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As_4 Activation

Selective Formation and Unusual Reactivity of Tetraarsabicyclo[1.1.0]butane Complexes**

*Christoph Schwarzmaier, Alexey Y. Timoshkin, Gábor Balázs, and Manfred Scheer**

Dedicated to Professor Hubert Schmidbaur on the occasion of his 80th birthday

Abstract: *The selective formation of the dinuclear butterfly complexes [{Cp'''Fe(CO)$_2$}$_2$(μ,η$^{1:1}$-E$_4$)] (E = P (**1a**), As (**1b**)) and [{Cp*Cr(CO)$_3$}$_2$(μ,η$^{1:1}$-E$_4$)] (E = P (**2a**), As (**2b**)) as new representatives of this rare class of compounds was found by reaction of E$_4$ with the corresponding dimeric carbonyl complexes. Complexes **1b** and **2b** are the first As$_4$ butterfly compounds with a bridging coordination mode. Moreover, first studies regarding the reactivity of **1b** and **2b** are presented, revealing the formation of the unprecedented As$_8$ cuneane complexes [{Cp'''Fe(CO)$_2$}$_2${Cp'''Fe(CO)}$_2$(μ$_4$,η$^{1:1:2:2}$-As$_8$)] (**3b**) and [{Cp*Cr(CO)$_3$}$_4$(μ$_4$,η$^{1:1:1:1}$-As$_8$)] (**4**). The compounds are fully characterized by NMR and IR spectroscopy as well as by X-ray structure analysis. In addition, DFT calculations give insight into the transformation pathway from the E$_4$ butterfly to the corresponding cuneane structural motif.*

The coordination and activation of white phosphorus (P_4) and its heavier congener yellow arsenic (As_4) has become a research area of interest during the last decades. Especially in the case of P_4, the transition-metal- and main-group-element-based degradation of the tetrahedral framework has been extensively studied.[1] For As_4, much less is known about the reactivity towards transition-metal fragments, which is due to the highly unstable nature of the allotrope.[2] Recently, our group succeeded in stabilizing the intact As_4 tetrahedron by coordination to transition-metal cations or by encapsulation into polymeric matrices or spherical supramolecules.[3] These results prompted us to also investigate the activation of yellow arsenic by transition-metal fragments.

The activation of the E_4 tetrahedron (E = P, As) usually proceeds through the stepwise degradation of the six E–E bonds by reductive cleavage. The so-formed E_n ($n = 1$ to 4) ligands are either stabilized in the coordination sphere of transition-metal complexes, or they reaggregate to larger E_n ($n > 4$) ligands. However, the first step of the activation cascade is the cleavage of one E–E bond to form a tetrapnicto-bicyclo[1.1.0]butane unit, often entitled as a butterfly ligand. The E_4^{2-} unit can either coordinate to one or two Lewis acidic complex fragments to form mononuclear (side-on) or dinuclear (bridging) butterfly complexes. However, very few examples of characterized butterfly complexes derived from the E_4 tetrahedron are known (Figure 1). In the case of phosphorus, both butterfly coordination modes are known in [$L_2ClRh(\eta^2\text{-}P_4)$] (**A**) (L = PPh_3, P(*m*-Tol)$_3$, P(*p*-Tol)$_3$, $AsPh_3$) and [{Cp^{R}Fe(CO)$_2$}$_2$(μ,η$^{1:1}$-P$_4$)] (**C**) (Cp^R = Cp'' = 1,3-di-*tert*-butylcyclopentadienyl, Cp''' = 1,2,4-tri-*tert*-buytlcyclopentadienyl).[4] Only one mononuclear As_4 butterfly complex [Cp*(CO)Co(η$^{1:1}$-As$_4$)] (**B**) (Cp* = C_5Me_5) has been synthesiszed to date.[2c]

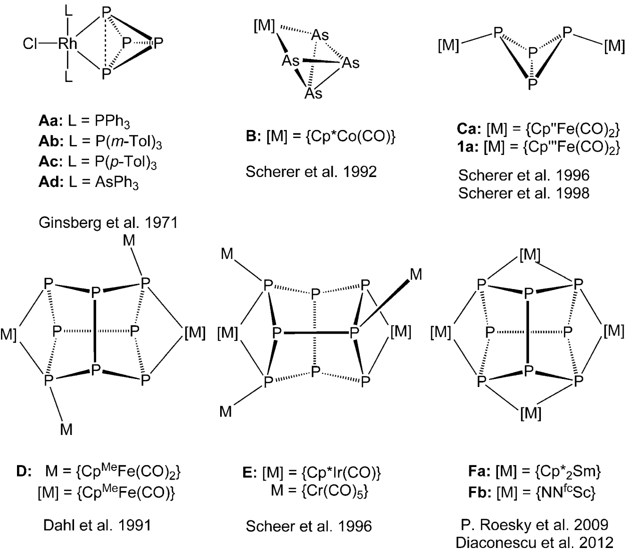

Figure 1. Mono- and dinuclear E_4 butterfly complexes derived from E_4 (E = P, As) as well as transition-metal complexes with P_8 cuneane motif.

