

Arsene Ligands

International Edition: DOI: 10.1002/anie.201802888
German Edition: DOI: 10.1002/ange.201802888The Influence of β -diiminato Ligands on As_4 Activation by Cobalt Complexes

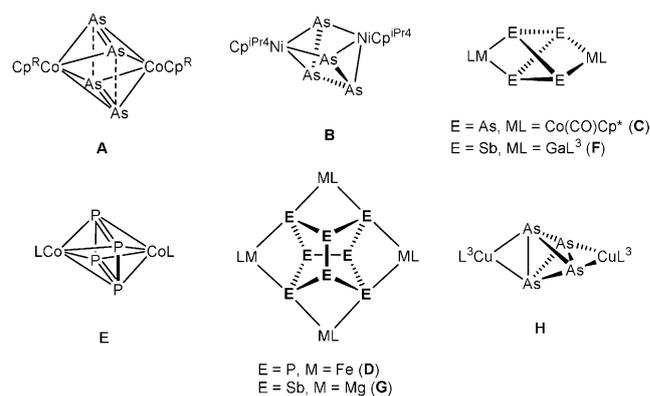
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Dedicated to Professor Alexander C. Filippou on the occasion for his 60th birthday

Abstract: In a systematic study of the activation of As_4 , three $[\text{LCo}(\text{tol})]$ ($\text{L} = \beta$ -diiminato) complexes have revealed different steric and electronic influences. 2,6-Diisopropylphenyl (Dipp) and 2,6-dimethylphenyl (dmp) flanking groups were used, one of the ligands with H backbone substituents (β -dialdiminato L^0) and two with Me substituents (β -diketiminato L^3 and L^1). In the reaction with As_4 , different dinuclear products $[(\text{LCo})_2\text{As}_4]$ ($\text{LM} = \text{L}^0$ (**1**), L^1 (**2**), L^3 (**3**)) were isolated, with all showing differently shaped $[\text{Co}_2\text{As}_4]$ cores in the solid state: octahedral in **1**, prismatic in **2**, and asterane-like in **3**. Thermal treatment of **3** leads to the abstraction of one arsenic atom to yield $[(\text{L}^3\text{Co})_2\text{As}_3]$ (**4**). All products were comprehensively characterized by single-crystal X-ray diffraction, FD-MS, and ^1H NMR spectroscopy. A rational explanation for the different reactivity is also proposed and DFT calculations shed light on the nature of the highly flexible $[\text{Co}_2\text{As}_4]$ cores.

Yellow arsenic (As_4) is the heavier homologue of white phosphorus (P_4), and both are metastable and the only soluble and, therefore, usually synthetically applicable allotropes. Regardless of their isostructural E_4 tetrahedra, they show differences in their E–E bond dissociation energies: 197 (P–P) and 151 kJ mol^{-1} (As–As).^[1] While P_4 is stable under ambient conditions, yellow arsenic tends to polymerize, especially in the presence of light (also in the solid state),

which prevents its storage and poses challenges regarding its handling.^[2] Over the last few decades, the reactivity of P_4 towards main-group and transition-metal compounds has been extensively investigated.^[3] In contrast, the reactivity of As_4 has been less explored and only a few reports have been published during the last few years.^[4] Most of the synthesized compounds have cyclopentadienyl (Cp^R) and strongly donating carbonyl ligands, for example $[(\text{Cp}^R\text{Co})_2\text{As}_4]$ (**A**),^[5] $[(\text{Cp}^{\text{IPr}4}\text{Ni})_2\text{As}_4]$ (**B**),^[6] and $[(\text{Cp}^*(\text{CO})\text{Co})_2\text{As}_4]$ (**C**)^[7] (Scheme 1). Recently, complexes containing β -diiminato



Scheme 1. Selected examples of E_n ligand complexes ($\text{E} = \text{P}, \text{As}, \text{Sb}$) containing Cp^R , CO, and β -diketiminato (L) ligands.

