$[Cp_4Fe_4(E_2)_2]$ Clusters with Triangulated Dodecahedral Fe_4E_4 Skeletons (E = P, As)☆

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The thermolysis of $[CpFe(CO)_2]_2$ (**1**) and P_4 or As_4 affords the iron clusters $[Cp_4Fe_4(E_2)_2]$, E = As (**2a**), P (**2b**), the Fe_4E_4 skeleton of which consists of a triangulated dodecahedron. S_8 and gray Se oxidize the P_2 ligands of **2b** with formation of $[Cp_4Fe_4(P_2X_2)_2]$, X = S (**3a**), Se (**3b**), complexes with the hitherto unknown P_2X_2 ligands. **2a, b** and **3a, b** have been characterized by X-ray crystallography.

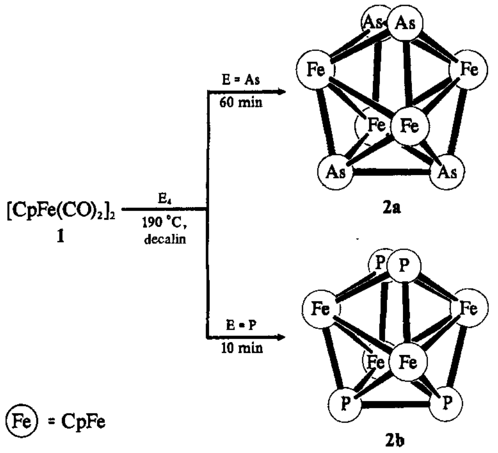
Among the P_n and As_n ligands the P_2 and As_2 building blocks occupy a key position[1]. Thus, for example, P_2 could recently be incorporated into a tantalum trinuclear complex[2]; furthermore, two P_2 ligands could be connected to a P_4 chain within the coordination sphere of cobalt[3].

Concerning the 8-corner polyhedra, there are several examples in the coordination chemistry (ML_8, $M(\widehat{LL})_4$ etc.) where the ligand sphere forms as a polyhedron a triangulated dodecahedron[4]. "Empty" polyhedra of this structural type are very rare and have been characterized by X-ray structural analysis only for molecules possessing an A_8, A_7B, A_6B_2, and A_4B_4 skeleton (cf. Table 3).

Synthesis of Clusters $[Cp_4Fe_4(E_2)_2]$, E = As (2a), P (2b)

The thermolysis of $[CpFe(CO_2)_2]_2$ (1) with As_4 or P_4, gives in satisfactory and moderate yield the iron clusters **2a** and **2b** (Scheme 1) which contain two μ_4-$\eta^{2:2:1:1}$ ligands As_2 and P_2, respectively. Both complexes can be handled in air for a short period. They are poorly soluble in benzene, but they dissolve easily in dichloromethane. In solution, **2** decomposes on exposure to air.

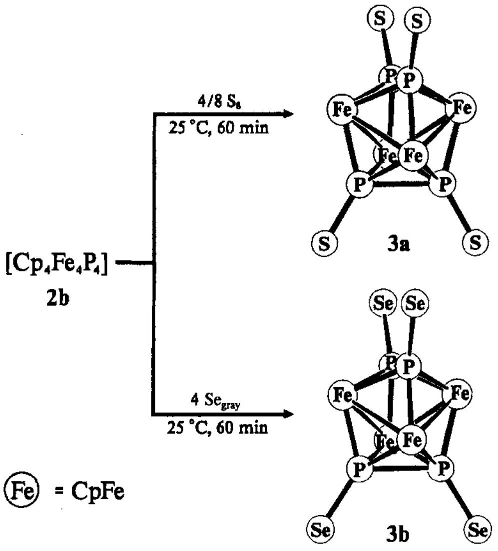
Scheme 1. Synthesis of Fe Clusters **2a**, **b**



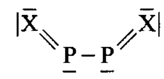
Oxidation of P_2 to P_2X_2 Ligands (X = S, Se) in the Case of $[Cp_4Fe_4(P_2)_2]$ (2b)

The two P_2 fragments in **2b** may be oxidized even at room temperature with S_8 and gray selenium to the ligands P_2X_2 (X = S, Se) (Scheme 2) which, to our knowledge, are unknown. For these ligands, the structural type I, among others can be discussed.