The reaggregation of small E_n ($n = 1$ to 4) fragments to form extended phosphorus frameworks is known for transition-metal-mediated as well as main-group-mediated activation of P_4.[5] One of the most interesting polyphosphorus structural motifs is the P_8 cuneane cage which can be found in elemental, Hittorf's phosphorus.[6] Dahl and co-workers reported the formation of [{Cp^{Me}Fe(CO)$_2$}$_2$-{Cp^{Me}Fe(CO)}(μ$_4$,η$^{1:1:2:2}$-P$_8$)] (**D**; Cp^{Me} = C_5H_4Me) by the photolytic reaction of [{Cp^{Me}Fe(CO)$_2$}$_2$] with P_4.[7] The

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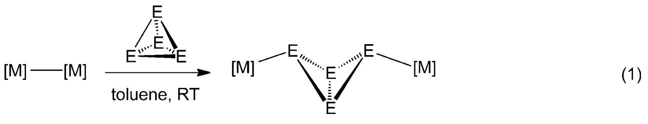
formation of **D** which contains a P_8^{4-} cuneane unit was explained by the formation of P_2 intermediates. A few years later, we used photolytical or thermal reaction conditions for the synthesis of $[\{Cp^*Ir(CO)\}_2\{Cr(CO)_5\}_3(\mu,\eta^{1:1:1:2:2}P_8)]$ (**E**).[8] Finally, the groups of Roesky and Diaconescu extended the family of transition-metal cuneane complexes by two f-block element examples $[\{L_2M\}_4(\mu_4,\eta^{2:2:2:2}\text{-}P_8)]$ (L = Cp*, M = Sm (**Fa**); $L_2 = NN^{fc}$, M = Sc (**Fb**)). For all these studies, a formation pathway was not described.[9] Therefore, this question was open, and we speculated that transient P_4 butterfly complexes could play an important role on the way to P_8 cuneanes. Moreover, because cuneane complexes of arsenic are unknown to date, the syntheses of As_4 butterfly complexes as well as As_8 cuneanes became worthwhile synthetic targets.

The published procedure for the synthesis of **1a** includes a brief thermolysis (toluene, 110 °C, 3 to 5 min) followed by a chromatographic work-up.[4b] However, our preparative attempts showed an immediate and clean reaction of $[\{Cp'''Fe(CO)_2\}_2]$ with P_4 already at room temperature, to afford the bright orange **1a** as the only reaction product in almost quantitative yield [Eq. (1)].



(1)

1a: [M] = $\{Cp'''Fe(CO)_2\}$; E = P; >95%
1b: [M] = $\{Cp'''Fe(CO)_2\}$; E = As; 77%
2a: [M] = $\{Cp^*Cr(CO)_3\}$; E = P; >95%
2b: [M] = $\{Cp^*Cr(CO)_3\}$; E = As; 75%

In the $^{31}P\{^1H\}$ NMR spectrum of **1a** (C_6D_6), two characteristic triplets at $\delta = -81.4$ and -325.0 ppm of an A_2M_2 spin system are found, which compare well to those reported by Scherer et al.[4b] The reaction most likely proceeds by the homolytic cleavage of the Fe–Fe bond in $[\{Cp'''Fe(CO)_2\}_2]$. The so-formed 17 valence electron (VE) metal-centered radicals react with white phosphorus and cleave one of the six P–P bonds to afford the P_4^{2-} butterfly ligand stabilized by two $\{Cp'''Fe(CO)_2\}$ fragments.

