Mixed-Element Ligands

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An Approach to Mixed P_nAs_m Ligand Complexes[**]

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Dedicated to Professor Bernt Krebs on the occasion of his 75th birthday

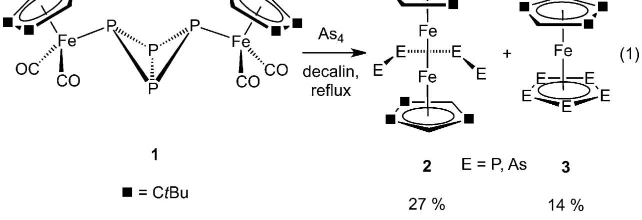
Abstract: *The reaction of a P_4 butterfly complex with yellow arsenic yields the largest mixed P_nAs_m ligand complexes synthesized to date. $[\{Cp'''Fe(CO)_2\}_2(\mu,\eta^{1:1}\text{-}P_4)]$ reacts with As_4 to yield $[\{Cp'''Fe\}_2(\mu,\eta^{4:4}\text{-}P_nAs_{4-n})]$ and $[Cp'''Fe(\eta^5\text{-}P_nAs_{5-n})]$. Mass spectrometry together with NMR spectroscopy and X-ray crystallography give clear evidence about the arrangement of the E positions within the cyclo-E_5 and E_4 moieties of the products. Moreover, the results of DFT calculations agree well with the experimental determined outcomes. By coordinating the E_4 complex $[\{Cp'''Fe\}_2(\mu,\eta^{4:4}\text{-}P_nAs_{4-n})]$ with CuCl, a rearrangement of the E positions occurs in favor with a preferred phosphorus coordination towards copper atoms in the resulting 1D polymeric chain.*

Since their discovery in 1969,[1] unsubstituted heavier Group 15 element ligand complexes have become an important class of compounds at the intersection of main-group and transition-metal chemistry.[2] As the Group 15 atoms are only bound to themselves or to the metal, they still bear free electron pairs that are capable of coordinating Lewis acidic metal centers. Besides their use in catalytic processes,[3] several examples of polymers,[4] supramolecular structures,[5] and even spherical aggregates[6] exist, which are built up mainly by P_n ligand complexes.

Until now, many E_n ligand complexes are known in which E represents either phosphorus or arsenic, but only a few examples exhibit mixed $E_nE'_m$ ligands (E, E′ = P, As, Sb). The first example was reported by Mays et al., who reacted the anion $[\{CpMo(CO)_2\}_2(\mu,\eta^{1:1}\text{-}PH_2)]^-$ with $AsCl_3$ to obtain the mixed E_2 ligand complex $[\{CpMo(CO)_2\}_2(\mu,\eta^{2:2}\text{-}PAs)]$.[7] Two years later, in our group, $[CpCr(CO)_2(\eta^3\text{-}P_2E)]$[8] (E = As, Sb) was synthesized by the reaction of $[\{CpCr(CO)_2\}_2(\mu,\eta^{2:2}\text{-}P_2)]$ with ECl_3. Cummins et al. have shown some examples of mixed P_nAs_m ligand complexes by using the interpnictide molecule P_3As[9] in reactions with various transition-metal complexes and organic compounds.[10] The formed P_3As ligand complexes are the largest mixed E_n ligand complexes known to date. However, the quest for novel sources to build up such compounds and, especially, larger moieties was still open. Interestingly, yellow arsenic has not been used as an alternative source instead of the hitherto used $AsCl_3$ (AsP_3 is also synthesized from $AsCl_3$), which is obviously due to the extreme difficulty of preparing and handling As_4.

Herein, by using yellow arsenic, we present the synthesis and characterization of novel mixed P_nAs_m ligand complexes with an E_4 and a *cyclo*-E_5 unit, respectively, as the largest examples of this rare class of compounds. Additionally, the E_4 ligand complex is used to build up a 1D polymeric chain that shows the different coordination behavior of phosphorus and arsenic towards Lewis acids.