Scheme 2. Oxidation of **2b** to **3a**, **b**



Ab initio calculations on different uncomplexed (free) P_2X_2 isomers (X = O, S, Se) revealed that **I** is energetically very unfavourable[5].



I

The iron clusters **3a, b** are sparingly soluble in benzene but dissolve well in dichloromethane. They are air-stable as solids.

[+] Crystal structural analyses.

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Discussion of the Molecular Structures of 2 and 3

Molecular structures in the crystal are compiled in Figures 1–3, selected bond lengths and angles in Table 1 and crystallographic data in Table 2.

Table 1. Selected bond lengths [Å] and angles [°] of the complexes **2a, b** and **3a, b**

	$[Cp_4Fe_4(E_2)_2]$ **2a** (E = As)	$[Cp_4Fe_4(E_2)_2]$ **2b** (E = P)	$[Cp_4Fe_4(E_2X_2)_2]$ **3a** (E = P, X = S) [a]	$[Cp_4Fe_4(E_2X_2)_2]$ **3b** (E = P, X = Se) [a]
E1-E2	2.539(2)	2.310(4)	2.374(8)	2.399(9)
E3-E4	2.540(2)	2.302(4)	2.361(7)	2.376(9)
average	2.54	2.31	2.37	2.39
Fe1-E2	2.303(2)	2.193(3)	2.155(6)	2.162(8)
Fe2-E3	2.298(2)	2.195(3)	2.171(6)	2.166(8)
Fe3-E1	2.287(2)	2.199(3)	2.160(7)	2.184(7)
Fe4-E4	2.297(2)	2.192(3)	2.164(6)	2.166(7)
average	2.30	2.195	2.16	2.17
Fe1-E3	2.381(2)	2.267(3)	2.251(5)	2.215(7)
Fe1-E4	2.378(2)	2.259(3)	2.224(6)	2.222(7)
Fe2-E1	2.383(2)	2.268(4)	2.227(6)	2.226(7)
Fe2-E2	2.376(2)	2.259(3)	2.240(5)	2.218(7)
Fe3-E3	2.379(2)	2.261(3)	2.236(6)	2.239(7)
Fe3-E4	2.384(2)	2.257(3)	2.213(5)	2.237(8)
Fe4-E1	2.379(2)	2.261(3)	2.221(6)	2.247(8)
Fe4-E2	2.376(2)	2.258(3)	2.217(6)	2.255(7)
average	2.38	2.26	2.23	2.23
Fe1-Fe2	2.768(2)	2.659(2)	2.713(4)	2.713(5)
Fe2-Fe3	2.750(3)	2.662(3)	2.730(4)	2.714(5)
Fe3-Fe4	2.736(2)	2.667(2)	2.721(4)	2.737(5)
Fe4-Fe1	2.758(2)	2.660(3)	2.736(4)	2.726(5)
average	2.75	2.66	2.725	2.72
Fe4-Fe1-Fe2	78.02(6)	78.90(6)	77.1(1)	77.2(1)
Fe3-Fe2-Fe1	78.20(5)	79.08(6)	77.5(1)	77.5(1)
Fe4-Fe3-Fe2	78.70(7)	78.72(6)	77.1(1)	77.0(1)
Fe3-Fe4-Fe1	78.60(7)	78.97(5)	77.3(1)	76.8(1)
average	78.4	78.9	77.3	77.1
E2-E1-Fe3	101.43(7)	104.05(14)	103.9(3)	103.0(3)
E1-E2-Fe1	102.20(7)	104.35(14)	103.8(3)	103.5(3)
E4-E3-Fe2	102.07(7)	103.89(13)	102.8(3)	103.2(3)
E3-E4-Fe4	101.49(7)	104.56(13)	104.9(3)	103.9(3)
average	101.8	104.2	103.8	103.4

[a] P1–S1 1.965(9), P2–S2 1.944(9), P3–S3 1.920(9), P4–S4 1.965(8), average 1.95. P1–Se1 2.096(7), P2–Se2 2.089(7), P3–Se3 2.103(7), P4–Se4 2.115(7), average 2.10.

