The Synthesis and Characterization of Cobalt Complexes with Diphosphorus–Sulphur and –Selenium Cyclic Units as Trihapto Ligands. X-Ray Crystal Structures † of [Co{CMe(CH2PPh2)3}(P2X)]BF4·C6H6 (X = S or Se)

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The reaction of $Co(BF_4)_2 \cdot 6H_2O$ with P_4S_3 or P_4Se_3 in the presence of 1,1,1-tris(diphenylphosphino-methyl)ethane (tppme) yielded complexes $[Co(tppme)(P_2X)]BF_4 \cdot C_6H_6$ [X = S (1) or Se (2)]. The molecular structures of the complexes have been determined by single-crystal X-ray diffraction methods. Both compounds crystallize in the monoclinic space group $P2_1/n$ with $Z = 4$ and unit-cell dimensions: $a = 17.193(7)$, $b = 20.164(8)$, $c = 13.136(7)$ Å, $\beta = 103.35(8)°$ [for (1)]; and $a = 17.049(8)$, $b = 20.119(9)$, $c = 13.188(8)$ Å, $\beta = 102.74(8)°$ [for (2)]. The metal atom in both compounds is in a six-co-ordinate environment formed by the tppme P atoms and by the atoms of the heterocyclic P_2S or P_2Se unit, as shown by the crystallographic investigations and by ^{31}P n.m.r. studies.

As part of a study on the reactivity of phosphorus chalcogen-ides toward transition-metal moieties [1,2] the reactions of the P_4S_3 and P_4Se_3 cage molecules with cobalt(II) salts in the presence of the tripod ligand 1,1,1-tris(diphenylphosphinomethyl)-ethane, tppme, have been investigated. Complexes of formula $[Co(tppme)(P_2X)]BF_4$ [X = S (1) or Se (2)] have been obtained and their structures have been elucidated by X-ray analyses and ^{31}P n.m.r. measurements. The complexes contain the heterocyclic P_2S or P_2Se unit η^3-bonded to the cobalt atom. The ^{31}P n.m.r. features of such compounds are compared to those of cyclic triphosphanes and of cyclotriphosphorus complexes. Several complexes of the latter type, reported in recent years, have provided the first examples of compounds in which the homocyclic P_3 unit is co-ordinated to one or more metal centres.[3,4] To the best of our knowledge the present compounds provide the first examples of hetero-atomic phosphorus chalcogenide rings π-bonded to metal atoms. A preliminary account of part of this work has already appeared.[5]

Experimental

All solvents were reagent grade and were dried by distillation from suitable agents.[6] All reactions and manipulations were carried out under dry nitrogen. Electronic spectra, conduc-tivity, and magnetic susceptibilities were measured by pro-cedures already described.[7] ^{31}P N.m.r. spectra were collected (at 32.19 MHz) on a Varian CFT20 spectrometer. The ^{31}P probe was locally modified for investigation of the high-field region. Phosphorus-31 positive chemical shifts are downfield relative to H_3PO_4 at 0.0 p.p.m. Changes in chemical shifts on co-ordination are reported in p.p.m. relative to the corres-ponding phosphorus in the free ligand. The compound P_4S_3 was purchased from Fluka AG and used after recrystallization from benzene; P_4Se_3 [8] and the ligand 1,1,1-tris(diphenyl-phosphinomethyl)ethane (tppme) [9] were prepared according to published procedures.

† η^3-Thiadiphosphirene- and η^3-selenadiphosphirene-[1,1,1-tris(diphenylphosphinomethyl)ethane]cobalt(I) tetrafluoroborate benzene solvate.

Supplementary data available (No. SUP 23775, 36 pp.): structure factors, thermal parameters, H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Preparation of the Complexes $[Co(tppme)(P_2X)]BF_4$ [X = S (1) or Se (2)].—A warm solution of tetraphosphorus chalco-genide (P_4S_3 or P_4Se_3) (1 mmol) in benzene (40 cm³) was added to a solution of $Co(BF_4)_2 \cdot 6H_2O$ (1 mmol) in ethanol (5 cm³) and tppme (1 mmol) in benzene (30 cm³). The resulting solu-tion was refluxed overnight and ethanol (10 cm³) was added. Orange crystals of the compounds were obtained by concen-trating the solution. The complexes were collected on a sin-tered-glass frit, in a closed system, and washed with ethanol-benzene (1 : 1) and then light petroleum (b.p. 40—70 °C) before being dried. The complexes were recrystallized from dichloromethane and benzene (yield, 50—55%). The com-plexes crystallize with one molecule of benzene. Analytical and conductivity data for the complexes are collected in Table 1.

