.825(5)
C(14)-P(1)	1.823(5)
C(15)-P(2)	1.833(4)
C(16)-P(2)	1.834(4)
C(17)-P(2)	1.836(5)
C(18)-P(3)	1.829(4)
C(19)-P(3)	1.846(4)
C(20)-P(3)	1.826(4)
Co(1)-P(3)	2.2252(11)
Co(1)-P(1)	2.2254(11)
Co(1)-P(2)	2.2812(11)
Co(1)-S(1)	2.3086(9)
C(3)-C(2)-C(11)	116.2(3)

C(3)-C(2)-Co(1)	126.1(3)
C(11)-C(2)-Co(1)	117.7(2)
C(2)-C(3)-C(4)	122.3(3)
C(5)-C(4)-C(3)	121.9(3)
C(4)-C(5)-C(6)	119.4(4)
C(7)-C(6)-C(5)	121.6(3)
C(7)-C(6)-C(11)	119.6(3)
C(5)-C(6)-C(11)	118.7(3)
C(8)-C(7)-C(6)	120.0(4)
C(7)-C(8)-C(9)	120.9(3)
C(10)-C(9)-C(8)	120.9(3)
C(9)-C(10)-C(11)	119.5(3)
C(9)-C(10)-S(1)	123.4(3)
C(11)-C(10)-S(1)	117.1(2)
C(10)-C(11)-C(6)	119.0(3)
C(10)-C(11)-C(2)	119.4(3)
C(6)-C(11)-C(2)	121.6(3)
C(2)-Co(1)-C(1)	94.39(15)
C(2)-Co(1)-P(3)	85.84(10)
C(1)-Co(1)-P(3)	84.77(12)
C(2)-Co(1)-P(1)	85.93(10)
C(1)-Co(1)-P(1)	85.38(12)
P(3)-Co(1)-P(1)	166.64(4)
C(2)-Co(1)-P(2)	170.28(9)
C(1)-Co(1)-P(2)	95.33(13)
P(3)-Co(1)-P(2)	94.86(4)
P(1)-Co(1)-P(2)	95.02(4)
C(2)-Co(1)-S(1)	86.29(9)
C(1)-Co(1)-S(1)	178.97(12)
P(3)-Co(1)-S(1)	94.51(4)
P(1)-Co(1)-S(1)	95.44(4)

P(2)-Co(1)-S(1)	83.99(4)
C(14)-P(1)-C(13)	98.9(2)
C(14)-P(1)-C(12)	103.2(2)
C(13)-P(1)-C(12)	98.5(2)
C(14)-P(1)-Co(1)	117.10(17)
C(13)-P(1)-Co(1)	118.30(17)
C(12)-P(1)-Co(1)	117.51(16)
C(15)-P(2)-C(16)	101.4(2)
C(15)-P(2)-C(17)	100.6(2)
C(16)-P(2)-C(17)	97.2(2)
C(15)-P(2)-Co(1)	119.96(15)
C(16)-P(2)-Co(1)	116.37(16)
C(17)-P(2)-Co(1)	117.51(17)
C(20)-P(3)-C(18)	99.0(2)
C(20)-P(3)-C(19)	98.5(2)
C(18)-P(3)-C(19)	102.6(2)
C(20)-P(3)-Co(1)	117.70(16)
C(18)-P(3)-Co(1)	118.58(15)
C(19)-P(3)-Co(1)	116.95(16)
C(10)-S(1)-Co(1)	99.34(11)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3)for **2**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	34(2)	28(2)	22(2)	-3(1)	-4(2)	6(2)
C(2)	26(2)	18(2)	21(2)	-1(1)	-2(1)	4(2)
C(3)	38(2)	26(2)	24(2)	2(1)	-1(2)	-4(2)
C(4)	48(2)	28(2)	24(2)	6(1)	1(2)	3(2)
C(5)	35(2)	21(2)	32(2)	5(1)	4(2)	-3(2)
C(6)	29(2)	19(2)	27(2)	-2(1)	2(1)	5(2)
C(7)	29(2)	22(2)	38(2)	-3(2)	-1(2)	-5(2)
C(8)	35(2)	36(2)	29(2)	-9(2)	-7(2)	-3(2)
C(9)	29(2)	28(2)	22(2)	-3(1)	-3(1)	0(2)
C(10)	24(2)	21(2)	19(1)	-4(1)	1(1)	2(2)
C(11)	26(2)	19(2)	17(1)	-1(1)	0(1)	2(2)
C(12)	51(3)	45(3)	30(2)	-10(2)	-3(2)	16(2)
C(13)	61(3)	38(3)	36(2)	3(2)	-6(2)	19(2)
C(14)	41(3)	45(3)	40(2)	-9(2)	-8(2)	11(2)
C(15)	38(3)	39(3)	41(2)	2(2)	-3(2)	-10(2)
C(16)	40(3)	50(3)	32(2)	6(2)	9(2)	-9(2)
C(17)	48(3)	35(2)	38(2)	12(2)	-1(2)	-7(2)
C(18)	36(2)	38(3)	33(2)	-1(2)	-4(2)	4(2)
C(19)	43(3)	33(2)	36(2)	-6(2)	0(2)	7(2)
C(20)	34(2)	41(3)	30(2)	-4(2)	8(2)	6(2)
Co(1)	24(1)	20(1)	14(1)	0(1)	-1(1)	1(1)
P(1)	31(1)	28(1)	20(1)	-3(1)	-3(1)	8(1)
P(2)	29(1)	30(1)	25(1)	3(1)	0(1)	-6(1)
P(3)	27(1)	26(1)	21(1)	-3(1)	0(1)	3(1)
S(1)	29(1)	27(1)	16(1)	2(1)	-2(1)	-1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **2**.

