Stereochemistry of Mixed Thiolate and Ditertiary Phosphine Cobalt(II) Complexes. Crystal Structures of $[Co\{Ph_2P(CH_2)_3PPh_2\}(SPh)_2]$ and $[Co\{Ph_2PCH_2CH_2P(Ph)CH_2CH_2PPh_2\}(SPh)_2]$‡

Guowei Wei, Maochun Hong, Zhiying Huang and Hanqin Liu *†
Fuzhou Laboratory of Structural Chemistry and Fujian Institute of Research on the Structure of Matter, Fuzhou, Fujian 350002, Chinese Academy of Sciences, China

The complexes [Co(dppp)(SPh)$_2$] [dppp = 1,3-bis(diphenylphosphino)propane] and [Co(bdpp)(SPh)$_2$] [bdpp = bis(2-diphenylphosphinoethyl)phenylphosphine] were prepared in good yields by treating Co(dppp)Cl$_2$ with NaSPh and elemental selenium in dimethylformamide and by treating $CoCl_2{\cdot}6H_2O$ and bdpp in acetonitrile with NaSPh, respectively. The complex [Co(dppp)(SPh)$_2$] crystallizes in the triclinic space group $P\bar{1}$, with $a = 9.665(2)$, $b = 10.075(1)$, $c = 18.288(2)$ Å, $\alpha = 102.41(1)$, $\beta = 93.89(1)$, $\gamma = 92.40(1)°$ and $Z = 2$, whereas the complex [Co(bdpp)(SPh)$_2$] is monoclinic, space group *Cc*, with $a = 16.374(2)$, $b = 26.033(3)$, $c = 10.873(5)$ Å, $\beta = 117.49(2)°$ and $Z = 4$.

Tertiary phosphine ligands have played an important role in modern co-ordination chemistry.[1] Transition-metal complexes of di- or poly-phosphines show facile electron-transfer properties and their molecular structures vary according to the possible combinations of metal atoms and ligands. Their applications in homogeneous or heterogeneous catalysis have stimulated recent extensive study in this field.[2] Brill and co-workers[3] synthesized and characterized a series of bis(tertiary phosphine) cobalt compounds and metal-thiolato complexes are known as ubiquitous biological electron-transfer mediators.[4,5] Yet complexes blending both diphosphine and thiolato ligands have received relatively little attention and only a few reports have been made.[6]

In an attempt to understand the synergetic effect between atoms or groups within a molecule, we have been exploring the co-ordination chemistry and reactivity of metal complexes with both thiolato and ditertiary phosphine ligands,[7,8] compounds [Co$_2$(μ-dppm)(μ-SPh)$_2$(SPh)$_2$] **1** [dppm = bis(diphenylphosphino)methane] and [Co$_2$(dppe)(μ-SPh)$_3$(SPh)] **2** [dppe = 1,2-bis(diphenylphosphino)ethane]. We now report the syntheses and stereochemistry of two monocobalt complexes, [Co(dppp)(SPh)$_2$] **3** [dppp = 1,3-bis(diphenylphosphino)propane] and [Co(bdpp)(SPh)$_2$] **4** [bdpp = bis(2-diphenylphosphinoethyl)phenylphosphine], which also contain both thiolato and ditertiary phosphine ligands.

Experimental

All operations were carried out under a dinitrogen atmosphere. The compound Co(dppp)Cl$_2$ was prepared according to the literature method.[9] The reagents dppp and bdpp were purchased from Aldrich, NaSPh from Merck, and the solvents and $CoCl_2{\cdot}6H_2O$ from the Shanghai Factory of Chemical Reagents. The solvents were dried, distilled and degassed prior to use. Elemental analyses were performed by the Analytical Chemistry Group of this Institute. Magnetic susceptibilities (χ_g) were measured using a powdered sample at room temperature on a home-made Gouy–Faraday magnetic balance using the Faraday method.[4] Effective magnetic moments (μ_{eff}) were calculated using the diamagnetic molar correction (χ_{diam}) of the ligands: $\mu_{eff}^2 = 3kT(M\,\chi_g - \chi_{diam})/N\beta^2$.