Collection and Reduction of X-Ray Data.—Diffraction data for the compounds $[Co(tppme)(P_2S)]BF_4 \cdot C_6H_6$ (1) and $[Co(tppme)(P_2Se)]BF_4 \cdot C_6H_6$ (2) were collected at room temp-erature on a Philips PW 1100 automated diffractometer using graphite-monochromated Mo-K_α radiation ($\lambda = 0.710\ 69$ Å). Details of crystal data are reported in Table 2. Lattice con-stants were determined for both compounds, which are iso-morphous to each other, by least-squares refinement of the angular settings of 24 reflections with $11 < \theta < 16°$ for (1) and $11 < \theta < 14°$ for (2). The intensities of all reflections with $k \geqslant 0$ and $l \geqslant 0$ were measured for (1) whereas those of all reflections with $l \geqslant 0$ (two forms) were measured for (2). Intensities in the range $5 < 2\theta < 44°$ for (1) and $5 < 2\theta < 40°$ for (2) were collected in the θ—2θ scan mode with a scan width of $(1.00 + 0.30 \tan\theta)°$ [for (1)] and $(1.20 + 0.30\tan\theta)°$ [for (2)] and scan speed 6° min⁻¹ [for (1)] and 5° min⁻¹ [for (2)]. Stationary background counts were taken at each end of the scan for a time equal to half the scan time. The intensities of three standard reflections monitored every 120 min showed small fluctuations ($<1\%$) about their mean values but no systematic trend during either data collection. Diffraction data were corrected for Lorentz, polarization, and absorption effects and were subsequently merged to unique sets. Trans-mission factors were in the range 0.75—0.83 for (1) and 0.76—0.83 for (2); crystal dimensions were $0.40 \times 0.30 \times 0.20$ mm for (1) and $0.25 \times 0.20 \times 0.12$ mm for (2). The principal computer programs used in the crystallographic calculations are listed in ref. 10.

Solution and Refinement of the Structures.—The structure of the sulphur derivative (1) was solved by standard heavy-

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Table 1. Analytical and conductivity data for the complexes

| Compound | Λ_M [a]$/\Omega^{-1}$ cm^2 mol^{-1} | Analysis (%) [b] | | | | |
		C	H	Co	P	Other
(1) [Co(tppme)(P$_2$S)]BF$_4$·C$_6$H$_6$	87	59.8 (59.9)	4.9 (4.8)	6.2 (6.2)	16.3 (16.4)	S, 3.3 (3.4)
(2) [Co(tppme)(P$_2$Se)]BF$_4$·C$_6$H$_6$	84	57.1 (57.0)	4.6 (4.6)	5.8 (6.0)	15.5 (15.6)	

[a] Molar conductance of ca. 10^{-3} mol dm^{-3} solution in nitroethane at 20 °C. [b] Calculated values in parentheses.

Table 2. Crystal data for [Co(tppme)(P$_2$S)]BF$_4$·C$_6$H$_6$ (1) and [Co(tppme)(P$_2$Se)]BF$_4$·C$_6$H$_6$ (2)

	(1)	(2)
Formula	C$_{47}$H$_{45}$BCoF$_4$P$_5$S	C$_{47}$H$_{45}$BCoF$_4$P$_5$Se
Space group	$P2_1/n$	$P2_1/n$
$a/\text{Å}$	17.193(7)	17.049(8)
$b/\text{Å}$	20.164(8)	20.119(9)
$c/\text{Å}$	13.136(7)	13.188(8)
$\beta/°$	103.35(8)	102.74(8)
$U/\text{Å}^3$	4 430.9	4 412.2
M	942.5	989.4
Z	4	4
$F(000)$	1 944	2 016
$D_c/\text{g cm}^{-3}$	1.41	1.49
$\mu(\text{Mo-}K_\alpha)/\text{cm}^{-1}$	6.57	14.32
Unique data	4 360	3 500
$F_o^2 > n\sigma(F_o^2)$	3 502 ($n = 3$)	1 512 ($n = 3.5$)