Table 2. Crystallographic data for **2a, b** and **3a, b**

	2a	**2b**	**3a**	**3b**
Formula	$C_{20}H_{20}As_4Fe_4$	$C_{20}H_{20}Fe_4P_4$ × 1/3 CH_2Cl_2	$C_{20}H_{20}Fe_4P_4S_4$ × 1 CH_2Cl_2	$C_{20}H_{20}Fe_4P_4Se_4$ × 1 CH_2Cl_2
Mol. mass	783.5	636.0	820.8	1008.4
Crystal size [mm]	0.1×0.22×0.22	0.12×0.17×0.3	0.25×0.13×0.1	0.27×0.07×0.07
Crystal system	orthorhombic	rhombohedral	monoclinic	monoclinic
Space group	*Pbca*	*R*3	$P2_1/c$	$P2_1/n$
a [Å]	13.330(3)	14.268(2)	13.427(2)	9.710(2)
b [Å]	17.650(4)	$a = b = c$	13.856(2)	20.293(4)
c [Å]	18.050(4)	$\alpha = \beta = \gamma$	15.174(2)	15.206(3)
β [°]		114.67(1)	91.85(1)	90.36(3)
V [$Å^3$]	4247(2)	1673.4(4)	2822(1)	2996(1)
Z	8	3	4	4
$d_{calcd.}$ [$g \cdot cm^{-3}$]	2.451	1.893	1.880	2.186
Measured reflections	3157	6797	8025	6669
Independent reflections	2784	4266	6478	5278
Observed reflections [$I > 2.5\,\sigma(I)$]			2887	1885
2Θ range [°]	2.22-22.52	2.25-25.91	1.52-27.51	1.67-25.01
Refined parameters	251	233	211	211
Diffractometer [a]				
*R*1	0.0952 [b]	0.1119 [b]	0.096 [c]	0.073 [c]
*wR*2	0.0993 [b]	0. 1203 [b]	0.119 [c]	0.084 [c]
Residual electron density [$e \cdot Å^{-3}$]	1.41	0.54	1.37	1.04
μ [mm^{-1}]	8.87	2.92	2.74	7.16
Transmission				
min.	0.27	0.46	0.47	0.14
max.	0.39	0.62	0.73	0.38

[a] Measuring temperature 298 K, Mo-K_α, Enraf-Nonius-CAD-4 for **2b**, Siemens-P4 for **2a**, **3a**, **b**. – [b] All data, refinement according to F^2. – [c] *R* values for observed reflections, refinement according to *F*.

Figure 1. X-ray crystal structure of $[(CpFe)_4(As_2)_2]$ (**2a**); only one Cp ligand is shown in **2a** and **3a**; the other Cp ligands have been omitted for clarity

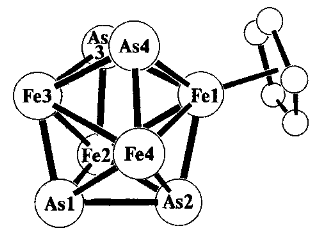


Figure 2. Crystal structure of $[(CpFe)_4(P_2)_2]$ (**2b**)

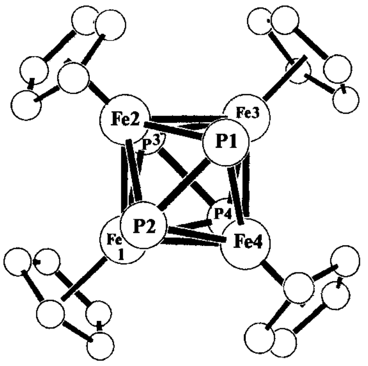
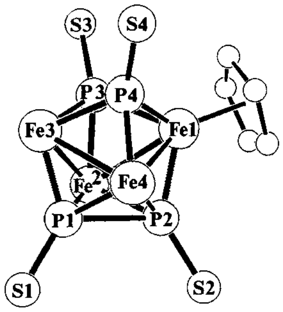


Figure 3. Crystal structure of $[(CpFe)_4(P_2S_2)_2]$ (**3a**)