ligands (L) have gained increasing importance because of their exceptionally mild and selective reactivity towards small molecules such as O_2 , N_2 , and P_4 .^[8] It has been shown that, for the activation of white phosphorus, the ligand design of the β -diiminato iron starting material, especially the nature of the flanking groups, has a decisive influence on the reaction outcome. Whereas tetranuclear $[(\text{LFe})_4\text{P}_8]$ ($\text{L} = \text{L}^1, \text{L}^2$ (**D**)) complexes are formed with dimethylphenyl (dmp) ligands, dinuclear products $[(\text{LFe})_2\text{P}_4]$ ($\text{L} = \text{L}^0, \text{L}^3$) are obtained exclusively with diisopropylphenyl (dipp) ligands.^[9] For the analogous Co^I-mediated reactions, dinuclear complexes $[(\text{LCo})_2(\mu-\eta^{4:4}\text{P}_4)]$ ($\text{L} = \text{L}^0, \text{L}^1, \text{L}^2, \text{L}^3$ (**E**)) are formed exclusively, with each of them stabilizing similar rectangular and neutral $[\text{P}_4]^0$ ligands.^[10] Recently, in the case of the heavier congener antimony, the synthesis of $[(\text{L}^3\text{Ga})_2\text{Sb}_4]$ (**F**)^[11] and $[(\text{LMg})_4\text{Sb}_8]$ (**G**)^[12] was reported. However, the only reported reaction of a β -diketiminato complex with As_4

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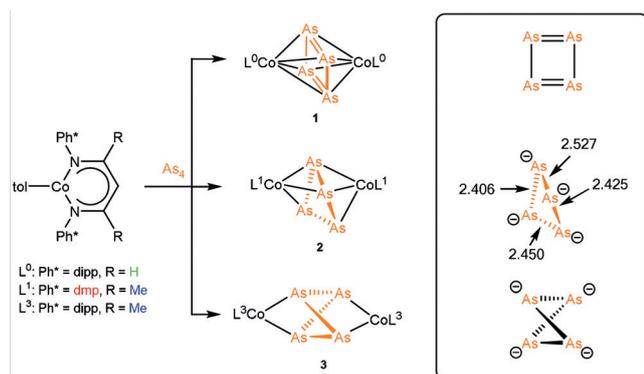
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yielded $[(L^3Cu)_2(\mu-\eta^2:\eta^2-As_4)]$ (**H**),^[13] which contains an intact $[As_4]^0$ tetrahedron fixed between two $[L^3Cu]$ fragments.

In view of this state of knowledge, the question arises as to whether a more electron-deficient β -diiminato-metal complex could open the As_4 tetrahedron by cleavage of one or more As–As bonds. Moreover, considering the known lower As–As bond energy compared with a P–P bond, there might be a good chance to gain more insight into the details of the preceding transformation process of an As_4 tetrahedron.

Herein, we report on the unprecedented and mild reactions of the Co^I - β -diiminato (L) complexes $[LCo(tol)]$ ($L = L^0, L^1, L^3$, Scheme 2) with yellow arsenic, which highlight



Scheme 2. Reactivity of As_4 with different $[LCo(tol)]$ complexes. High-lighted box: presumed electronic structure of the obtained As_4 ligands in the products and selected atomic distances in **2**.

the influence of the β -diiminato supporting ligands on the different reaction outcomes. The isolated As_4 derivatives provide remarkable insight into the reaction pathway, which is supported by DFT calculations. All reactions were performed under identical conditions (toluene, RT, 15 or 30 min) and led to three different dinuclear complexes $[(LCo)_2As_4]$ ($L = L^0$ (**1**), L^1 (**2**), L^3 (**3**))—each revealing a different and individually shaped As_4 ligand in the solid state. In addition, the thermolysis of **3** at 110 °C leads to the abstraction of one

As atom and the selective formation of $[(L^3Co)_2(\mu-\eta^{3:3}-As_3)]$ (**4**).

The reactions of $[L^0Co(tol)]$ and As_4 were performed under ambient conditions, and within 15 minutes $[(L^0Co)_2(\mu-\eta^4:\eta^4-As_4)]$ (**1**) was selectively formed as the main product (monitored by 1H NMR spectroscopy).^[14] The brown-colored **1** is readily soluble in toluene, C_6D_6 , and Et_2O solutions and decomposes slowly upon exposure to light.

