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PX (X = O, S, Se, Te) and P_4Se as Ligands in Multinuclear Cp^R–Cobalt Complexes

Otto J. Scherer, Sascha Weigel, and Gotthelf Wolmershäuser

Fachbereich Chemie der Universität Kaiserslautern, Erwin-Schrödinger-Straße, D-67663 Kaiserslautern, Germany

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ABSTRACT: *The room temperature oxidation of* $[\{Cp''Co\}_3(\mu_3\text{-}P)_2]$ (**1**), $Cp'' = C_5H_3Bu^t_2\text{-}1,3$, *with the whole series of chalcogens affords besides the double-oxidized complexes* $[\{Cp''Co\}_3(\mu_3\text{-}PX)_2]$ (**2a***:* X = O, **2b***:* X = S, **2c***:* X = Se) *the mono-oxidation products* $[\{Cp''Co\}_3(\mu_3\text{-}P)(\mu_3\text{-}PX)]$ (**3a***:* X = Se, **3b***:* X = Te). *The reaction of* $[\{Cp^*Fe\}\{Cp''Co\}_2(P_4)(P)]$ (**4**) *with* $Se_{(grey)}$ *at 0°C gives the trinuclear complex* $[\{Cp^*Fe\}\{Cp''Co\}_2(P_4Se)(P)]$ (**5**) *with the hitherto unknown* P_4Se *ligand.* **2a,b** *were additionally characterized by X-ray crystal structure determinations.* © 1999 John Wiley & Sons, Inc. Heteroatom Chem 10: 622–626, 1999

INTRODUCTION

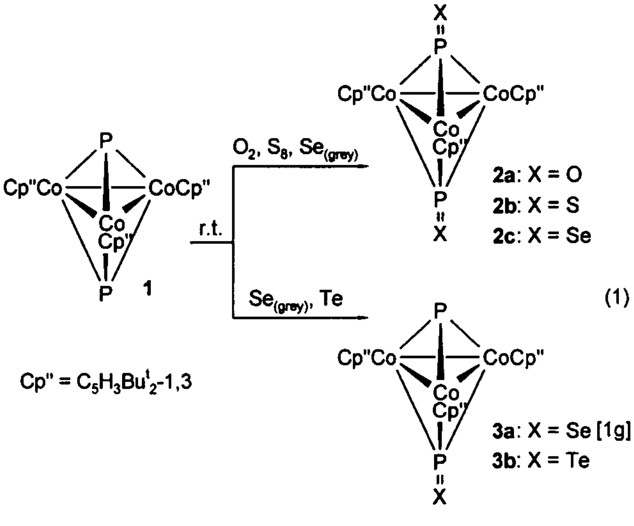
The coordinative stabilization of PX ligands, X = chalcogen, is a novel field in the chemistry of phosphorus with continuing interest. The preferred coordination mode is of the μ_3-PX type [1]. Until now, only one complex each is described with a terminal PO or PS ligand, respectively [2]. Also known are some examples with side-on coordinated PS [3], whereas only recently [1i,j], two cobalt complexes with μ_3-PSe ligands have been discovered. To the best of our knowledge, no compounds with P_4X; X = O, S, Se, as complex ligands are described.

RESULTS AND DISCUSSION

PX (X = O, S, Se, Te) as Ligands

The oxidation of $[\{Cp''Co\}_3(\mu_3\text{-}P)_2]$ (**1**) with chalcogens, according to Equation 1 (Scheme 1), affords the trinuclear cobalt complexes $[\{Cp''Co\}_3(\mu_3\text{-}PX)_2]$ (**2**) as well as $[\{Cp''Co\}_3(\mu_3\text{-}PX)]$ (**3**).

The following trends are remarkable. The reaction with O_2 or S_8 with **1** furnishes exclusively the dioxidation products **2a**, **b**, whereas reaction with grey selenium affords both **2c** and **3a**. On reaction



SCHEME 1

Correspondence to: Otto J. Scherer.

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Dedicated to Prof. Alfred Schmidpeter on the occasion of his 70th birthday.

X-ray crystal structure determinations.