Preparations.—[Co(dppp)(SPh)$_2$] **3**.—A mixture of NaSPh (0.26 g, 2 mmol) and elemental selenium (0.118 g, 1.5 mmol) in dimethylformamide (30 cm^3) was stirred for 40 min to produce a crimson solution. Addition of Co(dppp)Cl$_2$ (0.955 g, 1 mmol) to the solution gave a crimson-black mixture. Partial removal of the solvent by low-pressure evaporation at 45 °C formed a sticky liquid to which MeCN (25 cm^3) was added and the precipitate removed by filtration. The filtrate was kept at 0 °C for several weeks and the black crystals thus formed were washed with ethanol and diethyl ether, and dried in a vacuum, yield 0.448 g (65%) (Found: C, 66.90; H, 5.15; Co, 8.40; P, 9.10; S, 9.25. $C_{39}H_{36}CoP_2S_2$ requires C, 67.90; H, 5.25; Co, 8.55; P, 9.00; S, 9.30%). Magnetic moment at room temperature 4.28 μ_B.

[Co(bdpp)(SPh)$_2$] **4**. A mixture of $CoCl_2{\cdot}6H_2O$ (0.237 g, 1 mmol) and bdpp (0.535 g, 1 mmol) in MeCN (30 cm^3) was stirred for 1 h at room temperature. The solution immediately turned light green upon addition of NaSPh (0.264 g, 2 mmol) and then turned deep crimson. The precipitate was removed by filtration and the filtrate kept at 0 °C for several weeks to yield black crystals (0.438 g, 54%) (Found: C, 67.85; H, 5.30; Co, 7.10; P, 11.55; S, 7.80. $C_{46}H_{43}CoP_3S_2$ requires C, 68.05; H, 5.35; Co, 7.25; P, 11.45; S, 7.90%). Magnetic moment at room temperature 2.15 μ_B.

Crystal Structure Determinations.—A single crystal of

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† *Address for correspondence:* P.O. Box 143, Fuzhou, Fujian 350002, China.

‡ [1,3-bis(diphenylphosphino)propane-κ^2*P,P'*]bis(phenylthio-κ*S*)-cobalt(II) and [bis(2-diphenylphosphinoethyl)phenylphosphine-κ^3*P,P',P''*]bis(phenylthio-κ*S*)cobalt(II).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, xviii–xxii.

complex **3** or **4** suitable for X-ray diffraction was mounted on a glass fibre and data were collected at ambient temperature on an Enraf-Nonius CAD4 diffractometer using graphite-monochromatized Mo-Kα radiation (λ = 0.710 73 Å). The crystallographic and data collection and refinement parameters are summarized in Table 1. The cell parameters were obtained from a least-squares refinement using 25 high-angle reflections. All intensity data were corrected for standard decay, since the three standard reflections monitored periodically during data collection showed small fluctuations in intensity. The data were corrected for Lorentz and polarization effects. Absorption corrections were based on empirical psi-scans for crystals of complex **3** and on DIFABS [10] for complex **4**.

Calculations were performed on a VAX 11/785 computer with the SDP program package.[11] The structures were solved using direct methods and subsequently by Fourier difference maps. Anisotropic thermal refinements were applied to all non-hydrogen atoms. In the last stage of refinement, contributions were included for hydrogen atoms with fixed 'idealized' positions of C–H 0.95 Å and a group of isotropic thermal parameters varied according to the average thermal parameters of the carbon atoms in the corresponding benzene ring. The atomic coordinates for compounds **3** and **4** are listed in Tables 2 and 3, respectively, and their interatomic distances and bond angles are in Table 4.