In all four clusters, the triangulated dodecahedral skeleton is formally formed by two orthogonally inserted trapezoids (Fe3, E1, E2, Fe1 and Fe2, E3, E4, Fe4) which, on the one hand, leads to a compressed Fe_4- and on the other hand to a stretched E_4 "tetrahedron". In the former case, the species contains four bonding Fe–Fe distances (mean values: 2.75 Å for **2a**, 2.66 Å for **2b**, 2.725 Å or **3a** and 2.72 Å for **3b**) and two non-bonding distances greater than 3.38 Å. Compared with the starting compound **2b** (cf. Scheme 2), the oxidation products **3a**, **b** exhibit slightly longer Fe–Fe bonds (Δ ≈ 0.07 Å). In bridged iron dinuclear complexes, the Fe–Fe bond lengths were found to be in the range of 2.37–3.05 Å[6]. In cubane – like $[\{CpFe\}_4(\mu_3\text{-}S)_4]$, the two bonding Fe–Fe distances are 2.65 Å[7]; oxidation of this cluster to the dication $[Cp_4Fe_4S_4]^{2+}$ results in the formation of two additional Fe–Fe bonds and an elongation of the bond length to 2.83 Å[8]. The E_4 "tetrahedron" exhibits four non-bonding E–E distances greater than 3.37 Å and two bonding ones. The mean values are: for **2a** (E = As) 2.54, for **2b** (E = P) 2.31, for **3a** (E = P) 2.37, and for **3b** (E = P) 2.39 Å, bond lengths that are known for arsenic[9] and phosphorus compounds[10]. In $[Cp_4Co_4P_4]$, the strongly distorted Co_4P_4 cubane skeleton contains 4 shorter P···P distances with an average of 2.57 Å[11].

In the four clusters, the Fe–E bonds exhibit the four shorter distances required for a triangulated dodecahedron (18 edges: 12 × Fe–E, 4 × Fe–Fe, 2 × E–E), i.e. mean values: 2.30 for **2a** (E = As), 2.195 for **2b** (E = P), 2.16 for **3a** (E = P), and 2.17 Å for **3b** (E = P), likewise eight longer distances are required (average: 2.38 for **2a**, E = As, as well as 2.26, 2.23, and 2.23 Å for **2b** and **3a**, **b**, (E = P). Both sets differ by approximately 3% (Table 1).

In [$(\mu_3\text{-As})_2\{Fe(CO)_3\}_3$], which has a trigonal-bipyramidal As_2Fe_3 skeleton, the Fe–As bond lengths are 2.331(3) to 2.376(3) Å[12]; the corresponding Fe–P distances in [$(\mu_4\text{-P})_2\{Fe(CO)_3\}_3\{Mn(CO)_2Cp\}_2$] are 2.241(9) to 2.317(9) Å[13].

The four atoms of the P_2X_2 ligands of **3a**, **b** lie almost in a plane. The torsion angles are as follows: X2–P2–P1–X1 = 4.5° for **3a** (X = S) and 0.4° for **3b** (X = Se); X3–P3–P4–X4 = 0.5° for **3a** and 1.0° for **3b**). The mean values of α for the units $\mathrm{X}\diagdown_{\mathrm{P-P}}$ differ only slightly in the case of **3a** (X = S, α = 120.9°) and **3b** (X = Se, α = 122.4°). $\bar{d}$(P=S) and $\bar{d}$(P=Se) are in the typical double bond range with 1.95 Å (**3a**) and 2.10 Å (**3b**). This was also found for P_4S_5 (1.94 Å[14]) and P_4Se_5 (2.12 Å[15]). A comparison of the ^1J(PSe) and ^2J(PSe) coupling constants of **3b** with data found in the literature[16] indicates that the new P_2Se_2 ligand is not easily classified.

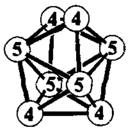
A slight shortening of the Fe–Cp(cent.) distance (mean values: **2a**, **b**: 1.74 Å; **3a**, **b**: 1.72, 1.71 Å) is observed on going from **2a**, **b** to **3a**, **b**.

Table 3. Examples of molecules with triangulated dodecahedral skeletal structure characterized by X-ray structural analysis and NMR data of clusters **2a**, **b** and **3a**, **b**