It is known that the thermolysis of the P_4 butterfly complex $[\{Cp'''Fe(CO)_2\}_2(\mu,\eta^{1:1}\text{-}P_4)]$ (**1**) (Cp‴ = 1,2,4-tri-*tert*-butylcyclopentadienyl) with white phosphorus leads to the P_4 and *cyclo*-P_5 ligand complexes $[\{Cp'''Fe\}_2(\mu,\eta^{4:4}\text{-}P_4)]$ (**2a**) and $[Cp'''Fe(\eta^5\text{-}P_5)]$ (**3a**).[11] Recent results[12] indicate that $[\{Cp'''Fe\}_2(\mu,\eta^{1:1}\text{-}P_1)(\mu,\eta^{3:3}\text{-}P_3)]$ could be an intermediate in this reaction and that it undergoes further fragmentation and reaggregation under harsh thermolytic conditions. The formation of a P_3-containing fragment was postulated earlier by Scherer and co-workers, who observed the formation of $[Cp'''Fe(\eta^5\text{-}P_3C_2Ph_2)]$ during the co-thermolysis of **1** with the acetylene derivative C_2Ph_2.[13] To obtain mixed E_4 and *cyclo*-E_5 ligand complexes, **1** was treated with yellow arsenic in boiling decalin until the carbonyl bands of **1** disappeared from the IR spectrum [Eq. (1)]. After chromatographic work-up, a reddish-brown solid **2** was obtained as a mixture of the complexes **2a**, $[\{Cp'''Fe\}_2(\mu,\eta^{4:4}\text{-}P_3As)]$ (**2b**) and $[\{Cp'''Fe\}_2(\mu,\eta^{4:4}\text{-}P_2As_2)]$ (**2c**), and a green solid **3** was isolated as a mixture of the complexes **3a**, $[Cp'''Fe(\eta^5\text{-}P_4As)]$ (**3b**), $[Cp'''Fe(\eta^5\text{-}P_3As_2)]$ (**3c**), and $[Cp'''Fe(\eta^5\text{-}P_2As_3)]$ (**3d**).



The mass spectrum of **2** shows peaks corresponding to the molecules **2a**, **2b**, and **2c**. Compounds **2** crystallize as a mixture of individual compounds in the space group $P\bar{1}$ with two independent molecules in the asymmetric unit.[14] In these molecules, every position E shows an occupancy

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Table 1: Phosphorus and arsenic occupancy in the two independent $[\{Cp'''Fe\}_2(\mu,\eta^{4:4}\text{-}P_nAs_{4-n})]$ molecules, determined by X-ray structure analysis.

	Molecule A				Molecule B			
position	E1	E2	E3	E4	E5	E6	E7	E8
ratio P [%]	65	85	100	97	95	94	84	85
ratio As [%]	35	15	0	3	5	6	16	15

disorder with a variable P/As content (Table 1) and leads to the sum formula $[\{Cp'''Fe\}_2(\mu,\eta^{4:4}\text{-}As_{0.48}P_{3.52})]$.

The molecular structure of **2** (Figure 1) reveals a cisoid E_4 chain bridging two {Cp‴Fe} fragments. The E2–E3 distance is with 2.393(1) Å longer than the E1–E2 and E3–E4 distances with 2.200(1) Å and 2.098(1) Å, which is consistent with the isolobal analogy between the E_4^{2-} chain and butadiene and the consequential double bonding character of the E1–E2 and E3–E4 bonds. Owing to the As content on positions E1, E2, and E4, the E–E bonds are longer than the corresponding bonds in **2a** (2.385(2), 2.081(2), and 2.094(2) Å).[11] As the As content on the positions E1 and E2 is higher than for the positions E3 and E4, the E1–E2 bond is 0.1 Å longer than the E3–E4 bond.