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with tellurium, only one phosphorus atom of **1** is oxidized to yield **3b**.

Compounds **2** and **3** form black crystalline powders. The solubility in pentane or dichloromethane decreases from **2a** (PO) to the heavier chalcogen congeners (**2b, 2c, 3a, 3b**) and increases from **3** to the double-oxidized series **2**. The hitherto unknown PTe ligand could be coordinatively stabilized in compound **3b** (cf. Ref. [4]). Until now, no single crystals could be obtained. In solution, even at −28°C, **3b** eliminates elemental tellurium, a process already described for the system R_3PTe/R'_3P [5]. ^{1}H, ^{31}P, and IR ($\tilde{\nu}$(PX)) data are summarized in Table 1.

In comparison with the starting material **1** (δ ^{31}P = 1058.7 ppm) [1h], the oxidation products **2** and **3** show a distinct high-field shift (581.9 for **2c** to 530.5 for **3b** Table 1). For **2c** and **3a** ^1J(PSe) coupling constants of −1047 Hz and −981.3 Hz could be observed (cf. Ref. [1j]).

Crystal and Molecular Structures of the Double-Oxidized Complexes [{Cp″Co}$_3$(μ_3-PX)$_2$] (**2**)

The crystallographic data for complexes **2a**, **b** are compiled in Table 2. Table 3 contains selected bond lengths (A) and angles (°). Figure 1 shows the structure of [{Cp″Co}$_3$(μ_3-PO)$_2$] (**2a**) in the crystal.

In analogy to the starting material [{Cp″Co}$_3$(μ_3-P)$_2$] (**1**) [1h], the Co_3P_2 skeleton of **2a**, **b** consists of a trigonal bipyramid with the PX ligands in the axial

TABLE 2 Crystallographic Data for Complexes **2a,b**^{a}

	2a^b	*2b*^{c}
Formula	$C_{39}H_{63}Co_3O_2P_2$	$C_{39}H_{63}Co_3P_2S_2$
M_r	802.6	834.7
Crystal Size (mm)	0.66 × 0.26 × 0.18	0.58 × 0.56 × 0.28
Crystal System	monoclinic	triclinic
Space Group	C2/c	$P\bar{1}$
a(Å)	44.449(2)	10.4646(13)
b(Å)	11.6035(5)	11.1308(12)
c(Å)	35.192(2)	18.073(2)
α(°)	90	79.038(14)
β(°)	116.572(6)	87.811(14)
γ(°)	90	88.685(14)
V(Å^3)	16233.5(15)	2065.0(4)
Z	16	2
ρcalcd (g cm^{-3})	1.314	1.342
μ (mm^{-1})	1.321	1.395
2 θ range (°)	1.83–24.10	2.67–27.98
Measured Refl.	64612	35769
Independent Refl.	12867	9116
Refined Parameters	865	636
RI [7 > 2 σ (I)]	0.0339	0.0294
wR2 (All Data)	0.885	0.0772
Residual Electron Density [e Å^{-3}]	0.863/−0.624	0.507/−0.469

[a] Diffractometer: Stoe IPDS; Structure solution by direct methods, SHELXS-97; refinement: full-matrix least-squares methods against F^2 (SHELXL-97) [10]. [b] There are two independent molecules in the asymmetric unit which differ only slightly.
[c] The Cp″ ligands show rotational disorder.

TABLE 1 ^{1}H, ^{31}P NMR, and IR Data of Complexes **2a,b,c, 3a,b,** and **5** (Cp″ = $C_5H_3Bu^t_2$-1,3)

