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Iron β -diiminate complexes with As₂-, As₄- and As₈-ligands⁺

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Different substituents at the β -diiminato ligand in low-valent [LFe(tol)] (L = β -diiminato) complexes fundamentally change their reactivity towards yellow arsenic. By using dmp (2,6-dimethylphenyl) as flanking groups, the tetranuclear complexes [(LFe)₄As₈] (L = L¹ (1), L² (2)) are isolated. For dipp (2,6-diisopropylphenyl) substituted ligands, dinuclear complexes [(LFe)₂(cyclo-As₄)] (L = L³ (3a), L⁴ (4a)) are obtained. Not only the choice of the ligand impacts the product formation, but also the temperature of the crystallization can shift their ratio in the solid state.

Group 15 element ligand complexes have become an important class of compounds at the intersection of main-group and transition-metal chemistry.¹ While in the past decades, extensive investigations towards the isolation of polyphosphorus compounds have been carried out, the number of polyarsenic ligand complexes still remains limited.² Most of the reported compounds are stabilized by cyclopentadienyl or strongly donating CO ligands.³ Recently, β-diiminato transitionmetal(I) systems have attracted attention as they enable the activation of yellow arsenic (As₄) under remarkably mild conditions.⁴ Thermodynamically unstable, but kinetically stable compounds were accessible and gave insight into the subsequent reactivity of As4 towards transition metal compounds. The first reported β-diiminato polyarsenic complex was $[(L^4Cu)_2As_4]$ (A), which contains an intact As₄ tetrahedron (Scheme 1).⁵ Recently, we reported about more electron deficient, binuclear cobalt complexes $[(LCo)_2As_4]$ (L = L³ (B), L² (C), L^{1} (**D**)), which in dependency of their used ligands and the corresponding Co---Co distance in the solid state, stabilize various rectangular (in **B**), prismatic (in **C**) or asterane-like (in **D**) As₄-ligands.⁴ The influence of ligand substituents on the product formation was also recognized in Fe^I-mediated P₄

activations, which yielded different dinuclear products $[(L^4Fe)_2P_4]$ or $[(L^3Fe)_2(P_2)_2]$, if dipp (2,6-diisopropylphenyl) flanking groups are used. However, for dmp (2,6-dimethylphenyl) substituted systems, exclusively tetranuclear $[(LFe)_4P_8]$ ($L = L^1$, L^2 (E)) with a realgar-like $[P_8]^{4-}$ core were obtained.⁶ However, for the heavier congener, antimony, this crucial influence of the 2,6-position of the aromatic substituents was not confirmed. Recently, the isostructural $[(LMg)_4Sb_8]$ ($L = L^4$, L^5 (F))⁷ was reported, which is supported by dipp as well as mes (2,4,6trimethylphenyl; L^5) substituted ligands. Therefore, the question arises about the reaction products of As_4 with β -diiminato iron(1) precursors in general and about the substituent dependency at the β -diiminato ligand towards the formed arsenic moiety in particular.

Herein, we report about the reactivity of yellow arsenic towards four [(LFe)(tol)] (L = L¹, L², L³, L⁴) complexes. Dependent from their distinct steric and electronic properties, different tetranuclear products $[(LFe)_4As_8]$ (L = L¹ (1), L² (2)) were obtained, as well as different dinuclear complexes $[(LFe)_2(cyclo As_4)]$ (L = L³ (3a), L⁴ (4a)) and $[(L^3Fe)_2(As_2)_2]$ (3b). These results confirm the decisive influence of the ligand's 2,6-substituents (Me $\nu s.$ ⁱPr). Moreover, they show the importance of the crystallization temperature on the solid-state structure composition of such highly dynamic systems (*vide infra*).



Scheme 1 Selected examples of E_n ligand (E = P, As, Sb) complexes supported by the β -diketiminato (L) ligand system.