atom procedures. That of the selenium isomorph (2) was refined using as initial values of the atomic co-ordinates those from the structure of (1). Both P$_2$X rings [X = S (1), Se (2)] were found to be affected by orientational disorder about the pseudo-three-fold axis of the respective cation. The amount of disorder was evaluated by examination of the residual electron density in difference-Fourier maps calculated without contributions from atoms of the P$_2$X rings, as well as from the results of least-squares refinements in which either the occupancy factors of the atomic sites of the rings or their thermal parameters were allowed to refine. The P$_2$S group in (1) was finally considered to be distributed with identical probability among the three possible orientations mainly based on the following considerations: (a) the R factor did not decrease when the S form factor was assigned in turn to each site in the ring; (b) use of identical form factors for the three sites led to closely similar values of their equivalent isotropic thermal parameters. Each atomic site in the P$_2$S ring was therefore assigned in the final cycles of refinement 0.33 and 0.67 occupancy factors for S and P, respectively. One orientation of the P$_2$Se group in (2) was found to be more populated than the other two; the Se occupancy factors of the three sites in the ring were finally set at 0.77, 0.17, and 0.06. In the final cycles of the full-matrix least-squares refinement all atoms heavier than carbon were assigned anisotropic thermal parameters, whereas C and B atoms were refined isotropically. Hydrogen atoms were introduced in calculated positions (C–H = 1.00 Å) with (a) fixed thermal parameters ca. 20% larger than those of the respective carbon atoms [for (1)], or (b) with overall thermal parameters [for (2)] whose values were separately refined for H atoms in the cation and for those in the benzene solvate molecule (0.11 and 0.27 Å², respective final values). Both the tppme ligand phenyl groups and the benzene molecule in compound (2) were refined as rigid groups with idealized geometry whereas no constraint was imposed on such groups in the structure of compound (1). The function $\Sigma w(|F_o| - |F_c|)^2$ was minimized in the least-squares refinement, with weights $w = 1/\sigma^2(F_o)$. The scattering factors of the neutral atoms were taken from ref. 11 and the anomalous dispersion corrections for Co and Se from ref. 12. The final values

of the discrepancy indices were $R = \Sigma(|F_o| - |F_c|)/\Sigma(|F_o|) = 0.061$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o^2)]^{\frac{1}{2}} = 0.064$ for complex (1) and $R = 0.069$ and $R' = 0.062$ for complex (2). The largest shift to error ratios in the final cycles were 0.09 for (1) and 0.20 for (2). Final difference-Fourier maps showed a few peaks with heights 0.5 e Å^{-3} (1) and 0.6 e Å^{-3} (2). The highest peaks in the map of (2) were located in the region of the P$_2$Se group. The final positional parameters for the non-hydrogen atoms in the structures of compounds (1) and (2) are listed in Tables 3 and 4, respectively.

Results and Discussion

The reaction of cobalt(II) tetrafluoroborate in the presence of the tripod ligand tppme with the appropriate phosphorus chalcogenide (P$_4$S$_3$ or P$_4$Se$_3$) affords complexes of formula [Co(tppme)(P$_2$X)]BF$_4$ (X = S or Se). The analytical data (Table 1) for the complexes, which crystallize with one molecule of benzene, are in good agreement with the proposed formula. The complexes behave as 1 : 1 electrolytes in nitroethane (Table 1).[13] The diamagnetic compounds are moderately air-stable in the solid state. They are soluble in acetone and dichloromethane whereupon they undergo decomposition in a few hours exposed to air.

The crystal structures of the isomorphous compounds [Co(tppme)(P$_2$S)]BF$_4$·C$_6$H$_6$ (1) and [Co(tppme)(P$_2$Se)]BF$_4$·C$_6$H$_6$ (2) consist of [Co(tppme)(P$_2$X)]$^+$ cations (X = S or Se), BF$_4^-$ anions, and an interposed benzene molecule from the solvent. Figures 1 and 2 show perspective views of the cations in compounds (1) and (2) respectively. Selected values of bond distances and angles in the two structures are listed in Table 5. The metal atom in each cation is in a six-co-ordinate environment formed by the tppme P atoms and by the atoms of the heterocyclic P$_2$X unit in a staggered arrangement similar to that previously found for the simple sandwich complexes formed by the P$_3$ homocyclic ring.[14]

The P$_2$S triangular unit in (1) is disordered about the pseudo-three-fold axis of the cation (see Experimental section) so that the sulphur atom resides on each vertex of the triangle with essentially identical probability. Although the presence of

Table 3. Atomic parameters for [Co(tppme)(P$_2$S)]BF$_4$·C$_6$H$_6$ (1) [a]