The 1H NMR spectrum of **1** in C_6D_6 displays seven characteristic signals in the range of 61 ppm to –49 ppm, which indicates the paramagnetic properties of **1** in solution. Its molecular composition was confirmed by FD mass spectrometry and single-crystal X-ray diffraction. The molecular structure of **1** consists of two parallel $[L^0Co]$ fragments, which are bridged by a rectangularly shaped *cyclo*- As_4 ring (Figure 1, left side).^[16] The $Co\cdots Co'$ distance (3.587 Å) excludes any bonding interaction between the cobalt centers. The As–As–As angles are 89.86(2) and 90.14(2)°. The central $[Co_2As_4]$ core reveals a slightly distorted octahedral shape: The Co–As distances are between 2.4638(5) and 2.4816(5) Å. Two pairs of longer (2.4884(5) Å) and shorter (2.3299(5) Å) As–As distances are present in the As_4 middle deck (Table 1).

Table 1: Comparison of selected distances in $[(LCo)_2As_4]$ ($L = L^0$ (**1**), L^1 (**2**), L^3 (**3**)) and $[(L^3Co)_2As_3]$ (**4**).

	1	2 ^[a]	3	4
$d(Co\cdots Co')$ [Å]	3.587	3.966	4.615	3.842
$d(As-As)$ [Å]	2.3299(5)	2.4064(11)	2.4466(12)	2.349(3) ^[b]
	2.4884(5)	2.4152(10)	2.4530(13)	2.398(4) ^[b]
		2.4501(11)	2.4561(13)	2.555(3) ^[b]
		2.5266(10)	2.4616(12)	
$d(Co-As)$ [Å]	2.4638(5)	2.3403(11)	2.3077(14)	2.3207(8)
	2.4748(5)	2.3411(12)	2.3139(14)	–
	2.4762(5)	2.3582(11)	2.3143(14)	2.496(3)
	2.4816(5)	2.3601(11)	2.3217(15)	
		2.5011(11)		
		2.5155(11)		

[a] Two molecules of **2** in the asymmetric unit. Only the values of one molecule are given. Further details are given in the Supporting Information. [b] The *cyclo*- As_3 ligand is disordered over four positions. Herein the values of only one component are given.^[15]

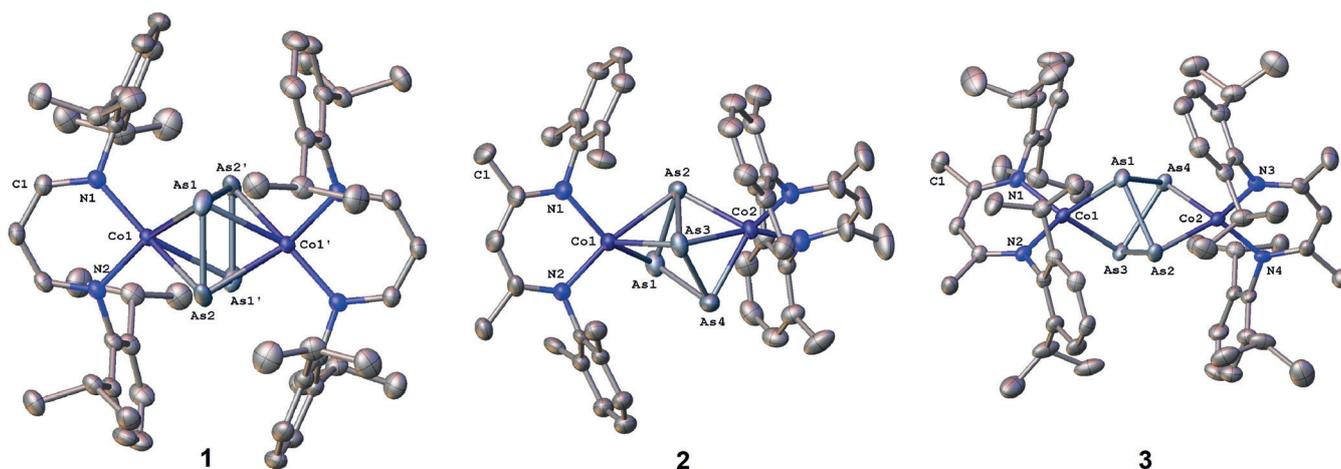


Figure 1. Molecular structure of $[(LCo)_2As_4]$ ($L = L^0$ (**1**, left side), L^1 (**2**, middle), L^3 (**3**, right side) in the crystal; ellipsoids are set at the 50% probability level, hydrogen atoms are omitted for clarity.