	x	y	z	U(eq)
H(8)	5210(60)	8790(60)	4600(20)	77(17)
H(10)	3700(50)	8010(50)	4791(17)	42(12)
H(13)	5110(50)	7190(50)	4721(17)	52(14)
H(11)	2880(40)	5860(40)	4761(14)	26(10)
H(28)	1160(50)	3980(50)	4893(17)	53(13)
H(1)	-250(40)	3140(40)	4234(13)	26(10)
H(4)	-970(40)	3100(50)	3363(15)	38(11)
H(9)	-840(40)	4130(50)	2563(16)	49(13)
H(18)	890(40)	6140(40)	2428(16)	41(11)
H(15)	4850(40)	4860(40)	3066(14)	30(11)
H(34)	6210(50)	5980(60)	2920(20)	74(17)
H(35)	6680(50)	4590(50)	3191(17)	58(14)
H(22)	6410(50)	3970(50)	4140(15)	46(12)
H(24)	4250(50)	3940(50)	4061(16)	50(13)
H(31)	5300(60)	4670(60)	4490(20)	86(19)
H(7)	8090(60)	5790(60)	3973(18)	69(16)
H(20)	7620(60)	7370(60)	3760(20)	63(16)
H(30)	7320(50)	7050(60)	4250(20)	60(15)
H(6)	5940(50)	11040(50)	4167(18)	55(14)
H(12)	7240(60)	9870(60)	4099(19)	69(16)
H(26)	7060(50)	11100(50)	3727(17)	49(13)
H(23)	6680(50)	9930(50)	2848(17)	50(13)
H(32)	7170(50)	8580(50)	3094(16)	43(13)
H(36)	5750(50)	8570(50)	2737(18)	56(14)
H(16)	3440(50)	10670(50)	2991(16)	44(12)

H(21)	3590(40)	11570(50)	3467(16)	39(12)
H(33)	4820(50)	11650(50)	3116(17)	47(13)
H(3)	290(40)	8990(40)	3478(14)	28(10)
H(5)	-50(50)	10390(50)	3783(16)	47(13)
H(14)	1210(40)	10360(50)	3346(16)	39(11)
H(17)	3000(60)	10440(60)	4720(20)	86(19)
H(19)	3100(40)	11320(50)	4262(16)	40(12)
H(29)	1450(60)	11260(60)	4562(19)	75(16)
H(2)	-20(50)	9060(50)	4602(15)	43(12)
H(25)	1310(50)	8100(60)	4870(20)	74(16)
H(27)	170(50)	7540(50)	4426(18)	57(15)

Table 6. Torsion angles [°] for **2**.