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Co	0.638 0(1)	0.546 9(1)	0.305 5(1)	C(33)	0.666 0(5)	0.753 1(4)	0.078 0(6)
P(1)	0.677 1(1)	0.461 1(1)	0.225 3(1)	C(34)	0.718 4(5)	0.748 3(4)	0.014 7(7)
P(2)	0.743 1(1)	0.606 9(1)	0.295 3(2)	C(35)	0.777 6(5)	0.703 7(4)	0.030 0(7)
P(3)	0.701 0(1)	0.514 9(1)	0.464 9(1)	C(36)	0.786 3(5)	0.658 3(4)	0.114 7(6)
P(4) [b]	0.547 2(1)	0.623 1(1)	0.328 7(2)	C(41)	0.784 0(4)	0.666 7(4)	0.401 7(6)
P(5) [b]	0.533 7(1)	0.582 8(1)	0.177 3(2)	C(42)	0.732 1(5)	0.705 3(4)	0.440 8(7)
P(6) [b]	0.507 6(1)	0.524 1(1)	0.300 0(2)	C(43)	0.759 3(6)	0.753 3(5)	0.518 3(8)
F(1)	0.515 3(3)	0.118 3(3)	0.259 9(6)	C(44)	0.840 6(6)	0.760 9(5)	0.552 8(8)
F(2)	0.413 0(4)	0.047 8(3)	0.214 7(7)	C(45)	0.893 3(6)	0.724 7(5)	0.516 6(8)
F(3)	0.393 0(4)	0.153 2(5)	0.246 8(7)	C(46)	0.864 8(5)	0.675 5(4)	0.438 3(7)
F(4)	0.427 4(6)	0.126 9(4)	0.107 6(6)	C(51)	0.697 6(4)	0.572 2(4)	0.572 3(6)
C(1)	0.827 8(4)	0.486 8(4)	0.362 2(6)	C(52)	0.765 1(5)	0.595 4(4)	0.642 7(6)
C(2)	0.771 7(4)	0.431 1(4)	0.305 6(6)	C(53)	0.757 5(5)	0.640 6(4)	0.720 5(7)
C(3)	0.826 2(4)	0.549 4(4)	0.292 0(6)	C(54)	0.684 1(5)	0.661 2(4)	0.728 3(7)
C(4)	0.808 4(4)	0.502 8(4)	0.468 6(6)	C(55)	0.616 2(5)	0.637 2(4)	0.662 0(7)
C(5)	0.915 5(5)	0.460 2(4)	0.385 1(7)	C(56)	0.623 3(5)	0.591 7(4)	0.584 7(7)
C(11)	0.610 2(4)	0.390 0(3)	0.200 2(6)	C(61)	0.672 9(4)	0.437 6(3)	0.521 4(5)
C(12)	0.539 0(4)	0.397 0(4)	0.125 1(6)	C(62)	0.717 7(4)	0.417 0(4)	0.618 9(6)
C(13)	0.484 7(5)	0.346 4(4)	0.107 1(6)	C(63)	0.698 3(5)	0.359 9(4)	0.665 8(7)
C(14)	0.498 1(5)	0.287 3(4)	0.160 5(6)	C(64)	0.635 2(4)	0.322 0(4)	0.616 3(6)
C(15)	0.568 6(5)	0.279 1(4)	0.233 4(6)	C(65)	0.591 5(5)	0.340 0(4)	0.519 2(6)
C(16)	0.625 3(5)	0.329 3(4)	0.253 2(6)	C(66)	0.609 5(4)	0.398 9(4)	0.472 6(6)
C(21)	0.697 9(4)	0.472 5(4)	0.095 1(6)	C(71)	−0.011(1)	0.339(1)	0.000(1)
C(22)	0.666 3(5)	0.523 9(4)	0.030 9(6)	C(72)	−0.035(1)	0.304(1)	0.071(1)
C(23)	0.682 8(6)	0.530 9(5)	−0.067 7(7)	C(73)	−0.018(1)	0.321(1)	0.175(1)
C(24)	0.730 3(6)	0.488 7(5)	−0.102 0(8)	C(74)	0.018(1)	0.380(1)	0.196(2)
C(25)	0.767 0(7)	0.437 2(6)	−0.037 3(9)	C(75)	0.036(1)	0.420(1)	0.123(2)
C(26)	0.745 7(6)	0.427 9(6)	0.060 2(9)	C(76)	0.028(1)	0.400(1)	0.025(2)
C(31)	0.735 2(4)	0.622 2(4)	0.180 9(6)	B	0.440(1)	0.109(1)	0.208(1)
C(32)	0.675 0(5)	0.708 4(4)	0.163 8(6)				

[a] Atoms Co, P(1)—P(6), and C(1)—C(66) belong to the complex cation, atoms B and F(1)—F(4) to the anion, and C(71)—C(76) to the solvate benzene molecule. [b] Each of the P(4)—P(6) sites has 0.67 P and 0.33 S population parameters.
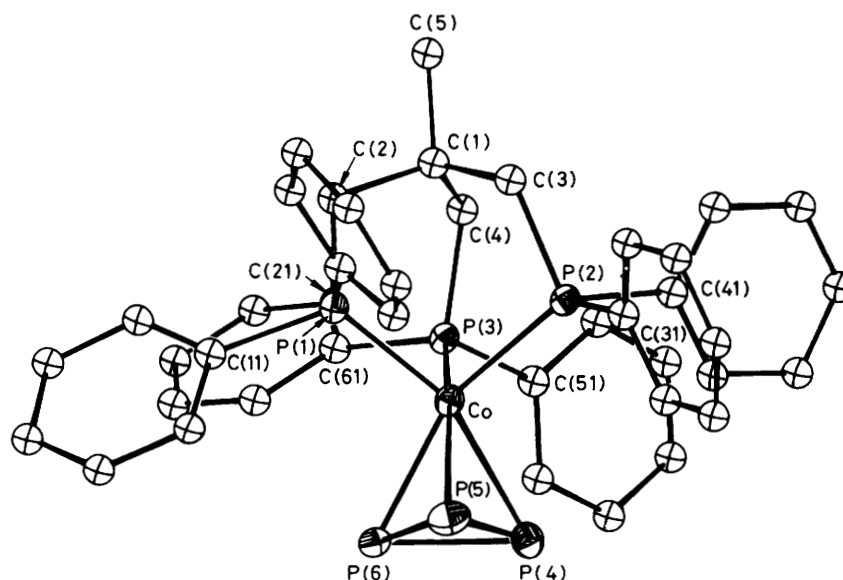