	[{Cp″Co}$_3$(μ_3-PX)$_2$] (**2**)	*[{Cp″Co}$_3$(μ_3-P)(μ_3-PX)]* (**3**)	*[{Cp*Fe}{Cp″Co}$_2$(P_4Se)(P)]* (**5**)
^{1}H^a δ [ppm]	**2a**: X = O 4.22 (s, 6H), 4.16 (s, 3H), 1.29 (s, 54H) **2b**: X = S 4.28 (s, 6H), 4.19 (s, 3H), 1.34 (s, 54H) **2c**: X = Se [1i] 4.40 (s, br, 9H), 1.39 (s, 54H)	**3a**: X = Se [1i] 4.36 (s, br, 9H), 1.41 (s, 54H) **3b**: X = Te 4.21 (s, 6H), 4.17 (s, 8H), 1.46 (s, 54H)	4.85 (s, 1H), 4.63 (s, 1H), 4.56 (s, 2H), 4.32 (s, 1H), 4.11 (s, 1H), 1.78 (s, 15H), 1.41 (s, 9H), 1.39 (s, 18H), 1.25 (s, 9H)
^{31}P{^{1}H}^{b} δ [ppm] ^nJ(PP) [Hz]	**2a**: 538.5 (s, 2P) **2b**: 586.2 (s, 2P) **2c**: 581.9 (s, 2P) ^1J(PSe) = −1047 [1i]	**3a**: 1143.8 (d, 1P), 565.7 (s, br, 1P), ^2J(PP) = 56.6, ^1J(PSe) = −981.3 [1i] **3b**: 1130.6 (d, 1P), 530.5 (d, 1P), ^2J(PP) = 61.1,	ABMXY-Spin System [11] 611.5 (dd, P_A), 518.8 (d, P_B), 307.4 (dd, P_M), 9.6 (dd, P_X), −129.0 (m, P_Y) ^2J (P_AP_M) = 30.5, ^1J (P_BP_Y) = −94, ^1J (P_MP_Y) = −167, ^2J (P_AP_X) = 83, ^1J(P_XP_Y) = −265
IR^c $\tilde{\nu}$(PX) [cm^{-1}]	**2a**: 1182 (X = O) **2b**: 643 (X = S) **2c**: 438 (X = Se)	**3a**: 436 (X = Se) **3b**: 402 (X = Te) (attempted assignment)	483 (X = Se)

[a] WP-200 (Bruker), ^{1}H (C_6D_6, TMS int., 200 MHz); [b] ^{31}P{^{1}H} (C_6D_6, 85% H_3PO_4 ext., 81 MHz; s, singlet; d, doublet; dd, doublet of doublet; m, multiplet; br, broad); [c] n-hexane.

TABLE 3 Selected Bonds Lengths (Å) and Angles (°) for Complexes **2a,b**

	$[\{Cp''Co\}_3(\mu_3\text{-}PO)_2]$ (**2a**)^a	$[\{Cp''Co\}_3(\mu_3\text{-}PS)_2]$ (**2b**)
Co1-Co2	2.6506(5)	2.6632(15)
Co1-Co3	2.5725(5)	2.6656(14)
Co2-Co3	2.6085(5)	2.6034(12)
Co1-P1	2.1309(8)	2.1460(14)
Co2-P1	2.1251(8)	2.1671(16)
Co3-P1	2.1156(8)	2.1316(15)
Co1-P2	2.1242(8)	2.1499(17)
Co2-P2	2.1233(8)	2.1368(14)
Co3-P2	2.1171(8)	2.1409(12)
P1-O1(S1)	1.482(2)	1.9435(16)
P2-O2(S2)	1.480(2)	1.9337(12)
P1···P2	2.989	3.014
$Cp''_{(centr.)}$-Co1	1.71	1.73
$Cp''_{(centr.)}$-Co2	1.71	1.72
$Cp''_{(centr.)}$-Co3	1.70	1.73
Co1-Co2-Co3	58.563(13)	60.80(4)
Co2-Co1-Co3	59.899(14)	58.49(4)
Co1-Co3-Co2	61.537(14)	60.71(4)
P1-Co1-P2	89.25(3)	89.13(6)
P1-Co2-P2	89.43(3)	88.91(6)
P1-Co3-P2	89.85(3)	89.75(4)
Co1-P1-O1(S1)	132.6	138.0
Co2-P1-O1(S1)	136.5	132.2
Co3-P1-O1(S1)	135.1	133.6
Co1-P2-O2(S2)	136.1	133.9
Co2-P2-O2(S2)	134.8	139.2
Co3-P2-O2(S2)	133.2	130.2