Molecule	SEP	Structure type [a]	Connectivity of the atoms in the skeleton of the polyhedron [b]		^1H NMR [c]	^{31}P NMR [c]	Ref.
			4	5			
B_8Cl_8 (**4**)	8	*n*	4 x B	4 x B			[17]
[$(CpCo)_4B_4H_4$] (**5**)	8	*n*	4 x B	4 x Co			[18]
[$(CpFe)_4As_4$] (**2a**)	8	*n*	4 x As	4 x Fe	4.11 (s, 20 H)		this
[$(CpFe)_4P_4$] (**2b**)	8	*n*	4 x P	4 x Fe	4.29 (s, 20 H)	848 (s, 4 P)	work
[$(CpFe)_4(P_2S_2)_2$] (**3a**)	8	*n*	4 x P	4 x Fe	4.40 (s, 20 H)	495 (s, 4 P)	this
[$(CpFe)_4(P_2Se_2)_2$] (**3b**)	8	*n*	4 x P	4 x Fe	4.38 (s, 20 H)	477 (s, 4 P) [d]	work
[B_8H_8]$^{2-}$ (**6**)	9	*n* + 1	4 x B	4 x B			[19]
[CB_7H_7I]$^-$ (**7**)	9	*n* + 1	3 x B	4 x B			
			1 x C				[20]
[$C_2B_6H_6(CH_3)_2$] (**8**)	9	*n* + 1	2 x B	4 x B			
			2 x C				[21]
[$(CpNi)_4B_4H_4$] (**9**)	10	*n* + 2	4 x Ni	4 x B			[22]
[$(iPr_3PCu)_4Te_4$] (**10**)	10	*n* + 2	4 x Te	4 x Cu			[23]

SEP = skeletal electron pairs. – [a] According to the Wade-Mingos electron counting rules[24]: *n* = hypercloso[25], *n* + 1 = closo, *n* + 2 = nido. – [b] Terminal ligands not considered. – [c] In $CHCl_3$. – [d] $^1J(^{31}P^{77}Se) = -596$, $^2J(PSe) = \pm 82$ Hz.

Figure 4. Triangulated dodecahedron with atom connectivities



Comparative Studies of Molecules Containing a Triangulated Dodecahedral Skeleton

Application of the Wade-Mingos electron counting rules[24] to the molecules listed in Table 3 leads to the expected (*n* + 1)-closo structural type of a triangulated dodecahedron only for the boron-rich examples $B_8H_8^{2-}$ (**6**)[19], [CB_7H_7I]$^-$ (**7**)[20], and [$C_2B_6H_6\text{-}1,7\text{-}(CH_3)_2$] (**8**)[21]. The number of electrons available for the skeleton from single atoms and for fragments decreases as follows: four for Te (complex **10**)[23]; three for CpNi (complex **9**)[22], P and As (complexes **2a**, **b** and **3a**, **b**, this work) as well as CH and CR (complexes **7** and **8**); two for BR (complexes **4**[17], **5**[18], **6**, **7**, and **8**) and CpCo (complex **5**)[18]; and one for CpFe (complexes **2a**, **b** and **3a**, **b**) and R_3PCu (complex **10**)[23]. Polyhedra containing different skeletal atoms or skeletal complex fragments were characterized by X-ray structural analysis. The results show that the building blocks providing the most skeletal electrons occupy, up to now and without exception, the vertices with connectivity 4 in the triangulated dodecahedron. The more electron-deficient units are located in the vertices with connectivity 5 (see Table 3 and Figure 4). Complexes **5** and **9** were the subject of various theoretical studies[26] also dealing in detail with the problem of the *n*, (*n* + 1) and (*n* + 2) structural type in the triangulated dodecahedron.

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Experimental

All experiments were performed under argon in anhydrous solvents. ^{1}P-, ^{31}P-NMR spectra: Bruker AC 200 and AMX 400, FT-IR: Perkin-Elmer 16 PC. Starting materials: [$CpFe(CO)_2]_2$ (**1**)[27], As_4[28].

[$Cp_4Fe_4(As_2)_2$] (**2a**): To a freshly prepared solution of yellow arsenic, As_4 (ca. 13 mmol), in 200 ml of boiling decalin 1950 mg (5.5 mol) of [$CpFe(CO)_2]_2$ (**1**) was added with stirring. After 1 h, the CO bands in the IR spectrum had disappeared. After the mixture was cooled with an ice-bath, the gray arsenic was separated by means of a D3 frit. The solvent was evaporated under oil pump vacuum, the residue dissolved in 60 ml of diethyl ether, then ca. 10 g of Al_2O_3 was added and the mixture dried until it was free-flowing. The mixture was eluted with petroleum ether/diethyl ether (5:1) on a column (35 × 3 cm, Al_2O_3, activity grade II) to afford a pale yellow first fraction containing ca. 15 mg of $FeCp_2$ followed by a green fraction of **2a** (yield 590 mg, 27%). Elution with petroleum ether/diethyl ether (1:1) furnished 460 mg (24%) of [$\{CpFe(\mu\text{-}CO)\}_3(\mu_3\text{-As})$] (**11**). Complex **2a** was recrystallized from pentane/diethyl ether (2:1). – $C_{20}H_{20}As_4Fe_4$ (783.5): calcd. C 30.66, H 2.57; found C 30.15, H 2.51. – **11**: $C_{18}H_{15}AsFe_3O_3$ (521.8): calcd. C 41.43, H 2.90; found C 41.06, H 3.03. – IR (xylene): ν(CO) = 1808 (s), 1760 (m) cm^{-1}. – ^{1}H NMR ($CHCl_3$): δ = 4.45 (s, 15H).