Figure 1. Perspective view of the [Co(tppme)(P$_2$S)]$^+$ cation with 20% probability ellipsoids. The P(4)—P(6) atomic sites have 0.67 P and 0.33 S occupancy. Only the first carbon atom of each phenyl group is labelled

a sulphur atom in the triatomic ring was not unambiguously detected by the X-ray analysis, it is proved by the analytical data and, indirectly, by the diamagnetism and ^{31}P n.m.r. properties of the compound (see below). Due to the above disordering, the P$_2$S group appears to be almost symmetrically bonded to the metal atom. The mean of the interatomic

distances in the P$_2$S ring [2.119(10) Å] is shorter than the value of 2.141(2) Å found for the cyclotriphosphorus unit in the neutral complex [Co(tppme)(P$_3$)] [15] and is close to that of 2.122(4) Å existing in the [Ni(tppme)(P$_3$)]$^+$ cation.[1] The mean distance from the metal to atoms of the P$_2$S ring [2.270(9) Å] is shorter than the 2.301(1) and 2.306(5) Å

Table 4. Atomic parameters for [Co(tppme)(P₂Se)]BF₄·C₆H₆ (2) ^{a}

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Co	0.637 4(2)	0.547 8(1)	0.304 7(2)	C(33)	0.664 1(6)	0.752 8(6)	0.081 0(8)
P(1)	0.678 9(3)	0.461 3(3)	0.223 5(4)	C(34)	0.716 4(6)	0.748 5(6)	0.013 5(8)
P(2)	0.743 0(3)	0.607 9(3)	0.295 0(5)	C(35)	0.777 6(6)	0.701 1(6)	0.030 5(8)
P(3)	0.699 2(3)	0.516 6(3)	0.463 5(4)	C(36)	0.786 5(6)	0.657 9(6)	0.115 1(8)
P(4) ^{b}	0.547 2(3)	0.626 6(3)	0.326 8(5)	C(41)	0.783 0(6)	0.667 3(6)	0.401 4(9)
P(5) ^{b}	0.532 3(3)	0.585 7(3)	0.173 6(4)	C(42)	0.729 1(6)	0.707 0(6)	0.439 7(9)
Se ^{b}	0.498 4(2)	0.523 9(1)	0.299 2(2)	C(43)	0.757 7(6)	0.754 9(6)	0.515 4(9)
F(1)	0.511 7(8)	0.118 8(7)	0.252 9(12)	C(44)	0.840 3(6)	0.762 9(6)	0.552 7(9)
F(2)	0.409 3(8)	0.049 1(8)	0.213 2(14)	C(45)	0.894 3(6)	0.723 2(6)	0.514 4(9)
F(3)	0.390 1(8)	0.155 6(10)	0.243 4(13)	C(46)	0.865 6(6)	0.675 3(6)	0.438 7(9)
F(4)	0.420 4(13)	0.128 2(9)	0.102 1(14)	C(51)	0.696 6(6)	0.573 3(5)	0.571 2(9)
C(1)	0.827 3(11)	0.486 2(10)	0.362 7(15)	C(52)	0.765 0(6)	0.596 7(5)	0.640 5(9)
C(2)	0.773 2(11)	0.431 2(9)	0.306 0(14)	C(53)	0.757 3(6)	0.641 2(5)	0.718 8(9)
C(3)	0.823 9(11)	0.548 6(9)	0.288 1(14)	C(54)	0.681 3(6)	0.662 4(5)	0.727 8(9)
C(4)	0.809 0(10)	0.504 1(9)	0.468 5(14)	C(55)	0.612 9(6)	0.639 0(5)	0.658 6(9)
C(5)	0.917 2(11)	0.459 7(10)	0.385 6(15)	C(56)	0.620 5(6)	0.594 5(5)	0.580 3(9)
C(11)	0.612 6(7)	0.389 6(5)	0.197 2(8)	C(61)	0.671 6(5)	0.439 4(5)	0.521 6(8)
C(12)	0.541 3(7)	0.398 3(5)	0.122 7(8)	C(62)	0.714 3(5)	0.422 5(5)	0.621 1(8)
C(13)	0.484 6(7)	0.347 3(5)	0.102 9(8)	C(63)	0.695 7(5)	0.364 2(5)	0.668 0(8)
C(14)	0.499 1(7)	0.287 6(5)	0.157 6(8)	C(64)	0.634 4(5)	0.322 8(5)	0.615 4(8)
C(15)	0.570 4(7)	0.278 9(5)	0.232 1(8)	C(65)	0.591 7(5)	0.339 7(5)	0.515 9(8)
C(16)	0.627 1(7)	0.329 9(5)	0.251 9(8)	C(66)	0.610 3(5)	0.398 0(5)	0.469 0(8)
C(21)	0.703 2(6)	0.471 2(5)	0.094 5(9)	C(71)	0.984 7(7)	0.325 1(7)	0.169 5(11)
C(22)	0.666 7(6)	0.522 2(5)	0.029 2(9)	C(72)	0.967 0(7)	0.303 6(7)	0.066 3(11)
C(23)	0.685 6(6)	0.531 4(5)	−0.067 5(9)	C(73)	0.988 3(7)	0.342 8(7)	−0.010 6(11)
C(24)	0.741 0(6)	0.489 5(5)	−0.098 9(9)	C(74)	1.027 3(7)	0.403 4(7)	0.015 5(11)
C(25)	0.777 5(6)	0.438 5(5)	−0.033 6(9)	C(75)	1.045 0(7)	0.424 8(7)	0.118 7(11)
C(26)	0.758 6(6)	0.429 3(5)	0.063 1(9)	C(76)	1.023 7(7)	0.385 6(7)	0.195 7(11)
C(31)	0.734 2(6)	0.662 2(6)	0.182 6(8)	B	0.434 9(20)	0.108 2(17)	0.199 9(26)
C(32)	0.673 0(6)	0.709 6(6)	0.165 6(8)				