Table 1 Crystallographic data

	3	**4**
(*a*) Crystal data		
Formula	$C_{39}H_{36}CoP_2S_2$	$C_{46}H_{43}CoP_3S_2$
M	689.73	811.84
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	*Cc* (no. 9)
a/Å	9.665(2)	16.374(2)
b/Å	10.075(1)	26.033(3)
c/Å	18.288(2)	10.873(5)
α/°	102.41(1)	
β/°	93.89(1)	117.49(2)
γ/°	92.40(1)	
U/Å³	1732.30(86)	4111.50(273)
Z	2	4
D_c/g cm^{-3}	1.322	1.311
F(000)	718	1692
μ(Mo-Kα)/cm^{-1}	7.26	6.6
(*b*) Data collection at 23 °C		
Crystal dimensions/mm	0.12 × 0.18 × 0.20	0.16 × 0.20 × 0.24
$\theta_{min,max}$/°	1, 24	1, 25
Total data measured	5622	3858
Total data refined [significance test $I > 3.0\sigma(I)$]	3870	3023
(*c*) Refinement		
Parameters refined	506	467
Final *R*[a]	0.038	0.039
Final *R'*[b]	0.041	0.048

[a] $R = \Sigma|F_o - F_c|/\Sigma|F_o|$. [b] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{\frac{1}{2}}$.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

The structures of the two neutral cobalt compounds **3** and **4** have been determined and their structures are shown in Figs. 1 and 2, respectively. The Co atom in compound **3** is at the centre of a distorted tetrahedron, the co-ordinated angles varying between 93.26 [P(1)–Co–P(2)] and 120.62(5) [S(1)–Co–S(2)], with mean atomic distances Co–S 2.228(5) and Co–P 2.345(2) Å. The six-membered ring Co–P–C–C–C–P is non-planar and both the Co–P–C angles [107.2(1) and 108.4(2)°] deviate slightly from the standard tetrahedral angle (109.5°). The Co atom in compound **4** is co-ordinated by five atoms, PPPSS, with no symmetric element for the whole molecule. The tridentate ligand bdpp chelates to the Co atom forming a CoPPP triangular pyramid with Co–P distances varying between 2.196(2) and 2.306(2) Å. The two SPh$^-$ ligands are attached to the Co atom from the other side with the Co–S distances varying slightly between 2.247(2) and 2.272(2) Å. There is thought to be no structural strain of the ring at the P atoms as their angles Co–P–C (107.1–111.0°) differ only slightly from the standard tetrahedral angle.

Comparison of the Molecular Structures of Compounds **1**–**4**.—Ditertiary phosphines react with cobalt(II) and thiolate ligands to form disparate molecular structures. In $[Co_2(\mu\text{-dppm})(\mu\text{-SPh})_2(SPh)_2]$ **1** the dppm ligand bridges the two cobalt atoms forming a symmetric compound. Compound **2**, [Co$_2$(dppe)(μ-