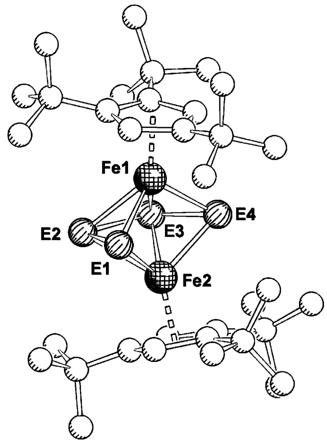

Figure 1. Molecular structure of $[\{Cp'''Fe\}_2(\mu,\eta^{4:4}\text{-}P_nAs_{4-n})]$ (**2**). Only molecule A is displayed; hydrogen atoms are omitted for clarity.

In the ^1H NMR spectrum of **2**, three sets of signals at $\delta =$ 1.22–1.25, 1.28–1.29, and 4.43–4.56 ppm can be detected that represent the two slightly different *tert*-butyl groups and the aromatic ring protons of the Cp‴ ligand. Each set consists of three peaks with an integral intensity ratio of 1:0.32:0.14. As the increasing arsenic content in the E_4^{2-} chain has an influence on the chemical shift of the Cp‴ protons, these peaks can be assigned to the molecules **2a**, **2b**, and **2c** and therefore can be used to determine the relative amount of the different species **2**. Thus, the composition of **2** is 68% of **2a**, 22% of **2b**, and 10% of **2c** leads to the sum formula $C_{34}H_{58}Fe_2As_{0.42}P_{3.58}$ and compares very well to the composition calculated from crystal structure analysis. In the $^{31}P\{^1H\}$ NMR spectrum, five broad signals can be observed that do not show any fine structure upon cooling to 193 K. For **2a**, this broadening has been explained with a fluxional bonding within the P_4^{2-} chain and the intermediate formation of a 30 VE triple-decker complex.[15] The signal at $\delta = 92$ ppm can be assigned to complex **2a**.[11] The signals at $\delta = 59$ and 112 ppm as well as the signals at $\delta = -13$ and 212 ppm show equal integral intensities. Further assignment of these signals to the compounds **2b** and **2c** is not possible owing to the broadening and missing fine resolution for determining coupling constants.

To investigate the different constitutional isomers of **2b** and **2c** further, calculations were carried out.[16] For **2b**, the occupation of a terminal position of the E_4 chain with arsenic is favored by 0.5 kJ mol^{-1} over an occupation of an inner position. In the case of **2c**, four different isomers are possible, of which AsAsPP is the energetically most favored. The isomers PAsAsP, AsPAsP, and AsPPAs are higher in energy by 3.7, 7.1, and 9.4 kJ mol^{-1}, which compares well to the results of the X-ray structure analysis (Table 1).

In the mass spectrum of **3**, the individual complexes $[Cp'''Fe(\eta^5\text{-}P_5)]$ **3a**, $[Cp'''Fe(\eta^5\text{-}P_4As)]$ (**3b**), $[Cp'''Fe(\eta^5\text{-}P_3As_2)]$ (**3c**), and $[Cp'''Fe(\eta^5\text{-}P_2As_3)]$ (**3d**) can be detected. The compounds crystallize as a mixture in the space group $P2_1/c$.[14] Again, the molecule in the asymmetric unit shows an allocation disorder of phosphorus and arsenic at the positions E (Table 2). The calculated molecular formula in the crystal is $C_{17}H_{29}FeAs_{0.54}P_{4.46}$.

Table 2: Phosphorus and arsenic occupancy in $[Cp'''Fe(\eta^5\text{-}P_nAs_{5-n})]$ **3** determined by X-ray structure analysis.

	Position				
	E1	E2	E3	E4	E5
ratio P [%]	83	86	80	98	98
ratio As [%]	17	14	20	2	2

In the molecular structure of **3** (Figure 2), the *cyclo*-E_5 and the Cp‴ ligand are almost coplanar (deviation 2°). The average E–E bond (2.146(1) Å) is longer than that found in pure **3a** (2.08 Å)[11] and shorter than the As–As distances found in $[Cp^*Fe(\eta^5\text{-}As_5)]$ (2.32 Å)[17] because of the mixed P/As population of the ring positions.