^{a} Atoms Co, P(1)—P(5), Se, and C(1)—C(66) belong to the complex cation, atoms B and F(1)—F(4) to the anion, and C(71)—C(76) to the solvate benzene molecule. ^{b} These sites have occupancies: P(4) (0.94 P, 0.06 Se), P(5) (0.83 P, 0.17 Se), and Se (0.23 P, 0.77 Se).
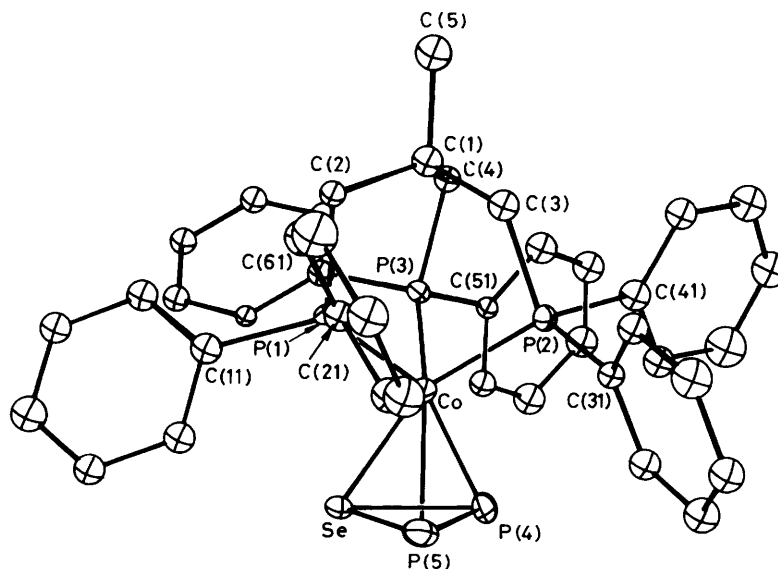

Figure 2. Perspective view of the [Co(tppme)(P₂Se)]⁺ cation with 20% probability ellipsoids. Atomic sites of the P₂Se ring have fractional P and Se occupancies as follows: P(4) (0.94 P, 0.06 Se), P(5) (0.83 P, 0.17 Se), and Se (0.23 P, 0.77 Se). Only the first carbon atom of each phenyl group is labelled

respectively found for the above neutral and cationic complexes. The shortening in (1) seems therefore to be due to replacement of one P by one S atom in the ring rather than to an effect of increased overall charge from that of the neutral cobalt complex. The Co⁻P(tppme) distances in (1) [2.211(9)

Å, mean] are intermediate between those of 2.186(1) and 2.243(4) Å in [Co(tppme)(P₃)] [15] and [Ni(tppme)(P₃)]⁺,[1] respectively. This result confirms the trend previously noted,[1] of the increasing of M⁻P(tppme) distances with increasing overall charge in complexes of this type.