The first ones are slightly longer than an As–As single bond in yellow arsenic (determined in As₄ by electron diffraction: 2.435(4)^[17] and 2.44(3) Å,^[18] by DFT calculations:^[19] 2.437 Å), whereas the latter are significantly shorter. The shorter ones lie between the values of an arsenic single and double bond (As=As bond determined in diarsene (R¹As=AsR²) by SCD: 2.224(2)–2.2634(3) Å^[20]). To the best of our knowledge, no complex with a comparable *cyclo*-As₄ ligand has been reported so far. The As₄ ligand in **1** deviates from the ones found in [(Cp^RCo)₂As₄] (**A**: R = Cp^{'''}, 2.2795(5)/2.8209(4) Å, R = Cp^{Et}: 2.272(1)/2.844(1) Å).^[5] The bonding situation of **A** is better described as two As₂ bars with weak intramolecular interactions. The bonding situation in **1** resembles that of the recently reported phosphorus congener [(LCo)₂(μ-η^{4:4}-P₄)] (L = L⁰, L¹, L², L³), which possesses neutral [P₄]⁰ ligands.^[10] Therefore, **1** represents the first arsenic-containing complex with a [As₄]⁰ unit.

To gain further insight into the impact of changing the substituents (dipp versus dmp; H versus Me) in the β-diiminato ligand, the reaction of [L¹Co(tol)] with As₄ was performed. Despite applying identical reaction conditions (RT, 15 min), the dinuclear complex [(L¹Co)₂(μ-η³:η³-As₄)] (**2**) was isolated (Scheme 2). The ¹H NMR spectrum of **2** in C₆D₆ displays five characteristic resonances, which suggests a D_{2h} or D_{2d} symmetry of the molecule on the NMR timescale. The signals are in the range between 14.68 ppm and –14.88 ppm. The magnetic moment of **2** was determined by the Evans method in solution and amounts to 2.77 μ_B (C₆D₆).

The molecular structure of **2** reveals two individual molecules of **2** in the asymmetric unit. As they display only marginal deviations in terms of their structural parameters, only one molecule is discussed hereafter.^[21] The central [Co₂As₄] core of **2** is best described as distorted and between a trigonal prism and an antiprism (Figure 1, middle). The Co...Co distance is 3.966 Å, which is slightly elongated compared to that in **1** (3.587 Å). Each Co atom is η³-coordinated by three arsenic atoms with Co–As bonds in the range between 2.3403(11) and 2.5155(11) Å. All As–As distances in **2** are between 2.4064(11) and 2.5266(10) Å (see Scheme 2) and are, therefore, without doubt in the range of slightly shortened or elongated As–As single bonds, respectively. Its electronic structure can be best described as an [As₄]⁴⁻ ligand. Moreover, there are significant differences regarding the unprecedented *cyclo*-As₄ conformation in **2** compared to the *catena*-As₄ unit in [(Cp^{IPr4}Ni)₂(μ-η³:η³-As₄)] (**B**,^[6] Scheme 1).^[22]

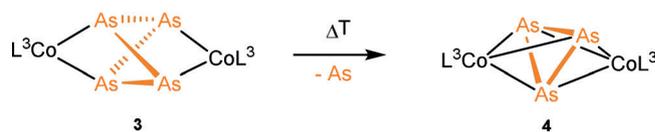
Finally, introducing the ligand system L³ into the reactivity study (Scheme 2), [L³Co(tol)] was reacted with As₄ under similar reaction conditions (RT, 30 min), with the complex [(L³Co)₂(μ-η^{1:1:1}-As₄)] (**3**) being formed selectively (monitored by ¹H NMR spectroscopy). For **3**, seven characteristic ¹H NMR signals are detected in the range between 10.47 and –5.92 ppm (C₆D₆), thereby revealing two equivalent L³ ligands. The composition of **3** was further verified by elemental analysis and mass spectrometry.

The magnetic moment of **3** amounts to 2.68 μ_B (determined by the Evans method in C₆D₆). This value is in good agreement with SQUID measurements, which show a magnetic moment of 2.5 μ_B at room temperature. The magnetic

behavior of **3** between 0 and 100 K is explained by a S_{tot} = 0 ground state. By continuously increasing the temperature (100–300 K), the excited triplet spin state becomes populated and shows, however, antiferromagnetic coupling between the two Co centers. At room temperature, the magnetic moments of **2** and **3** in C₆D₆ solutions are the same as in the crystals of **3**, which suggests both have similar conformations in solution. Therefore, the structure in solution might be similar to the molecular structure of **3** in the solid state (Figure 1).