Table 2 Positional parameters for compound **3** with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*	Atom	*x*		*z*
Co	0.861 60(6)	0.076 41(6)	0.760 83(3)	C(33)	0.655 1(5)	0.534 3(5)	0.786 2(3)
S(1)	1.046 5(1)	0.217 4(1)	0.764 55(7)	C(34)	0.523 1(6)	0.564 0(5)	0.795 7(4)
S(2)	0.883 6(1)	−0.123 8(1)	0.792 72(7)	C(35)	0.437 3(6)	0.477 6(6)	0.819 7(5)
P(1)	0.678 3(1)	0.157 7(1)	0.832 45(6)	C(36)	0.481 4(5)	0.356 2(6)	0.833 2(4)
P(2)	0.725 4(1)	0.045 8(1)	0.646 68(6)	C(41)	0.696 7(4)	0.166 9(4)	0.932 8(2)
C(1)	0.526 8(5)	0.039 8(5)	0.798 6(3)	C(42)	0.824 3(5)	0.169 0(5)	0.969 6(3)
C(2)	0.470 5(5)	0.033 6(6)	0.717 8(3)	C(43)	0.840 6(6)	0.181 9(6)	1.046 2(3)
C(3)	0.558 4(5)	−0.039 9(5)	0.656 5(3)	C(44)	0.731 2(6)	0.190 3(6)	1.087 2(3)
C(11)	1.113 9(4)	0.257 1(4)	0.859 6(3)	C(45)	0.604 0(6)	0.187 5(8)	1.051 6(3)
C(12)	1.162 9(5)	0.158 7(5)	0.895 1(3)	C(46)	0.585 3(5)	0.177 3(7)	0.976 4(3)
C(13)	1.213 4(5)	0.190 4(6)	0.969 0(3)	C(51)	0.782 6(5)	−0.064 4(5)	0.562 8(3)
C(14)	1.216 5(6)	0.322 0(7)	1.008 4(3)	C(52)	0.816 5(6)	−0.195 5(5)	0.566 4(3)
C(15)	1.169 3(6)	0.419 9(6)	0.975 1(4)	C(53)	0.858 4(7)	−0.282 2(6)	0.503 6(3)
C(16)	1.116 9(5)	0.390 1(5)	0.901 5(3)	C(54)	0.865 3(6)	−0.240 9(6)	0.438 6(3)
C(21)	1.007 7(5)	−0.220 4(4)	0.742 7(3)	C(55)	0.835 6(6)	−0.111 6(6)	0.434 4(3)
C(22)	1.026 3(5)	−0.351 8(4)	0.752 0(3)	C(56)	0.794 2(5)	−0.025 1(5)	0.496 1(3)
C(23)	1.121 1(6)	−0.429 7(5)	0.714 1(4)	C(61)	0.683 1(4)	0.198 6(5)	0.614 7(2)
C(24)	1.200 6(6)	−0.381 9(5)	0.665 4(4)	C(62)	0.784 7(5)	0.301 4(5)	0.623 4(3)
C(25)	1.184 8(6)	−0.252 9(6)	0.654 7(4)	C(63)	0.762 2(6)	0.419 8(6)	0.599 5(3)
C(26)	1.092 3(5)	−0.170 1(5)	0.692 3(3)	C(64)	0.635 4(7)	0.435 4(7)	0.567 6(4)
C(31)	0.616 0(4)	0.322 0(4)	0.822 2(3)	C(65)	0.533 7(7)	0.337 1(7)	0.559 0(4)
C(32)	0.702 2(5)	0.412 5(5)	0.798 8(3)	C(66)	0.556 5(6)	0.218 3(6)	0.581 5(3)