A similar disorder of occupancy was described for $[CpFe(\eta^5\text{-}C_2tBu_2AsP_2)W(CO)_5]$.[18] The P–As bond in this

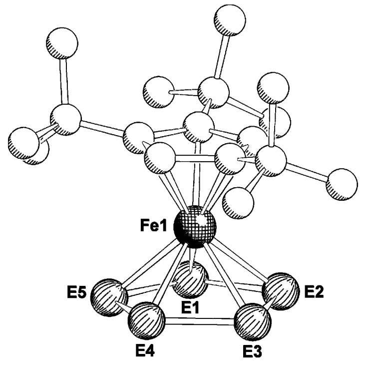

Figure 2. Molecular structure of $[Cp'''Fe(\eta^5\text{-}P_nAs_{5-n})]$ (**3**). Hydrogen atoms are omitted for clarity.

pseudo E_n-ligand complex (2.161(3) Å) is slightly longer than in **3**. This may be caused by the coordinating $\{W(CO)_5\}$ fragment. The shortest bond in **3** (2.1078(7) Å) is found between positions E4 and E5 with the lowest arsenic content.

The ^{1}H NMR spectrum shows three sets of signals at $\delta =$ 1.04–1.07, 1.17–1.20, and 3.76–3.94 ppm for the Cp‴ ligand consisting of four peaks each. The integral intensity ratio of these peaks is 1:0.63:0.18:0.02 that can be found in any of the three signal sets (Figure 3). The most upfield shifted signal of every group can be assigned to **3a**.[11] The rising arsenic content in the *cyclo*-E_5 ligand seems to be responsible for the staggering of the signals, so they can further be assigned to the complexes **3b**, **3c**, and **3d**. This again allows the determination of the total composition of **3** by using the ratio of integral intensities. The mixture of complexes **3** consists of 54% **3a**, 34% **3b**, 10% **3c**, and 2% **3d**, which adds up to the total molecular formula of $C_{17}H_{29}FeAs_{0.6}P_{4.4}$; this also corresponds well with that found in the crystal structure.

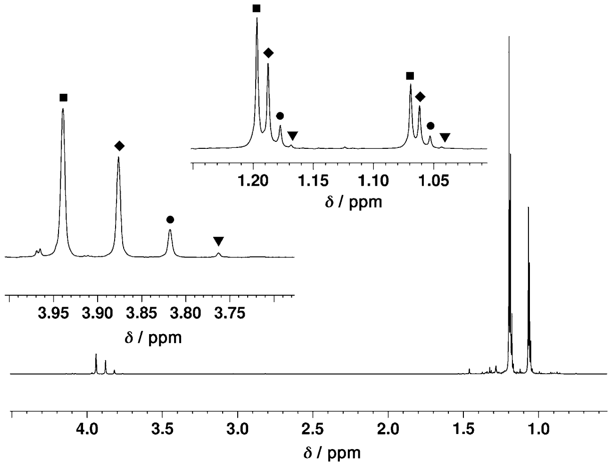

Figure 3. ^{1}H NMR spectrum (300 K in C_6D_6) of **3** with marked signals for **3a** (■), **3b** (◆), **3c** (●), and **3d** (▼).

The $^{31}P\{^1H\}$ NMR spectrum of **3** shows a singlet at $\delta =$ 165 ppm that can be assigned to **3a**[11] as well as higher-order spectra of **3b** and **3c** (AA′MM′ and AA′M spin system, respectively) that are partially superimposed. The simulation of the higher-order spectra[16] points to a neighbored constitution of the three phosphorus atoms in **3c**, but no conclusions can be drawn about the constitution of **3d**.

Furthermore, calculations show a neighbored constitution of the P atoms being favored by 6.1 kJ mol^{-1} for **3c** and 5.5 kJ mol^{-1} for **3d**. This is in good agreement with the occupancy of As calculated during the crystal structure refinement, which also shows the highest arsenic content at neighbored positions (Table 2).