Since the new synthetic method describes an easy and high-yielding way to the rare butterfly complexes, we used yellow arsenic instead of white phosphorus and also varied the dinuclear metal compound. The chromium carbonyl complex $[\{Cp^*Cr(CO)_3\}_2]$ has a long Cr–Cr bond of 3.310(1) Å,[10] and is known to dissociate in solution to form the radical species $[Cp^*Cr(CO)_3]^\bullet$.[11] The reactions of $[\{Cp'''Fe(CO)_2\}_2]$ with As_4 and those of $[\{Cp^*Cr(CO)_3\}_2]$ with E_4 (E = P, As) in toluene at room temperature afforded the three new butterfly complexes $[\{Cp'''Fe(CO)_2\}_2(\mu,\eta^{1:1}\text{-}As_4)]$ (**1b**) and $[\{Cp^*Cr(CO)_3\}_2(\mu,\eta^{1:1}\text{-}E_4)]$ (E = P (**2a**), As (**2b**)) in good to excellent yields [Eq. (1)]. The products were isolated as orange solids, which show good solubility in toluene (**1b**) or dichloromethane (**2**) but are only sparingly soluble in hexane. As solids, they can be stored under an inert atmosphere for months without noticeable decomposition. Complex **1b** shows a typical set of signals for the Cp''' ligand in the ^1H NMR spectrum. Mass spectrometry reveals the molecular-ion peak at *m/z* 990.0. In the IR spectrum, two strong CO absorption bands are detected at 1990 and 1940 cm^{-1} which are red-shifted by 10 cm^{-1} compared to **1a**. The ^1H NMR spectra of **2a** and **2b** reveal one characteristic singlet for the protons of the Cp* ligands. The $^{31}P\{^1H\}$ NMR spectrum (CD_2Cl_2) of **2a** reveals two triplets of an A_2M_2 spin system at $\delta = -95.2$ and -327.4 ppm. The mass spectra of both chromium butterfly complexes did not show the molecular-ion peaks. The detected fragments indicate a slightly increased instability of complexes **2** compared to **1a** and **1b**. While **2a** shows strong CO absorption bands in the IR spectrum at 1983 (vs), 1967 (vs), 1916 (vs), 1900 (vs), the respective signals of **2b** are red-shifted by about 10 cm^{-1}. The observed red-shift in the IR spectra of **1b** and **2b** indicates the As_4^{2-} ligand as a stronger σ-donor and/or weaker π-acceptor ligand compared to its phosphorus derivative independently from the chosen metal fragment.

The molecular structures of **1b** and **2b** are depicted in Figure 2 (for the X-ray structure of **2a**, see the Supporting Information).

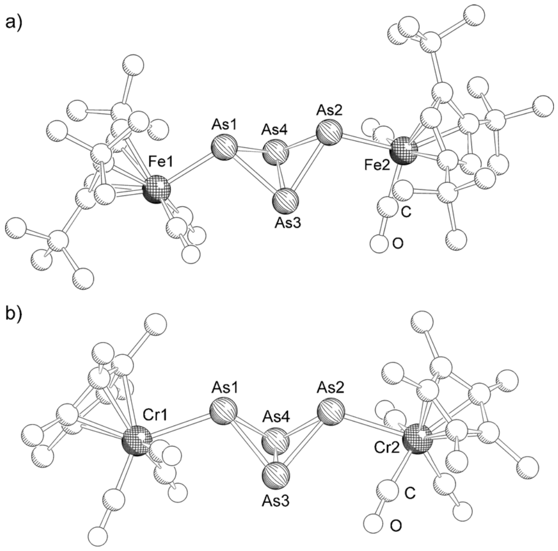
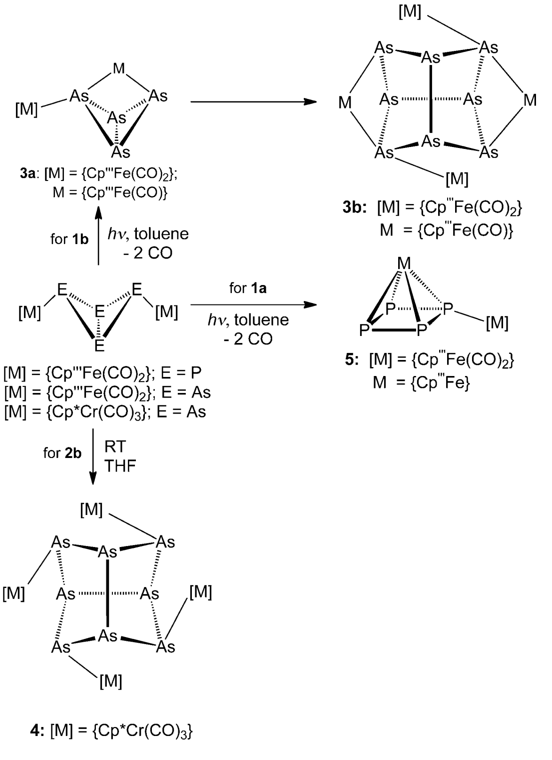