Table 3 Positional parameters for compound **4** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Co	0.238 1(0)	0.179 56(3)	0.414 0(0)	C(35)	0.142 7(5)	0.110 1(3)	0.738 1(7)
S(1)	0.286 1(1)	0.112 43(6)	0.330 3(1)	C(36)	0.172 0(5)	0.141 1(3)	0.661 5(6)
S(2)	0.365 8(1)	0.186 63(7)	0.618 2(2)	C(41)	0.209 2(4)	0.283 5(3)	0.612 9(6)
P(1)	0.165 2(1)	0.226 43(6)	0.502 2(1)	C(42)	0.271 3(4)	0.277 2(3)	0.751 0(6)
P(2)	0.099 0(1)	0.160 46(6)	0.252 7(1)	C(43)	0.303 6(5)	0.319 7(3)	0.834 1(7)
P(3)	0.248 2(1)	0.231 64(6)	0.250 0(1)	C(44)	0.180 1(5)	0.332 9(3)	0.560 2(7)
C(1)	0.056 1(4)	0.248 3(3)	0.357 7(6)	C(45)	0.212 3(6)	0.374 7(3)	0.646 2(9)
C(2)	0.012 0(4)	0.202 3(3)	0.265 2(6)	C(46)	0.274 0(6)	0.368 2(4)	0.782 4(8)
C(3)	0.091 0(4)	0.178 7(3)	0.083 5(5)	C(51)	0.046 3(4)	0.097 1(2)	0.221 2(6)
C(4)	0.134 7(4)	0.230 3(3)	0.095 0(6)	C(52)	0.061 9(4)	0.062 0(3)	0.137 1(7)
C(11)	0.294 7(4)	0.056 1(2)	0.425 2(5)	C(53)	0.021 8(6)	0.014 1(3)	0.111 7(9)
C(12)	0.358 2(4)	0.019 7(3)	0.432 2(6)	C(54)	−0.034 7(6)	0.000 3(3)	0.170(1)
C(13)	0.369 3(6)	−0.025 5(3)	0.504 8(7)	C(55)	−0.048 8(5)	0.034 4(3)	0.252 2(9)
C(14)	0.315 7(6)	−0.035 7(3)	0.569 2(7)	C(56)	−0.007 9(5)	0.081 7(3)	0.280 2(7)
C(15)	0.252 6(5)	−0.000 0(3)	0.560 9(7)	C(61)	0.328 5(4)	0.208 4(2)	0.189 1(6)
C(16)	0.241 9(4)	0.044 7(3)	0.489 5(6)	C(62)	0.421 1(4)	0.207 2(3)	0.284 9(7)
C(21)	0.444 0(4)	0.134 8(2)	0.661 6(6)	C(63)	0.485 2(5)	0.187 7(3)	0.249 8(9)
C(22)	0.505 9(5)	0.130 2(3)	0.613 0(8)	C(64)	0.458 7(5)	0.169 2(3)	0.117 2(7)
C(23)	0.570 5(5)	0.092 1(4)	0.658(1)	C(65)	0.368 9(5)	0.169 9(3)	0.024 5(7)
C(24)	0.575 1(6)	0.057 2(4)	0.756(1)	C(66)	0.302 6(5)	0.189 2(3)	0.057 5(6)
C(25)	0.513 8(6)	0.061 7(3)	0.807 3(8)	C(71)	0.278 3(4)	0.299 8(2)	0.269 3(6)
C(26)	0.448 1(5)	0.099 8(3)	0.759 7(7)	C(72)	0.309 5(4)	0.323 3(3)	0.396 5(7)
C(31)	0.127 9(4)	0.186 3(2)	0.606 5(5)	C(73)	0.334 2(5)	0.374 4(3)	0.412 4(8)
C(32)	0.054 8(5)	0.201 6(3)	0.629 7(7)	C(74)	0.326 9(5)	0.402 5(3)	0.302 4(9)
C(33)	0.027 4(5)	0.170 4(3)	0.708 1(7)	C(75)	0.296 1(5)	0.379 8(3)	0.175 7(8)
C(34)	0.071 5(5)	0.125 6(3)	0.763 2(6)	C(76)	0.270 6(5)	0.328 9(3)	0.157 8(7)

Table 4 Selected atomic distances (Å) and angles (°) for complexes **3** and **4**