As P_n- and As_n-ligand complexes prefer different coordination modes towards Lewis acidic metal fragments (σ- versus π-coordination),[4–6,19] it was of interest to investigate the coordination behavior of these mixed complexes. Therefore, **2** was reacted with two equivalents of CuCl to yield the polymeric 1D chain compound $[\{Cp'''Fe\}_2(\mu,\eta^{4:4:1:1}\text{-}E_4)\{Cu(\mu\text{-}Cl)\}_2(MeCN)]_\infty\cdot(CH_2Cl_2)_2$ (**4**) as crystalline brown bars. X-ray structure analysis[14] of these crystals reveals an undulated chain in which the $[\{Cp'''Fe\}_2(\mu,\eta^{4:4}\text{-}E_4)]$ units are linked together by Cu_2Cl_2 four-membered rings (Figure 4). Whereas one of the two copper atoms bears an additional acetonitrile ligand to complete its coordination sphere, the other copper atom is only three-fold coordinated, which is due to the large steric demand of the Cp‴ ligands. In contrast to **2**, only the two non-coordinating positions E2 and E3 show an arsenic content of 10 and 30%, respectively, whereas only phosphorus occupies the coordinating positions 1 and 4. This leads to a molecular formula of $[\{Cp'''Fe\}_2(\mu,\eta^{4:4:1:1}\text{-}As_{0.4}P_{3.6})\{Cu(\mu\text{-}Cl)\}_2(MeCN)]_\infty$. The occupancy pattern is inverted compared to **2** in which the terminal positions showed the highest arsenic content. This may be explained by phosphorus being the harder Lewis base compared to arsenic. That makes an interaction of phosphorus with the rather hard Lewis acid copper more reasonable. As **2** shows a dynamic behavior in solution (see above), the molecule can rearrange itself and form the energetically most favored polymeric chain. Thus, the coordination to Lewis acids can be used as a method to influence the constitution in these larger mixed P_nAs_m ligand complexes and may be used to separate them.

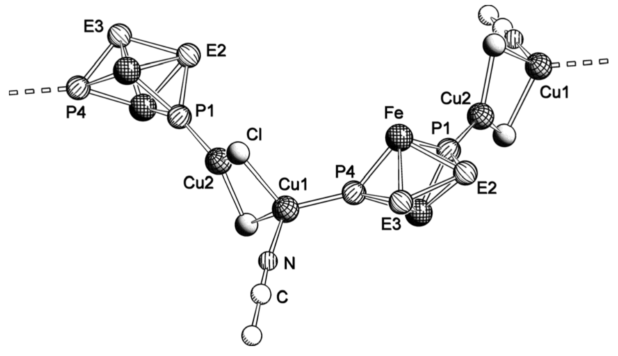

Figure 4. Section of the 1D structure of $[\{Cp'''Fe\}_2(\mu,\eta^{4:4:1:1}\text{-}E_4)\{Cu(\mu\text{-}Cl)\}_2(MeCN)]_\infty$. Hydrogen atoms and Cp‴ ligands are omitted for clarity.

The analogous all-phosphorus polymer $[\{Cp'''Fe\}_2(\mu,\eta^{4:4:1:1}\text{-}P_4)\{Cu(\mu\text{-}Cl)\}_2(MeCN)]_\infty$ (**5**)[4b,20] exhibits a similar undulated chain motif as observed in **4** with slightly longer E–E bond lengths (2.136(2), 2.149(2), and 2.382(2) Å) than the P–P distances in **5** (2.096(2), 2.102(2), and 2.372(2) Å), because of the partial arsenic population in **4**. The Cu1–P4 and Cu2–P1 distances of 2.214(2) and 2.151(2) Å are slightly shorter than the corresponding distances in **5** (2.229(1) and 2.163(1) Å).