Table 5. Selected interatomic distances (Å) and angles (°) for [Co(tppme)(P$_2$S)]BF$_4$·C$_6$H$_6$ (1) and [Co(tppme)(P$_2$Se)]BF$_4$·C$_6$H$_6$ (2)

(a) Compound (1)

Co–P(1)	2.209(2)	P(1)–Co–P(2)	93.3(1)
Co–P(2)	2.203(2)	P(1)–Co–P(3)	95.0(1)
Co–P(3)	2.220(2)	P(2)–Co–P(3)	89.4(1)
Co–P(4)	2.260(3)	P(4)–Co–P(5)	55.5(1)
Co–P(5)	2.276(2)	P(4)–Co–P(6)	55.6(1)
Co–P(6)	2.275(2)	P(5)–Co–P(6)	55.8(1)
P(4)–P(5)	2.111(3)	P(4)–P(5)–P(6)	59.8(1)
P(4)–P(6)	2.115(3)	P(5)–P(6)–P(4)	59.6(1)
P(5)–P(6)	2.130(4)	P(6)–P(4)–P(5)	60.5(1)

(b) Compound (2)

Co–P(1)	2.238(6)	P(1)–Co–P(2)	92.9(2)
Co–P(2)	2.195(6)	P(1)–Co–P(3)	95.5(2)
Co–P(3)	2.218(6)	P(2)–Co–P(3)	89.2(2)
Co–P(4)	2.272(6)	P(4)–Co–P(5)	55.6(2)
Co–P(5)	2.327(6)	P(4)–Co–Se	56.9(2)
Co–Se	2.403(4)	P(5)–Co–Se	56.7(2)
P(4)–P(5)	2.144(8)	P(4)–P(5)–Se	60.9(2)
P(4)–Se	2.228(6)	P(5)–Se–P(4)	57.3(2)
P(5)–Se	2.247(6)	Se–P(4)–P(5)	61.8(2)

resonances (Table 6) with an intensity ratio of 3 : 2. The more intense signal [33.30 and 32.70 p.p.m. for compounds (1) and (2) respectively] is assigned to the three phosphorus atoms of the ligand: it shows a co-ordination chemical shift (Table 6) comparable to that found for analogous cobalt complexes having tppme as a coligand.[1] The other signal [−210.90 (1), −145.50 p.p.m. (2)] has to be assigned to the two phosphorus atoms in the P$_2$X groups. The former resonance, strongly affected by the cobalt quadrupole moment, becomes sharper on cooling but it is not resolved into a fine structure even at −70 °C. The latter resonance is less affected by the cobalt quadrupole, decreasingly so, on going from the P$_2$S to the P$_2$Se derivative. In fact, the broad signal appearing at room temperature in the spectrum of compound (1) is resolved in a quartet ($J = 12$ Hz) at −70 °C, whereas a quartet ($J = 12$ Hz) is observed even at room temperature for compound (2); the latter is not subject to splitting or broadening on cooling to −70 °C.* The larger quadrupolar effects on the tppme resonance than on the P$_2$X resonance might be due to the involvement of the phosphine ligand in lower-energy molecular orbitals than the P$_2$X cyclic unit.[14] The same fact may be at the origin of the low sensitivity of the tppme chemical shift to replacement of the heteroatom in the P$_2$X group: the

Table 6. ^{31}P-{^{1}H} n.m.r. and electronic spectral data of the complexes

Compound	T/K	δ/p.p.m.[a]		^2J(P–P)/ Hz	ΔP[b]	v$_{max.}$/nm (ε/dm^3 mol^{-1} cm^{-1})
		P(phosphine)	P(P$_2$X)			
(1) [Co(tppme)(P$_2$S)]BF$_4$·C$_6$H$_6$	301	33.30 (br)	−210.90 (br)		58.55	440 (sh), 370 [c]
						440 (sh) (~800), 370 (1 600) [d]
	203	33.30 (br)	−210.90 (q)	12	58.55	
(2) [Co(tppme)(P$_2$Se)]BF$_4$·C$_6$H$_6$	301	32.70 (br)	−145.50 (q)	12	58.25	470 (sh), 380 [c]
						460 (sh) (~730), 370 (1 650) [d]
	203	32.70 (br)	−145.50 (q)	12	58.25	
[Co(tppme)(P$_3$)] [e,f]	203	38.16 (br) P(apical)	−276.21 (br) P(basal)		63.41	
P$_4$S$_3$ [e,g]		71 (q)	−120 (d)	86		
P$_4$Se$_3$ [e,h]		38 (q)	−106 (d)	85		