The molecular structure of **3** consists of two orthogonal [L³Co] fragments, which are bridged by a twofold edge-opened As₄ tetrahedron (Figure 1, right side). The coordinating arsenic atoms are separated by 3.057(1) or 3.070(1) Å, which excludes any bonding interaction. In contrast, the remaining As–As distances are single bonds in the range of 2.4466(12) to 2.4616(12) Å. Therefore, the electronic structure is best described as an [As₄]⁴⁻ ligand. The Co–As bonds are between 2.3077(14) and 2.3217(15) Å. The Co...Co distance in **3** amounts to 4.615 Å and, therefore, exceeds those in **1** (3.587 Å) and **2** (3.966 Å). Besides the almost tetrahedral coordination geometry of the Co centers in **3**, the central [Co₂As₄] core is more comparable to the As₄ ligand in [(Cp*(CO)Co)₂(μ-η^{1:1:1}-As₄)] (**C**).^[7]

It is noteworthy that fragmentation of the initial *cyclo*-As₄ ligand of compound **C** after further CO elimination under thermolytic conditions results in a *catena*-As₄ structure or a pair of As₂ ligands, as in **A**.^[7] However, no such leaving groups are present in **3** and we were intrigued by its reactivity under elevated temperatures. The thermolysis of **3** in [D₈]toluene was monitored by ¹H NMR spectroscopy up to 378 K, which showed the selective transformation into the new product [(L³Co)₂(μ-η^{3:3}-As₃)] (**4**), in which one As atom is removed (Scheme 3). The VT-NMR spectra of this reaction are shown in Figure S12.^[15]



Scheme 3. Thermolytic extrusion of one As atom from [(L³Co)₂(μ-η^{1:1:1}-As₄)] (**3**) and formation of [(L³Co)₂(μ-η^{3:3}-As₃)] (**4**).

The molecular structure of **4** (Figure 2) confirms a dinuclear product, which consists of two parallel [L³Co] fragments. The Co atoms are separated by 3.842 Å. They are bridged by a *cyclo*-As₃ middle deck, which is localized on an inversion center and, therefore, is disordered.^[15,23] The As–As distances are between 2.349(3) and 2.563(3) Å (see Table 1 and the Supporting Information), which is clearly in the range of single bonds. Comparable *cyclo*-As₃ ligands have so far only been reported in ionic complexes, such as [(triphos)-Co)₂As₃]²⁺ with As–As distances of 2.42(2), 2.45(1), and 2.45(2) Å.^[24] The As–As–As angles in **4** are 56.51(10), 58.37(9), and 65.13(8)°. Therefore, the molecular structure of **4** confirms the formation of a *cyclo*-As₃ middle deck, which is additionally supported by mass spectrometry, elemental

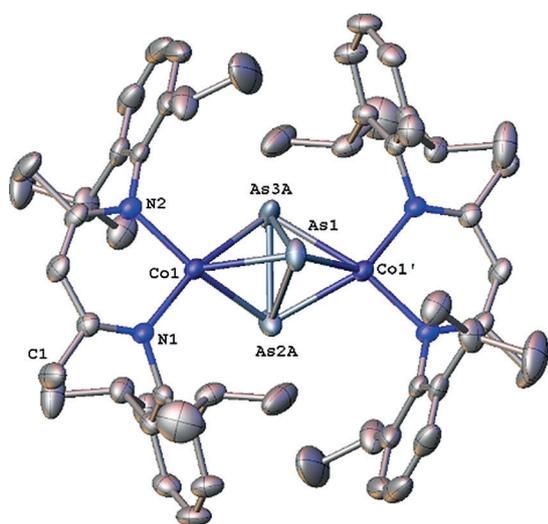
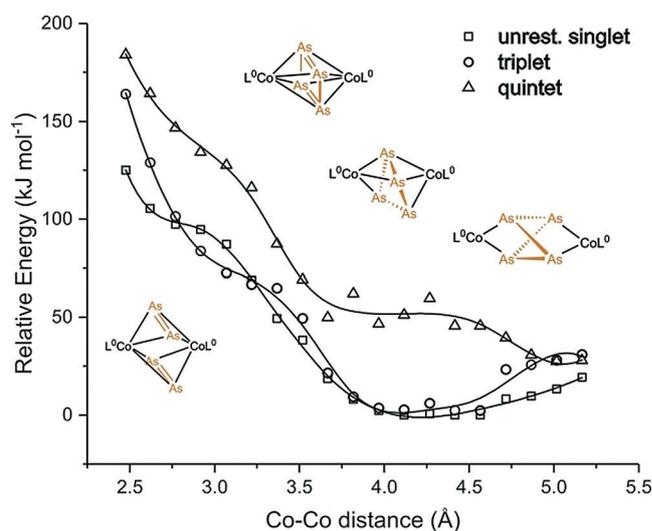