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All reactions were performed under rigorous exclusion of light and under comparable conditions: A solution of approx. 200 mg [LFe(tol)] (L = L¹, L², L³, L⁴) in 10 mL toluene was transferred onto a freshly prepared load of purified yellow arsenic (excess).⁸ The reaction mixture was stirred at ambient temperature for 15 – 60 minutes. The solvent was removed in vacuum and the remaining solid was stored (at least) overnight in order to complete the desired decomposition of unreacted yellow arsenic into grey arsenic. The remaining solid was dissolved in Et₂O or toluene and filtered over Celite in order to remove the formed grey arsenic. After investigation of the reaction solution by ¹H NMR spectroscopy and FD-mass spectrometry, the solution was concentrated and stored at 8 °C or -30 °C for crystallization.

The reactions of [LFe(tol)] (L = L¹, L²) with As₄ leads to the formation of two tetranuclear and isostructural products $[(LFe)_4As_8]$ (L = L¹ (1), L² (2)) in 3% and 9% for 1 and 2, respectively. Both compounds are highly soluble in toluene and are red-brown in color. LIFDI mass spectrometry as well as elemental analysis (for 2) confirms their molecular composition. Both complexes are paramagnetic in solution. Compound 2 has a magnetic moment (μ_{eff}) of 5.62 μ_{B} in C₆D₆ solution.⁹ In the ¹H NMR spectrum of 1 in C₆D₆ solution, a signal pattern is detected between 311.15 and -22.82 ppm corresponding to a half of the ligand, which suggests a D_{2d} symmetry on the NMR time scale.

Single-crystal X-ray structural analysis reveal that the molecular structures of 2.2.5 toluene and 1-toluene are isostructural (Fig. 1 for 1). Both compounds contain a realgar-like $[As_8]^{4-}$ ligand coordinating to four [LFe] (L = L¹ (1), L² (2)) fragments. The coordination geometry of the Fe metal centres in 1 and 2, respectively, is best described as distorted tetrahedral. All As–As



Fig. 1 Core structure of 1 in crystals of 1-toluene (hydrogen and carbon atoms are omitted for clarity; thermal ellipsoids are drawn at 50% probability level). A representation of 1 with its complete ligands is shown in the inset.

distances are in the range of 2.4379(5)-2.4430(5) Å in 1 and 2.4250(3)-2.4423(3) Å in 2; and therefore, are in line with As-As single bonds (for comparison: As-As single bond in yellow arsenic determined by electron diffraction: 2.435(4)¹⁰ and 2.44(3)¹¹ Å, by DFT calculations:¹² 2.437 Å). The distance between the bridgehead arsenic atoms are between 2.4929(5) and 2.4973(3) Å, which corresponds to a moderately elongated As-As single bond. Those findings agree with previously reported As-As bond lengths in [{Cp^{'''}Fe(CO)₂}₂{Cp^{'''}Fe(CO)}₂ $(\mu_4 - \eta^{1:1:2:2} - As_8)$ (G), [{Cp*Cr(CO)}_3]_4($\mu_4 - \eta^{1:1:1:1} - As_8$)] (H) and [(Cp*₂Sm)₄($\mu_4 - \eta^{1:1:1:1:1:1:1:1:As_8$)] (I), which are the only examples for realgar-type $[As_8]^{4-}$ ligand complexes so far.^{8,13} While the coordination mode in I is similar to that found in 1 and 2, this differs in **G** and **H**. The As–As distances within their $[As_8]^{4-}$ ligands are not significantly changed by the different nature of the metal centers (Fe or Cr), their coordination modes ($\eta^1 vs$. $\eta^{1:1}$) or the supporting ligand systems (Cp^R vs. L¹, L²). A detailed comparison is given in Table S3 in ESI.[†]

Changing the aromatic substituent in 2,6-position from Me to the more bulky ⁱPr, the reactions of [LFe(tol)] (L = L³, L⁴) with As₄ leads to formation of only dinuclear products [(LFe)₂(μ - $\eta^{4:4}$ -As₄)] (L = L³ (**3a**), L⁴ (**4a**)) (Scheme 2). By crystallization solid solutions containing **3a** and [(L³Fe)₂(As₂)₂] (**3b**) (2% crystalline yield) as well as **4a** and [(L⁴Fe)₂(As₃)] (**4b**) (10% crystalline yield) are obtained (Scheme 2).¹⁵ All compounds are readily soluble in Et₂O and are red-brown in color. LIFDI mass spectrometry confirms their molecular composition and excludes the formation of possible tetranuclear products (like in **1** or **2**).