^{a}Two independent molecules that do not differ significantly.

position and the Cp″Co fragments in the equatorial position (Figure 1). According to the Wade–Mingos electron counting rules [6], the clusters belong to the closo type with $n + 1 = 6$ skeleton electron pairs (SEPs). The mean values of the Co–Co bond lengths are 2.53 for **1**, 2.61 for **2a**, and 2.64 Å for **2b** with an increasing trend on going from the pristine complex **1** to the compounds with PX ligands (**2a**: X = 0; **2b**: X = S). The six Co–P bond distances (Table 3) lie in the range of 2.12 to 2.13 (**2a**) and 2.13 to 2.17 Å (**2b**); values that are slightly shorter than those of **1** (2.16–2.17 Å [1h]) have μ_3-P ligands. This type of contraction was also found on the oxidation of $[\{Cp^4Ni\}_2(\mu_3\text{-}P)_2\{W(CO)_4\}]$(**6**) [1a,b] to $[\{Cp^4Ni\}_2(\mu_3\text{-}PX)_2\{W(CO)_4\}]$ (**7**) [1a,b, X = 0; 3b, X = S] and $[\{CpFe\}_4(P_2)_2]$ (**8**) to $[\{CpFe\}_4(P_2X_2)_2]$ (**9**), X = S, Se [7], as well as to tetraphosphacubanes [8].

P1-O1 and P2-O2 have bond lengths of 1.48 Å each, whereas the corresponding P1-S1 and P2-S2 distances are 1.94 and 1.93 Å (Table 3). These results are in good agreement with values found for other complexes with PO and PS ligands [1a–h, 2]. The average Co–P–X bond angles are 134.7 (**2a**, X = 0), 134.5 (**2b**, X = S) and 135.7° in $[\{Cp''Co\}_3(\mu_3\text{-}P)(\mu_3\text{-}PSe)]$ (**3a**) [1i].

P_4Se as Ligand

The mild oxidation of $[\{Cp^*Fe\}\{Cp''Co\}_2(P_4)(P)]$ (**4**) [1h] with grey selenium affords, according to Equation 2 (Scheme 2), the trinuclear cluster **5** with a P_4Se and a μ_3-P ligand.

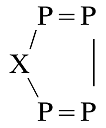
Compound **5** forms a brown microcrystalline powder that is poorly soluble in hexane but dissolves readily in toluene and still better in dichloromethane. Until now, all attempts to obtain suitable crystals for an X-ray structure determination failed. Fortunately, the structure of the synthon **4** is known. Its P_5Co_2Fe cluster skeleton consists of a distorted cubane-like arrangement (Figure 3) with a tripodal P_4 (trigonal pyramid) and a μ_3-P ligand [1h].

An ABMXY-spin system (Figure 2, Table 1) was derived for complex **5** using ^{31}P-NMR.

Formally, the oxidation of P1 in the educt (Figure 3) gives the P_XSe part of the P_4Se ligand in **5** with the expected high-field shift (9.6 ppm, Table 1). Contrary to Ref. [1i] and in agreement with findings in Ref. [1j], no ^1J(PSe) coupling could be detected. Compared to the ^{31}P-NMR shift of 562 ppm for P4 in complex **4** (Figure 3) [1h], atom P_A in **5**, which is also coordinated to three L_nM fragments, shows a still further down-field shift of 611.5 ppm (Table 1).

In the mass spectrum, no peak for the parent ion was found. EIMS (70 eV): *m/z* = 818.4(100) [M-Se]$^+$, 787.3(52) [M-P-Se]$^+$, 581.5(25) [M-{CoCp″}-Se]$^+$ (31 VE-triple decker $[\{Cp^*Fe\}\{Cp''Co\}P_5]^+$?) and 519.7 (37) [M-2P-{CoCp″}-Se]$^+$ (29 VE-triple decker $[\{Cp^*Fe\}\{Cp''Co\}P_3]^+$?).