[$Cp_4Fe_4(P_2)_2$] (**2b**): To 250 ml of boiling decalin, 1.0 g (8.1 mmol) of P_4, 0.5 g (1.90 mmol) of Ph_3P as stabilizer of an intermediate, and 6.0 g (17 mmol) of **1** were added successively with stirring. Then stirring was continued under reflux for 10 min. The mixture turned green but the CO bands of **1** had not yet completely disappeared. Work-up of the mixture was carried out largely as with **2a**. Elution with diethyl ether/dichloromethane (1:1 to 1:3)

afforded 800 mg (15%, related to **1**) of **2b** as a green fraction. From the first fraction a small amount (ca. 20 mg) of $FeCp_2$ was also isolated. – $C_{20}H_{20}Fe_4P_4$ (607.7): calcd. C 39.53, H 3.31; found C 39.81, H 3.26.

[$Cp_4Fe_4(P_2S_2)_2$] (**3a**): To a stirred solution of 170 mg (0.28 mmol) of **2b** in 50 ml of THF 54 g (0.21 mmol) of S_8 was added at room temperature and the mixture was stirred for 60 min. After the solvent had been evaporated under vacuum, the black residue was washed three times each with 20 ml of *n*-hexane. Recrystallization (diffusion apparatus) from *n*-hexane/dichloromethane furnished 190 g (83%, related to **2b**) of **3a** as green-black crystals. – $C_{20}H_{20}Fe_4P_4S_4 \cdot 1\ CH_2Cl_2$ (820.8): calcd. C 30.73, H 2.69; found C 30.92, H 2.70%.

In the IR spectrum (KBr pellet), we tentatively assign [in accordance with, e.g., free PS[29a] $\nu(P{=}S)$ = 729 cm^{-1}, P_4S_{10}[29b] $\nu(P{=}S)$ = 690 cm^{-1}, and [{CpFe(CO)$_2$}PPh(S)][29c] $\nu(P{=}S)$ = 597 cm^{-1}] the band at 676 cm^{-1} (vs) of **3a** to $\nu(P{=}S)$.

[$Cp_4Fe_4(P_2Se_2)_2$] (**3b**): To a solution of 160 mg (0.26 mmol) of **2b** in 30 ml of dichloromethane 80 mg (1.01 mmol) of grey selenium was added at room temp. The mixture was stirred for 60 min during which time it turned red. The solvent was evaporated under vacuum and the residue dissolved in a small amount of CH_2Cl_2. Then 3 g of silica gel (activity grade III) was added and the mixture was dried until it was free-flowing. Elution with diethyl ether/dichloromethane (5:1) on a column (30 × 3 cm, petroleum ether, silica gel) afforded a red-brown fraction containing **3b** which was isolated and recrystallized from dichloromethane. Yield: 190 mg (72%, related to **2b**). – $C_{20}H_{20}Fe_4P_4Se_4 \cdot 1\ CH_2Cl_2$ (1008.4): calcd. C 25.01, H 2.19; found C 25.03, H 2.22.

In the IR spectrum (KBr pellet) we tentatively assign [in accordance with, e.g., P_4Se_{10}[30], $\nu(P{=}Se)$ = 500 cm^{-1}] the band at 468 cm^{-1} (vs) to $\nu(P{=}Se)$.

Notes concerning the crystal structure analyses[31] of complexes **3a**, **b**: All studied crystals of both compounds exhibited only a very weak diffraction (36 and 44%, respectively, of the independent reflections were considered observed). Moreover, all crystals of **3b** exhibited side grows leading to reflections with negative intensities. The carbon atoms of the two structures were only refined isotropically, the hydrogen atoms were not localized and not included in the refinement. Although both structures show no peculiarities concerning their bond lengths and bond angles the latter should not be overinterpreted.

☆ Dedicated to Professor *Herbert Schumann* on the occasion of his 60th birthday.

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