C(11)-C(2)-C(3)-C(4)	-0.3(5)
Co(1)-C(2)-C(3)-C(4)	177.5(3)
C(2)-C(3)-C(4)-C(5)	0.4(6)
C(3)-C(4)-C(5)-C(6)	0.6(6)
C(4)-C(5)-C(6)-C(7)	-179.7(4)
C(4)-C(5)-C(6)-C(11)	-1.6(5)
C(5)-C(6)-C(7)-C(8)	175.9(4)
C(11)-C(6)-C(7)-C(8)	-2.1(5)
C(6)-C(7)-C(8)-C(9)	1.1(6)
C(7)-C(8)-C(9)-C(10)	1.4(6)
C(8)-C(9)-C(10)-C(11)	-2.7(5)
C(8)-C(9)-C(10)-S(1)	177.4(3)
C(9)-C(10)-C(11)-C(6)	1.6(5)
S(1)-C(10)-C(11)-C(6)	-178.5(2)
C(9)-C(10)-C(11)-C(2)	-177.4(3)
S(1)-C(10)-C(11)-C(2)	2.5(4)
C(7)-C(6)-C(11)-C(10)	0.8(5)
C(5)-C(6)-C(11)-C(10)	-177.3(3)
C(7)-C(6)-C(11)-C(2)	179.8(3)
C(5)-C(6)-C(11)-C(2)	1.7(5)
C(3)-C(2)-C(11)-C(10)	178.3(3)
Co(1)-C(2)-C(11)-C(10)	0.3(4)
C(3)-C(2)-C(11)-C(6)	-0.7(5)
Co(1)-C(2)-C(11)-C(6)	-178.7(3)
C(3)-C(2)-Co(1)-C(1)	-0.6(3)
C(11)-C(2)-Co(1)-C(1)	177.2(3)
C(3)-C(2)-Co(1)-P(3)	-85.0(3)
C(11)-C(2)-Co(1)-P(3)	92.8(3)
C(3)-C(2)-Co(1)-P(1)	84.4(3)

C(11)-C(2)-Co(1)-P(1)	-97.8(3)
C(3)-C(2)-Co(1)-P(2)	-179.5(4)
C(11)-C(2)-Co(1)-P(2)	-1.8(8)
C(3)-C(2)-Co(1)-S(1)	-179.8(3)
C(11)-C(2)-Co(1)-S(1)	-2.1(2)
C(2)-Co(1)-P(1)-C(14)	-147.5(2)
C(1)-Co(1)-P(1)-C(14)	-52.7(2)
P(3)-Co(1)-P(1)-C(14)	-95.4(3)
P(2)-Co(1)-P(1)-C(14)	42.24(19)
S(1)-Co(1)-P(1)-C(14)	126.66(19)
C(2)-Co(1)-P(1)-C(13)	-29.2(2)
C(1)-Co(1)-P(1)-C(13)	65.6(2)
P(3)-Co(1)-P(1)-C(13)	22.9(3)
P(2)-Co(1)-P(1)-C(13)	160.51(18)
S(1)-Co(1)-P(1)-C(13)	-115.07(18)
C(2)-Co(1)-P(1)-C(12)	88.8(2)
C(1)-Co(1)-P(1)-C(12)	-176.4(2)
P(3)-Co(1)-P(1)-C(12)	141.0(3)
P(2)-Co(1)-P(1)-C(12)	-81.5(2)
S(1)-Co(1)-P(1)-C(12)	3.0(2)
C(2)-Co(1)-P(2)-C(15)	-178.1(6)
C(1)-Co(1)-P(2)-C(15)	2.9(2)
P(3)-Co(1)-P(2)-C(15)	88.1(2)
P(1)-Co(1)-P(2)-C(15)	-82.9(2)
S(1)-Co(1)-P(2)-C(15)	-177.9(2)
C(2)-Co(1)-P(2)-C(16)	-55.4(6)
C(1)-Co(1)-P(2)-C(16)	125.7(2)
P(3)-Co(1)-P(2)-C(16)	-149.15(18)
P(1)-Co(1)-P(2)-C(16)	39.85(19)
S(1)-Co(1)-P(2)-C(16)	-55.11(18)
C(2)-Co(1)-P(2)-C(17)	59.2(6)