Calculations were performed on different structures/constitutions; the ring

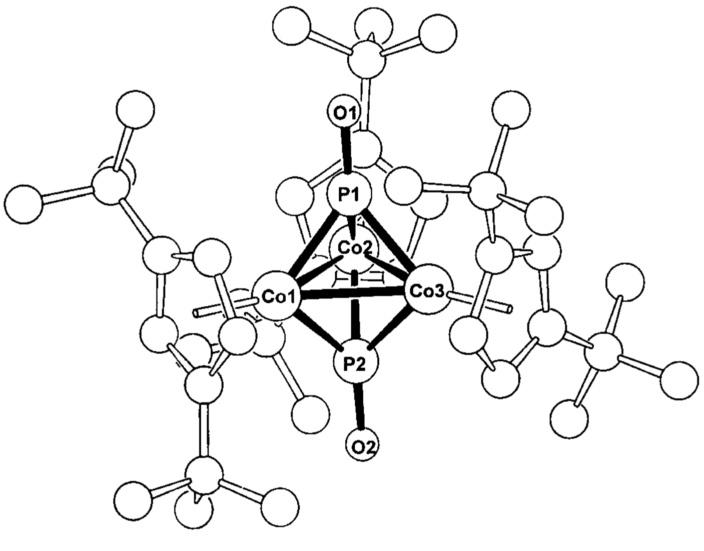


is the most stable constitution when it adopts a planar conformation [9].

EXPERIMENTAL

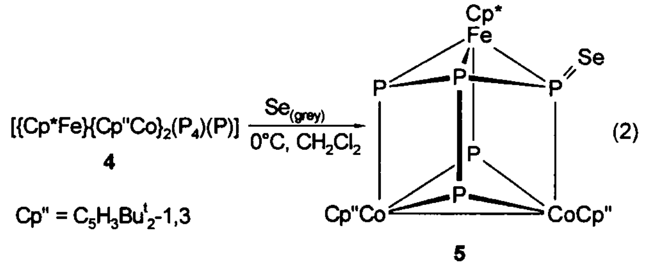
General

All experiments were performed under an argon atmosphere in dry solvents. $[\{Cp''Co\}_3(\mu_3\text{-}P)_2]$(**1**)[1h] and $[\{Cp^*Fe\}\{Cp''Co\}_2(P_4)(P)]$(**4**) [1h] as well as $[\{Cp''Co\}_3(\mu_3\text{-}PSe)_2]$(**2c**)[1i] and $[\{Cp''Co\}_3(\mu_3\text{-}P)(\mu_3\text{-}PSe)]$(**3a**)[1i] were synthesized according to the procedures cited in the literature. IR spectra were re-

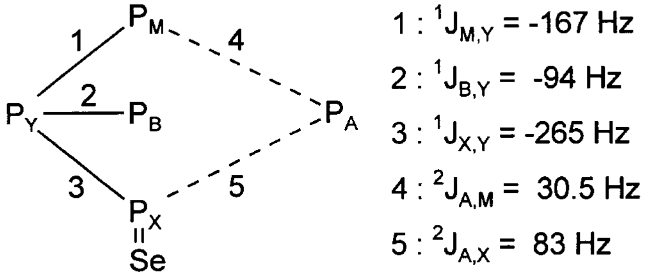


2a

FIGURE 1 Molecular structure of **2a** in the solid state.



SCHEME 2



1 : $^1J_{M,Y}$ = -167 Hz

2 : $^1J_{B,Y}$ = -94 Hz

3 : $^1J_{X,Y}$ = -265 Hz

4 : $^2J_{A,M}$ = 30.5 Hz

5 : $^2J_{A,X}$ = 83 Hz

FIGURE 2 ABMXY-spin system of [{Cp*Fe}{Cp″CO}$_2$(P$_4$Se)(P)](**5**).

corded on a Perkin-Elmer 881. MS spectra: MAT 90, Finnigan.