All complexes are paramagnetic in solution and for each a signal pattern of a quartered ligand (two perpendicular mirror planes) is detected in C_6D_6 solution, which suggests D_{2h} or D_{2d} symmetry on NMR time scale. For **4a**, the assigned signals in the ¹H NMR spectrum (C_6D_6) are between 9.41 and -5.71 ppm. Since the compounds **3a** and **3b** co-crystallize in their crystal



 $\label{eq:scheme 2} \begin{array}{l} \mbox{Reactivity of } As_4 \mbox{ towards different [LFe(tol)] complexes. Highlighted boxes: Products obtained as "solid solution" (vide infra) of two components 'a' and 'b' in the crystal. \end{array}$

structure, signals of two different sets of L^3 ligands are expected in the ¹H NMR spectrum. To our surprise, exclusively one set of signals is detected between 109.1 and -15.0 ppm in C_6D_6 solution. This, on the one side confirms their paramagnetic character (range of chemical shifts), on the other side suggests a fast dynamic isomerization in solution. It was expected, that the hypothetical coalescence and signal splitting of **3a** and **3b** could be detected by ¹H NMR spectroscopy of a sample of crystals dissolved at low temperature and by successively increasing the temperature of the solution. However, the low solubility of crystals at lower temperature $(-100 \ ^{\circ}C)$ prevents this investigation.

Therefore, we assume that the existence of the two different isomers **3a** and **3b** is only present in the solid state and cannot be observed in solution. Surprisingly, we found that the crystallization temperature influences the ratio of **3a:3b** in the crystals. In single crystals, grow at 8 °C the ratio of **3a:3b** is 61.5:38.5, while in single crystals grown at -30 °C the ratio is 82:18.

Due to their similarities, the molecular structure of $[(L^{4}Fe)_{2}(\mu-\eta^{4}:\eta^{4}-As_{4})]$ (4a) and $[(L^{3}Fe)_{2}(\mu-\eta^{4}:\eta^{4}-As_{4})]$ (3a) are described comparatively. Both structures are centrosymmetric and consist of two parallel [LFe] (L³, L⁴) fragments. They are bridged by a square-planar cyclo-As₄ ring with As-As-As angles of 89.62(2)/90.38(2)° in 3a and 88.54(3)/91.46(3)° in 4a. The central [Fe₂As₄] core reveals a slightly distorted octahedral shape and is depicted in Fig. 2, left side (exemplified for 3a). The As-As distances are almost equidistant (2.4276(7) and 2.4423(6) Å in 3a and 2.3898(8) and 2.4200(10) Å in 4a). The values in 4a are comparable to the ones found in the Zintl phase [(K@18-crown-6)₂As₄] (2.3871(4) and 2.3898(4) Å) containing a cyclo- $[As_4]^{2-}$ unit.¹⁶ The As-As distances in **3a** are in the range of As–As single bonds $(2.44(3) \text{ Å})^{10-12}$ and resemble best the ones (2.3905(8)-2.4562(7) Å) found in [(Cp^{BIG}Fe)₂ $(\mu-\eta^{4:4}-As_4)$] (J, see Table 1).¹⁷ The most remarkable differences between complexes 3a and 4a are the $Fe \cdots Fe'$ distances $(3.787 \text{ \AA in } 3a \text{ vs. } 3.982 \text{ \AA in } 4a)$ and the orientation of the As₄ ligand related to the [L^{3,4}Fe] planes (see ω_1/ω_2 and further details in Table 1).