C(1)-Co(1)-P(2)-C(17)	-119.7(2)
P(3)-Co(1)-P(2)-C(17)	-34.55(18)
P(1)-Co(1)-P(2)-C(17)	154.45(18)
S(1)-Co(1)-P(2)-C(17)	59.49(18)
C(2)-Co(1)-P(3)-C(20)	25.05(18)
C(1)-Co(1)-P(3)-C(20)	-69.8(2)
P(1)-Co(1)-P(3)-C(20)	-27.1(3)
P(2)-Co(1)-P(3)-C(20)	-164.68(16)
S(1)-Co(1)-P(3)-C(20)	110.99(16)
C(2)-Co(1)-P(3)-C(18)	-94.1(2)
C(1)-Co(1)-P(3)-C(18)	171.1(2)
P(1)-Co(1)-P(3)-C(18)	-146.2(2)
P(2)-Co(1)-P(3)-C(18)	76.17(18)
S(1)-Co(1)-P(3)-C(18)	-8.17(18)
C(2)-Co(1)-P(3)-C(19)	142.12(19)
C(1)-Co(1)-P(3)-C(19)	47.3(2)
P(1)-Co(1)-P(3)-C(19)	90.0(2)
P(2)-Co(1)-P(3)-C(19)	-47.60(17)
S(1)-Co(1)-P(3)-C(19)	-131.94(17)
C(9)-C(10)-S(1)-Co(1)	176.5(3)
C(11)-C(10)-S(1)-Co(1)	-3.5(3)
C(2)-Co(1)-S(1)-C(10)	2.72(15)
C(1)-Co(1)-S(1)-C(10)	-129(7)
P(3)-Co(1)-S(1)-C(10)	-82.80(12)
P(1)-Co(1)-S(1)-C(10)	88.27(12)
P(2)-Co(1)-S(1)-C(10)	-177.23(12)

Symmetry transformations used to generate equivalent atoms:

Perspective view of **2** with thermal ellipsoids at the 30 % probability level.

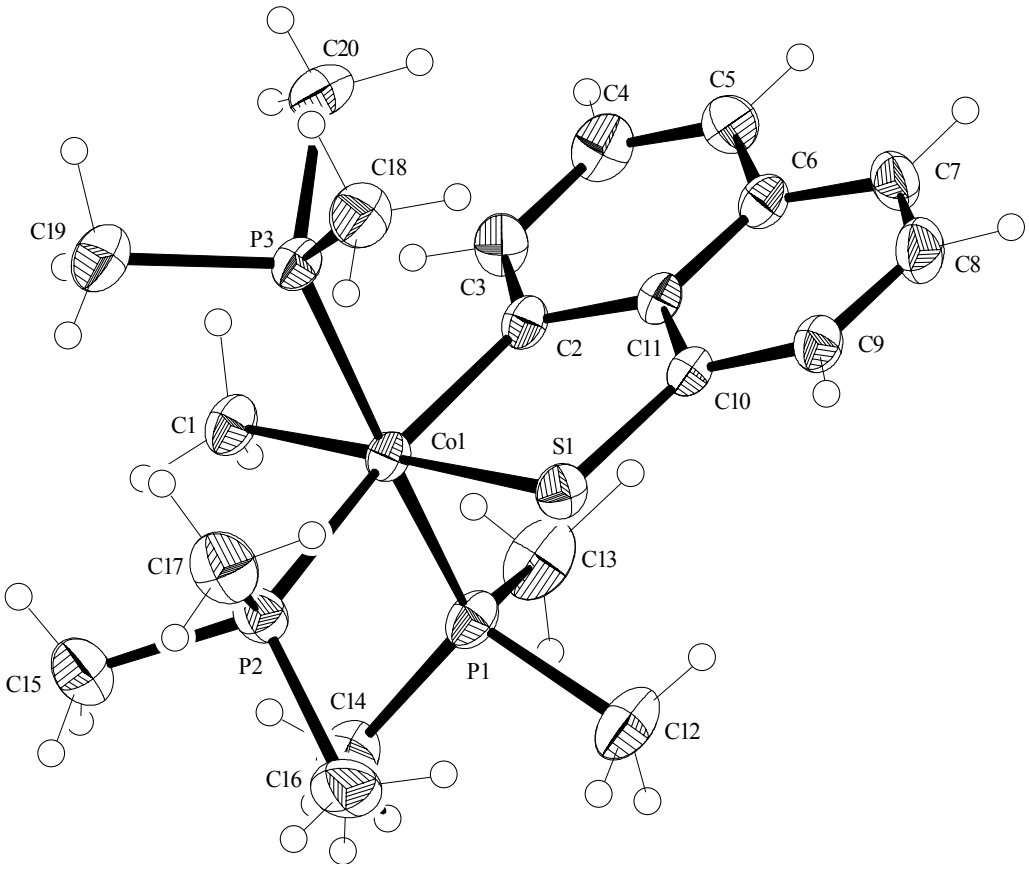

Figure 2. Molecular structure of **2**.