Figure 2. Molecular structure of a) **1b** and b) **2b**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: **1b**: Fe1-As1 2.443(3), Fe2-As2 2.458(3), As1-As3 2.449(2), As1-As4 2.461(3), As2-As3 2.452(2), As2-As4 2.460(3), As3-As4 2.405(3), As1···As2 3.184(2); As3-As1-As4 58.67(7), As3-As2-As4 58.63(8), As1-As3-As2 81.04(7), As1-As4-As2 80.65(9), As1-As3-As4 60.92(7), As1-As4-As3 60.42(7), As2-As3-As4 60.84(8), As2-As4-As3 60.53(8). **2b**: Cr1-As1 2.641(1), Cr2-As2 2.614(1), As1-As3 2.425(1), As1-As4 2.454(1), As2-As3 2.449(1), As2-As4 2.435(1), As3-As4 2.367(1) As1···As2 3.032(1); As3-As1-As4 58.06(3), As3-As2-As4 57.99(3), As1-As3-As2 76.93(4), As1-As4-As2 76.65(4), As1-As3-As4 61.58(3), As1-As4-As3 60.37(4), As2-As3-As4 60.73(4), As2-As4-As3 61.28(3).

Complexes **1b** and **2b** have an As_4 butterfly ligand bridging two $\{Cp'''Fe(CO)_2\}$ or $\{Cp^*Cr(CO)_3\}$ units, respectively. In both complexes, the bridgehead As3–As4 bond (2.405(3) and 2.367(1) Å) is shorter than the other As–As bonds (2.449(2) to 2.461(3) Å in **1b** and 2.425(1) to 2.454(1) Å in **2b**). A similar trend of the P–P bond lengths within the P_4 butterfly moiety is found in **1a**.[4b] The distance between the two coordinating atoms As1 and As2 (3.184(2) and 3.032(1) Å in **1b** and **2b**, respectively) is longer than an As–As single bond in As_4 (2.396(5)[3] to 2.435(4) Å)[12] but still below the sum of van der Waals radii (3.70 Å) pointing to a weak interaction of the two atoms. The As–M bond lengths are shorter in **1b** (2.443(3) and 2.458(3) Å) than in **2b** (2.641(1) and 2.614(1) Å) which indicates less steric shielding of the As_4 butterfly moiety in the chromium derivative than in the iron compound.

Surprisingly, the As_4 butterfly compound $[\{Cp^*Cr(CO)_3\}_2(\mu,\eta^{1:1}\text{-}As_4)]$ (**2b**) co-crystallizes together with the hitherto unknown As_8 cuneane complex $[\{Cp^*Cr(CO)_3\}_4(\mu_4,\eta^{1:1:1:1}\text{-}As_8)]$ (**4**) that has evidently formed by the dimerization of two complexes **2b**. The dimerization does not take place during the reaction but happens upon the crystallization time. Interestingly, all attempts to grow single crystals of only complex **2b** were unsuccessful. Initially formed orange crystals disappear within a few hours and reddish orange co-crystals of **2b** and **4** start to form. However, by stirring a solution of freshly prepared **2b** under ambient conditions, the color of the solution gradually changes from orange to reddish brown. From this solution, single crystals of complex **4** only could be obtained. The ^1H, $^{13}C\{^1H\}$ NMR as well as the IR spectra of the co-crystallized mixture of **2b** and **4** only show one set of signals for the methyl- and carbonyl groups of the $\{Cp^*Cr(CO)_3\}$ fragments. The two compounds are therefore not distinguishable by NMR or IR spectroscopy. Surprisingly, for the iron derivative **1b**, no cuneane formation could be detected under ambient conditions. Therefore, complex **1b** was irradiated with UV light (see Scheme 1) leading to a color change from bright orange to dark brown within 2 h.



Scheme 1. Formation of the As_8 cuneane complexes **3b** and **4** by the dimerization of the As_4 butterfly complexes **1b** and **2b**.