	3	**4**		**3**	**4**		**3**	**4**
Co–S(1)	2.224(1)	2.272(2)	S(1)–C(11)	1.770(4)	1.761(7)	P(2)–C(3)	1.837(5)	1.845(6)
Co–S(2)	2.231(1)	2.247(2)	S(2)–C(21)	1.757(5)	1.767(8)	P(2)–C(51)	1.823(4)	1.819(7)
Co–P(1)	2.345(1)	2.211(2)	P(1)–C(1)	1.831(4)	1.841(6)	P(2)–C(61)	1.813(6)	
Co–P(2)	2.346(1)	2.196(2)	P(1)–C(31)	1.828(5)	1.842(7)	P(3)–C(4)		1.846(7)
Co–P(3)		2.306(2)	P(1)–C(41)	1.814(5)	1.836(7)	P(3)–C(61)		1.827(7)
			P(2)–C(2)		1.848(7)	P(3)–C(71)		1.828(7)
S(1)–Co–S(2)	120.62(5)	97.03(7)	Co–S(1)–C(11)	105.2(1)	110.8(2)	C(3)–P(2)–C(51)	101.7(3)	
S(1)–Co–P(1)	117.78(4)	162.56(7)	Co–S(2)–C(21)	112.3(2)	115.5(2)	C(3)–P(2)–C(61)	105.9(2)	
S(1)–Co–P(2)	111.71(5)	85.92(7)	Co–P(1)–C(1)	107.2(1)	107.8(2)	C(51)–P(2)–C(61)	103.1(2)	
S(1)–Co–P(3)		88.91(6)	Co–P(1)–C(31)	116.6(2)	110.7(2)	C(2)–P(2)–C(3)		102.7(3)
S(2)–Co–P(1)	99.98(5)	88.23(7)	Co–P(1)–C(41)	118.4(1)	127.1(2)	C(2)–P(2)–C(51)		103.5(3)
S(2)–Co–P(2)	109.74(5)	163.06(8)	C(1)–P(1)–C(31)	103.3(3)	103.6(3)	C(3)–P(2)–C(51)		103.6(4)
S(2)–Co–P(3)		110.46(8)	C(1)–P(1)–C(41)	104.3(2)	104.1(3)	Co–P(3)–C(4)		107.1(2)
P(1)–Co–P(2)	93.26(4)	84.42(6)	C(31)–P(1)–C(41)	105.4(2)	101.3(3)	Co–P(3)–C(61)		114.0(2)
P(1)–Co–P(3)		104.87(7)	Co–P(2)–C(2)		111.0(2)	Co–P(3)–C(71)		126.4(2)
P(2)–Co–P(3)		86.21(7)	Co–P(2)–C(3)	108.4(2)	108.0(2)	C(4)–P(3)–C(61)		104.6(3)
			Co–P(2)–C(51)	119.5(2)	125.6(2)	C(4)–P(3)–C(71)		103.1(3)
			Co–P(2)–C(61)	116.7(1)		C(61)–P(3)–C(71)		99.4(3)

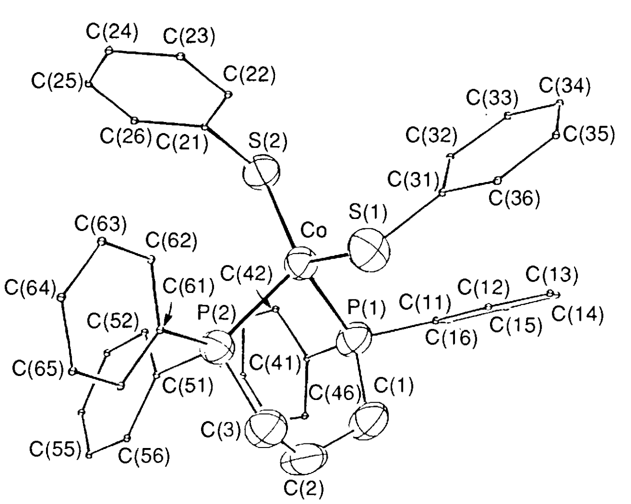

Fig. 1 Perspective view of the structure of [Co(dppp)(SPh)$_2$]

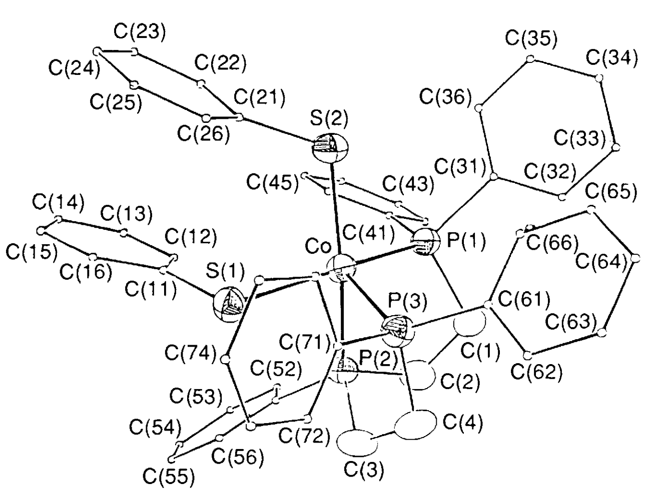

Fig. 2 Perspective view of the structure of [Co(bdpp)(SPh)$_2$]