[{Cp″Co}$_3$(μ$_3$-PO)$_2$] (2a)

A solution of 100 mg (0.13 mmol) [{Cp″Co}$_3$(μ_3-P)$_2$] (1) in 20 mL toluene was stirred at room temperature in an open vessel. After 30 minutes, the color of the reaction mixture change from red-violet to orange-red. After 18 hours, the solvent was evaporated under an oil-pump vacuum, the residue was dissolved in ca. 5 mL dichloromethane, ca. 1 g silylated silica gel was added, and the mixture was concentrated until it flowed freely. Column chromatography (column 10 × 1.0 cm, petroleum ether, water cooling), with petroleum ether affords an orange-red fraction of **2a**. Yield: 91 mg (87%, referred to **1**).

$C_{39}H_{63}Co_3P_2O_2$: Calcd: 802.6. Anal. calcd: C, 58.36; H, 7.91. Found: C, 57.91; H, 7.76%.

[{Cp″Co}$_3$(μ$_3$-PS)$_2$] (2b)

80 mg (0.1 mmol) **1** and 3.3 mg (0.013 mmol) S_8 was dissolved in 20 mL toluene and stirred at room temperature for 24 hours. For further preparative details, see compound **2a**. A 50:1 mixture of petroleum ether/toluene gave **2b** as a red-violet fraction. Yield 58 mg (70%, referred to **1**).

$C_{39}H_{63}Co_3P_2S_2$: calcd: 834.8. Anal. calcd: C, 56.12; H, 7.61. Found: C, 56.54; H, 7.73%.

[{Cp″Co}$_3$(μ_3-P)(μ_3-PTe)] (3b)

110 mg (0.14 mmol) **1** was dissolved in 20 mL dichloromethane. After addition of 182 mg (1.14 mmol) grey tellurium, the reaction mixture was stirred at room temperature. After only one hour, its color changed from red-violet to orange-red. After 24 hours, the mixture was worked up as described for compound **2a**. Petroleum ether eluted 53 mg (49%) unreacted starting material **1** as a red-violet fraction.

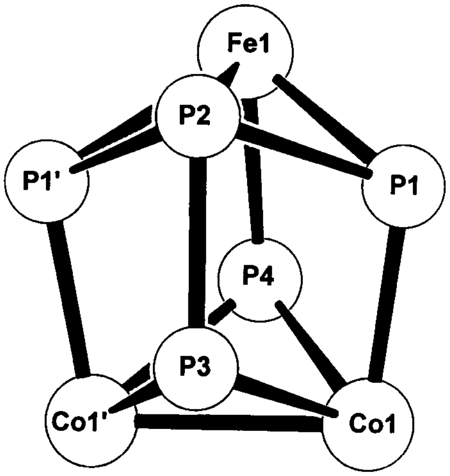


FIGURE 3 Skeleton structure of [{Cp*Fe}{Cp″Co}$_2$(P$_4$)(P)](**4**). Cp* and Cp″ ligands have been omitted for clarity [1h].

With dichloromethane, an orange-red fraction of **3b** was eluted. Yield of *3b*: 55 mg (44%, referred to **1**).

$C_{39}H_{63}Co_3P_2Te$: calcd: 898.2. Anal. calcd: C, 52.13; H, 7.07. Found: C, 52.41; H, 7.24%.

*[[Cp*Fe][Cp″Co]$_2$(P$_4$Se)(P)]* (**5**)

250 mg (0.31 mmol) [[Cp*Fe][Cp″Co]$_2$(P$_4$)(P)] (**4**) [1f] and 480 mg (6.1 mmol) grey selenium was dissolved in 40 mL dichloromethane and stirred for two hours at 0°C. The ^{31}P-NMR control showed that all signals of **4** disappeared. For further preparative details, see compound **2a**. The column used was 15 × 1.0 cm. With a 4:1 mixture of petroleum ether/toluene, **5** was eluted as a dark-brown fraction. A mixture of petroleum ether/diethylether (1:3) eluted a further dark-brown fraction, which, until now, was not characterized unequivocally. Yield of **5**: 80 mg (29 %, referred to **4**).

$C_{36}H_{57}Co_2FeP_5Se$: calcd: 897.4. Anal. calcd: C, 48.18; H, 6.40. Found: C, 48.87; H, 6.53.

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