Figure 2. Molecular structure of $[(L^3Co)_2(\mu-\eta^{3\cdot3}-As_3)]$ (**4**) in the crystal; ellipsoids are set at the 50% probability level, hydrogen atoms are omitted for clarity.

analysis, and 1H NMR spectroscopy. The 1H NMR spectrum displays seven characteristic signals in the range of 44.19 to -29.69 ppm at room temperature in $[D_8]$ toluene. Moreover, its magnetic moment was determined by the Evans method ($3.75 \mu_B$ in C_6D_6). Interestingly, the loss of one arsenic atom during the selective degradation of **3** into **4** is further indicated by the formation of an arsenic mirror.

The results show that despite applying similar conditions in the reactions of different complexes $[LCo(tol)]$ ($L = L^0, L^1, L^3$) with As_4 , the formation of differently structured As_4 moieties in the products **1**, **2**, and **3** occurred. To understand the driving forces that direct the elementarily different reaction outcome, we performed DFT calculations at the BP86/def2-SVP level of theory. $[(L^0Co)_2As_4]$ was chosen as a model system, and a potential energy surface (PES) scan was performed along the Co...Co reaction coordinate, in which the relative energy of the relaxed geometries with constrained Co...Co distances in different spin states ($S = 0, 1$, or 2) was computed (Scheme 4). A general feature is the flat PES surface, especially between 3.6 and 4.6 Å. The relative energies of the unrestricted singlet (\square) and triplet (\circ) spin states are very close to each other, while the quintet (\triangle) spin state is always higher in energy. Furthermore, several spin crossover points might be expected between the unrestricted singlet and triplet spin states. This is strongly supported by the results of the SQUID and magnetic moments measurements in solution.

The nature of the calculated $[Co_2As_4]$ core geometry is also very strongly influenced by the restricted Co...Co distance and the spin state.^[25] Representative geometries resulting from the constrained geometry optimization are depicted as inserts in Scheme 4. The slope of the function between 3.6 and 4.6 Å is very low regardless of the spin state, thus suggesting that the differences in the relative energy ΔE of all the observed $[Co_2As_4]$ cores in theory and furthermore experimentally (in crystal structures of **1**, **2**, and **3**) are low, especially compared to different energy contributions from



Scheme 4. Potential energy surface scan of $[(L^0Co)_2(As_4)]$ along the Co...Co reaction coordinate, calculated at the BP86/def2-SVP level of theory. Selected $[Co_2As_4]$ core geometries at the corresponding Co...Co distances are depicted. As a consequence of the possible antiferromagnetic couplings and the limited accuracy of DFT calculations for open-shell systems, the PES scan represents only an approximate qualitative description.

packing effects, dispersion interactions, thermal energy, etc. Therefore, the observed geometry in the solid state is suggested to be mainly driven by a combination of these factors, which explains the experimentally found variety of different $[Co_2As_4]$ cores in the solid state of the dinuclear compounds **1**, **2**, and **3**.

In conclusion, we demonstrated that the reaction of As_4 with three different $[LCo(tol)]$ ($L = L^0, L^1$, and L^3) complexes leads to the selective formation of the dinuclear products $[(LCo)_2As_4]$ ($L = L^0$ (**1**), L^1 (**2**), L^3 (**3**)), each of which reveals an individual As_4 core. In the solid state, each L^0, L^1 , and L^3 ligand system stabilizes a distinct octahedral (**1**), prismatic (**2**), or asterane-like (**3**)^[26] $[Co_2As_4]$ shape. The structure of the formed As_4 moiety is mainly directed by the Co...Co distances, which was determined by DFT calculations. Furthermore, the thermal extrusion of one As atom from **3** and the unique formation of the new triple decker complex $[(L^3Co)_2(\mu-\eta^{3\cdot3}-As_3)]$ (**4**) was monitored by 1H NMR spectroscopy.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: β -diiminato ligand · paramagnetic compounds · small-molecule activation · substituent effects · yellow arsenic

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