Table 5 Comparison of atomic distances (Å) and angles (°) for complexes **1**–**4***

	$\mathbf{1}^{7a}$	$\mathbf{2}^{8}$	**3**	**4**
Co–S	2.197(14)	2.215	2.228(5)	2.256
Co–P	2.343(8)	2.210(6)	2.345(2)	2.238(60)
S–C_{Ph}	1.75(1)	1.79	1.76	1.76
P–C_{Ph}	1.81(1)	1.81(2)	1.82(1)	1.83(1)
P–C_{alk}	1.84(1)	1.85	1.84(1)	1.85(1)
C_{alk}–C_{alk}		1.50	1.53(1)	1.51(1)
C_{Ph}–C_{Ph}		1.38(2)	1.367(7)	1.376(13)
S–Co–S			120.6	97.0
P–Co–P		86.7	93.3	84.4–104.9
S–Co–P			109.8 ± 7.3	85.9–163.1
Co–S–C		105.8	108.8 ± 5.0	113.2 ± 3.3
Co–P–C_{Ph}		119.2 ± 5.1	117.8	120.8 ± 7.8
Co–P–C_{alk}		107.4	107.8 ± 0.8	108.5 ± 1.5
C–C–C (Ph)		120.0 ± 2.0	120.0 ± 1.5	120.0 ± 1.5

* C_{Ph} and C_{alk} are the carbon atoms in the phenyl and alkyl groups respectively; average values are given with standard deviations $> 3\sigma$.

SPh)$_3$(SPh)], however, is asymmetric with the dppe acting as a bidentate ligand chelating to one of the cobalt atoms. The ligand dppp also acts as a bidentate ligand, and bdpp as a tridentate ligand, in the monocobalt complexes **3** (C_{2v}) and **4** (no molecular symmetry), respectively. Some atomic distances and angles for compounds **1**–**4** are listed in Table 5 for comparison.

The mean atomic distance between cobalt and the terminal sulphur atoms in compound **1** [2.197(14) Å] is close to that in compounds **2** [2.215(4) Å] and **3** [2.228(5) Å], but shorter than that in the five-co-ordinate cobalt complex **4** (2.256 Å) and much shorter than the 2.33(1) Å found in the tetrahedral complex $[Co(SPh)_4]^{2-}$.[12]

The mean Co–P distance in compound **1** [2.343(8) Å] is again comparable to that found in compound **3** [2.345(2) Å], but is significantly longer than the value of 2.210(6) or 2.238(60) Å found in compounds **2** and **4**, respectively, where the phosphorus atoms are bound to a five-co-ordinate cobalt atom.

Cobalt(II) (d^7) can assume either a low ($S = \frac{1}{2}$)- or a high ($S = \frac{3}{2}$)-spin configuration according to whether the energy separation between the two highest orbitals is higher or lower than the spin-pairing energy.[13] The magnetic moment of compound **3**, 4.28 μ_B, is somewhat larger than the value $g[S(S + 1)]^{\frac{1}{2}} = 2[\frac{3}{2}(\frac{3}{2} + 1)]^{\frac{1}{2}} = 3.87\ \mu_B$ and that of compound **4**, 2.15 μ_B, is larger than $2[\frac{1}{2}(\frac{1}{2} + 1)]^{\frac{1}{2}} = 1.73\ \mu_B$, indicating that there is a significant orbital contribution to the magnetic moment. The four-co-ordinated cobalt(II) is thus in the high-spin and the five-co-ordinated cobalt(II) is in the low-spin state.

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