The second component in the solid solution of 3ab is $[(L^3Fe)_2(\mu\text{-}\eta^{2:2}\text{-}As_2)_2]$ (3b). It is centrosymmetric and consists

Table 1 Comparison of the structural parameters in [(LFe)₂(μ - η ⁴: η ⁴-As₄)] (L = L³ (**3a**), L⁴ (**4a**)) and [(Cp^{BIG}Fe)₂(μ - η ⁴: η ⁴-As₄)] (**J**)¹⁴

Complex	3a	4a	\mathbf{J}^{14}	3b
$d(\text{Fe}\cdot\cdot\text{Fe}')$ [Å]	3.787	3.982	3.5414(7)	2.940(5)
d(As-As) [Å]	2.4276(7)	2.3898(8)	2.3909(7)	$2.2414(13)^{a}$
	2.4423(6)	2.4200(10)	2.4201(7)	$3.314(2)^{b}$
			2.4331(6)	
			2.4558(7)	
d(Fe–As) [Å]	2.5516(7)	2.5707(5)	2.4144(7)	2.461(2)
	_ ``	_ ``	_ ``	2.4673(17)
	2.5681(7)	2.6374(5)	2.5130(7)	2.499(2)
				2.5022(19)
$\omega_1, \omega_2 [^\circ]$	3.69(6)	41.26(5)	—	0.4(2)
	86.69(6)	50.21(5)		90(2)
Θ [°]	17.5(1)	15.19(8)	—	25.2(3)
$\Phi \left[\circ ight]$	0	0	—	0
^{<i>a</i>} Distance within As ₂ ligand. ^{<i>b</i>} Distance inter As ₂ ligands.				

of two [L³Fe] fragments bridged by a pair of As₂ ligands (Fig. 2, right). In comparison to the previously discussed complexes **4a** (3.982 Å) and **3a** (3.787 Å), the Fe···Fe' distance in complex **3b** is further decreased to a value of 2.940(5) Å.¹⁸ Doubtlessly, the shape of the arsenic ligands in **3b** is significantly different. The distance between both As₂ units is 3.314(2) Å, which excludes any bonding interaction of the arsenic atoms. The As-As distance within each As₂ ligand is 2.2414(13) Å and therefore, in the range of an As=As double bond (*e.g.* in diarsene R¹As=AsR²: 2.224(2)-2.2634(3) Å).¹⁹ Additionally, it is in accordance with the As-As distances (2.272(2)-2.300(2) Å) of other As₂-ligand containing complexes,²⁰ especially with [{(Cp^RCo)(μ - η^2 : η^2 -As₂)₂] (R = 1,2,4^{-t}Bu₃H₂ (2.2795(5) Å),^{19a} Me₄Et (2.272(1) and 2.279 Å)^{19b}), which display similar [Fe₂(μ - η^2 : η^2 -As₂)₂] cores.

In summary, the synthesis and characterization of the first polyarsenic containing β -diiminato iron complexes is reported. Low-valent iron(1) complexes [LFe(tol)] (L = β -diiminato) possessing different substituted β -diiminato ligands were reacted with yellow arsenic and several tetranuclear or dinuclear products are formed. β -diiminato ligands with dmp (2,6-dimethylphenyl) flanking groups yielded tetranuclear complexes of the type [(LFe)₄As₈] (L = L¹ (1), L² (2)), stabilizing a realgar-like [As₈]⁴⁻ unit revealing a unique bridging coordination mode of the metal moieties. For the sterically more bulky dipp (2,6-diisopropylphenyl) substituted ligands, the dinuclear complexes [(LFe)₂(*cyclo*-As₄)] (L = L³ (3a),



Fig. 2 Central core structures of complexes **3a** (left) and **3b** (right) in crystals of **3ab** (hydrogen and carbon atoms are omitted for clarity; thermal ellipsoids are drawn at 50% probability level).

L⁴ (4a)) and $[(L^3Fe)_2(As_2)_2]$ (3b) are formed. There is found a further dependency of the Fe···Fe distance on the formed *cyclo*-As₄ or double As₂ ligands in the complexes. If the β -diiminato ligands at the Fe centres allow a closer Fe···Fe distance, a rectangular shaped As₄ unit (double As₂ ligands) are formed whereas, if the distance gets longer a *cyclo*-As₄ unit results. The shape of the As_n-ligand in the solid state is influenced by the crystallization temperature, which leads to different ratios of the arsenic ligand in the solid solution of **3a**, **b**. Such effect has never seen before and will influence further studies definitively.

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Conflicts of interest

There are no conflicts to declare.

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