[a] Chemical shifts are relative to 85% H$_3$PO$_4$. Positive chemical shifts are downfield: br = broad, d = doublet, and q = quartet. The complexes were dissolved in CD$_2$Cl$_2$. [b] ΔP = δP$^{(co-ord.)}$ − δP$^{(free\ ligand)}$. [c] Absorption maxima for solid. [d] Absorption maxima for nitroethane solution. [e] ^{31}P n.m.r. data at room temperature for this molecule are reported for comparison purposes. [f] Ref. 1. [g] Ref. 16. [h] Ref. 8

The P$_2$Se group in compound (2) is affected by a similar type of disordering to that of the P$_2$S group in (1), although one of the three possible orientations of the P$_2$Se group is more populated than the other two (see footnote b to Table 4). In the most probable orientation the Se atom occupies the site of the ring which forms the longest contact distances with the rest of the cation. Both the distances within the P$_2$Se group, ranging from 2.144(8) to 2.247(6) Å, and the distances from this group to the metal atom, ranging from 2.272(6) to 2.403(4) Å, are considerably affected by the presence of the large Se atom in the heterocyclic ring, even though the effects of such asymmetry in bonding may be partly smeared out by the orientational disorder. A related asymmetry, never detected for cyclotriphosphorus complexes, is observed in the mode of bonding to the metal by the tppme ligand in (2). In fact, the Co–P(tppme) distances in this compound span a range [2.195(6)—2.238(6) Å] larger than usual,[14] the shortest Co–P(tppme) bond [Co–P(2) = 2.195(6) Å] being located in a *trans* position with respect to the site predominantly occupied by the Se atom in the co-ordination sphere.

In each of the above structures the BF$_4$ anion exhibits the usual effects of large thermal motion. There are no unusually short intermolecular contacts in either structure.

The ^{31}P-{^{1}H} n.m.r. spectra of the compounds exhibit two

tppme δ(^{31}P) values are indeed practically identical for complexes (1) and (2) (Table 6).

Each of the P$_2$X ^{31}P n.m.r. signals (Table 6) is considerably shifted upfield with respect to those of the corresponding P$_4$X$_3$ molecules.[8,16] Although the phosphorus atoms of P$_4$X$_3$ form with the chalcogen atom P–X–P moieties similar to the present P$_2$X triatomic units, they are however involved in higher-membered rings. The comparison with the ^{31}P resonances of the P$_2$X units suggests that the latter are strongly affected by the three-membered ring structure. Also the ^{13}C signals of cyclopropanes[17] and the ^{31}P signals of three-membered cyclophosphanes[18] are appreciably shifted upfield from the resonances of the corresponding higher-membered rings. In the case of the present P$_2$X units such upfield shift is particularly noticeable presumably as these units bear no other substituent than the π-bonded metal atom. The relative positions of the P$_2$X ^{31}P signals, the P$_2$Se occurring at lower

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* It has to be noted in this respect that the P$_3$ resonance in the spectrum of [Co(tppme)(P$_3$)][1] is unresolved even at −80 °C. It therefore essentially fits the above trend of increasing quadrupolar effects on the resonance of the P$_2$X group with decreasing atomic number of the X atom. The tppme resonance is not resolved either in the spectrum of the P$_3$ derivative.

field than P_2S, agree with the trend observed for heterocyclic three-membered phosphanes, which exhibit decreasing $\delta(^{31}P)$ values with increasing size of the heteroatom.[19]

The frequencies of the transitions, starting at *ca.* 440 nm for (1) and 470 nm for (2) in the electronic spectra of the compounds (Table 6) decrease slightly with increasing atomic number of the heteroatom in the P_2X ring. In spite of the fact that both compounds are cationic, such bands occur at lower energies than the corresponding bands (from 417 nm onward) in the spectrum of the neutral cyclotriphosphorus derivative $[Co(tppme)(P_3)]$.[14]

It should finally be stressed that the $[Co(tppme)(P_2X)]^+$ complexes described here are isoelectronic to the $[Ni(tppme)(P_3)]^+$ cation, which is obtained by reaction of P_4S_3 with a nickel(II) salt in the presence of tppme.[1] All of the above complexes in turn are isoelectronic to the neutral $[Co(tppme)(P_3)]$ complex, which is obtained by reaction of a cobalt(II) salt with P_4 under appropriate conditions and has been assigned the stable 18-electron configuration, on the basis of simple electron-counting procedures.[14] It may be noted in this connection that, although the mechanism of formation of the present compounds is not yet understood, an indication in this sense may be provided by the fact that the highest peaks in the mass spectra[20] of the P_4X_3 molecules are due to the P_3X^+ species isoelectronic with P_4, from which the triatomic fragments might originate.

Acknowledgements

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