In conclusion, we were able to extend the sparely investigated class of mixed P_nAs_m ligand complexes by two new examples revealing the largest mixed E_n moieties synthesized to date. As a new As source for such purposes, yellow arsenic was used in the reaction with $[\{Cp'''Fe(CO)_2\}_2(\mu,\eta^{1:1}\text{-}P_4)]$ to yield $[\{Cp'''Fe\}_2(\mu,\eta^{4:4}\text{-}P_nAs_{4-n})]$ and $[Cp'''Fe(\eta^5\text{-}P_nAs_{5-n})]$ as well. Calculations confirm the occupancy of the arsenic positions, which are in agreement with the obtained values by the X-ray structural analysis and with the atom arrangements determined by NMR spectroscopy. Moreover, $[\{Cp'''Fe\}_2(\mu,\eta^{4:4}\text{-}P_nAs_{4-n})]$ was used for the synthesis of a 1D polymer in which only the phosphorus atoms coordinate to the Lewis acids, revealing a different arrangement of atoms as found in the starting material. The different coordination tendencies of phosphorus and arsenic within one molecular building block could lead to novel coordination patterns and make them interesting for the construction of unprecedented coordination polymers and macromolecules.

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[14] The crystal structure analyses were performed either on an OXFORD Diffraction Gemini R Ultra CCD diffractometer or an OXFORD Diffraction Supernova CCD diffractometer using $Cu_{K\alpha}$ radiation (1.54178 Å). The structures were solved with the program SIR-97;[21] full-least-squares refinement on F^2 in SHELXL-97[22] was performed with anisotropic displacement parameters for all non-H atoms. The mixed P/As occupancy in **2**, **3**, and **4** were refined using free variables together with positional and displacement constraints (EXYZ and EADP) and fixed displacement parameters. After fixing the P/As content the displacement parameters were refined. This procedure was repeated until the values for P/As population and displacement parameters did not change any more during the refinement cycle. The hydrogen atoms were located in idealized positions and refined isotropically according to the riding model. **2**: $C_{34}H_{58}As_{0.42}Fe_2P_{3.58}$, $M_r = 1447.08$, crystal dimensions $0.117 \times 0.101 \times 0.067\ mm^3$, triclinic space group $P\bar{1}$ (No. 2), $a = 10.4598(2)$, $b = 15.2245(3)$, $c = 24.4120(5)$ Å, $\alpha = 72.234(2)$, $\beta = 88.072(2)$, $\gamma = 75.386(2)°$, $V = 3578.37(13)$ Å^3, $Z = 2$, $T = 123(1)$, $\rho_{calcd} = 1.343\ g\,cm^{-3}$, $\mu = 8.632\ mm^{-1}$, 26236 reflections collected, 14042 unique reflections ($R_{int} = 0.0212$), 764 parameters, $R_1 = 0.0248$, $wR_2 = 0.0589$. **3**: $C_{17}H_{29}As_{0.54}FeP_{4.46}$, $M_r = 467.97$, crystal dimensions $0.220 \times 0.130 \times 0.050\ mm^3$, monoclinic space group $P2_1/c$ (No.14), $a = 9.0468(2)$, $b = 25.6814(4)$, $c = 10.1456(2)$ Å, $\beta = 115.818(2)°$, $V = 2121.89(8)$ Å^3, $Z = 4$, $T = 123(1)$, $\rho_{calcd} = 1.465\ g\,cm^{-3}$, $\mu = 9.781\ mm^{-1}$, 21483 reflections collected, 3706 unique reflections ($R_{int} = 0.0265$), 222 parameters, $R_1 = 0.0251$, $wR_2 = 0.0611$. **4**: $C_{75}H_{128}As_{0.8}Cl_{10}Cu_4Fe_2N_2P_{7.2}$, $M_r = 2172.81$, crystal dimensions $0.246 \times 0.057 \times 0.037\ mm^3$, orthorhombic space group *Pbcn* (No.60), $a = 24.7652(7)$, $b = 16.6870(3)$, $c = 23.6559(6)$ Å, $V = 9776.0(4)$ Å^3, $Z = 4$, $T = 123(1)$, $\rho_{calcd} = 1.476\ g\,cm^{-3}$, $\mu = 9.772\ mm^{-1}$, 26862 reflections collected, 8495 unique reflections ($R_{int} = 0.0372$), 415 parameters, $R_1 = 0.0618$, $wR_2 = 0.1950$. CCDC 954182 (**2**), CCDC 954183 (**3**), and CCDC 954184 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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