Chromatographic work-up of the reaction mixture leads to a dark brown fraction, probably of $[\{Cp'''Fe(CO)_2\}\{Cp'''Fe(CO)\}(\mu,\eta^{1:2}\text{-}As_4)]$ (**3a**) as well as a dark green fraction of $[\{Cp'''Fe(CO)_2\}_2\{Cp'''Fe(CO)\}_2(\mu_4,\eta^{1:1:2:2}\text{-}As_8)]$ (**3b**; cf. Scheme 1). The IR spectrum of the dark brown fraction shows three carbonyl bands at 1988, 1938, and 1908 cm^{-1} indicating a terminal $\{Cp'''Fe(CO)_2\}$ group as well as a bridging $\{Cp'''Fe(CO)\}$ moiety.[13]

The IR spectrum of **3b** also shows three signals for the carbonyl groups at 1997, 1954, and 1885 cm^{-1}. In the mass spectrum, the molecular-ion peak is found (*m*/*z* 1924.5). The ^1H NMR spectrum shows signals for a freely rotating Cp''' ligand as well as a Cp''' ligand with hindered rotation. Single crystals of **3b** suitable for X-ray structure analysis could be obtained from concentrated solutions of the green as well as the brown fraction. The molecular structure of the cuneane complexes are depicted in Figure 3.

The central structural motif of the complexes **3b** and **4** is an As_8 cuneane unit that may best be described as an As_8^{4-} ligand. The As–As bond lengths (2.4317(5) to 2.4607(4) Å for **3b** and 2.4229(8) to 2.4600(8) Å for **4**) compare well to As–As single bonds (2.396(5)[3] to 2.435(4) Å[12]). The M–As bond lengths for the terminally coordinated metal fragments (2.4675(6) Å and 2.4692(6) Å for **3b** and 2.608(1) Å to

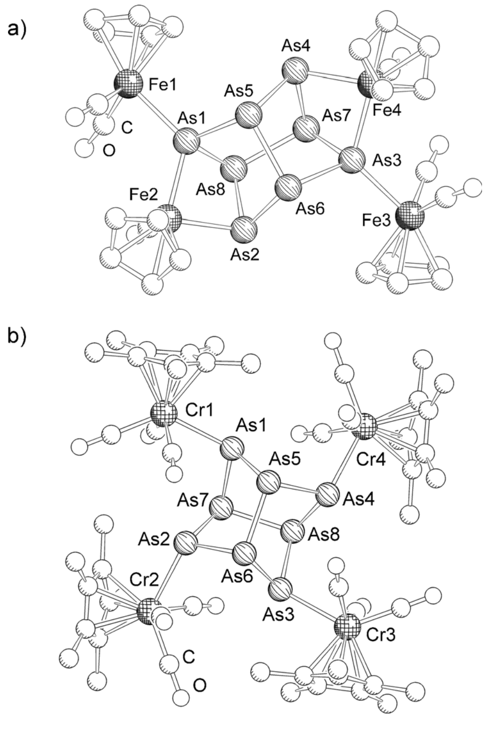


Figure 3. Molecular structures of a) **3b** and b) **4**. Hydrogen atoms and *tert*-butyl groups are omitted for clarity. Selected bond lengths [Å]: **3b**: Fe1-As1 2.4675(6), Fe2-As1 2.4253(5), Fe2-As2 2.4067(6), Fe3-As3 2.4692(6), Fe4-As3 2.4205(5), Fe4-As4 2.4213(6), As1-As5 2.4562(4), As1-As8 2.4557(4), As2-As6 2.4356(4), As2-As8 2.4323(4), As3-As6 2.4607(4), As3-As7 2.4499(4), As4-As5 2.4423(4), As4-As7 2.4317(5), As5-As6 2.4299(4), As7-As8 2.4348(5). **4**: Cr1-As1 2.608(1), Cr2-As2 2.628(1), Cr3-As3 2.626(1), Cr4-As4 2.635(1), As1-As5 2.4356(8), As1-As7 2.4246(8), As2-As6 2.4267(8), As2-As7 2.4412(8), As3-As6 2.4423(8), As3-As8 2.4266(8), As4-As5 2.4229(8), As4-As8 2.4470(8), As5-As6 2.4600(8), As7-As8 2.4543(8).

2.635(1) Å for **4**) resemble those found in the starting materials **1b** and **2b**. The main difference between the two cuneane complexes is the way in which the four transition-metal carbonyl fragments are coordinated. While in **3b** two terminal and two bridging coordination modes are found, the $\{Cp^*Cr(CO)_3\}$ moieties in **4** are terminally bound. This structural motif has never been observed before for cuneane complexes.

Surprisingly, the photolysis of **1a** did not lead to an analogous P_8 cuneane complex but to the loss of two carbonyl ligands and the formation of $[\{Cp'''Fe\}\{Cp'''Fe(CO)_2\}(\mu,\eta^{1:4}\text{-}P_4)]$ (**5**) as the only reaction product (for details see Supporting Information). In contrast, the arsenic derivative **1b** is only decarbonylated once and a re-aggregation process is observed. The formation of **3b** is likely to proceed by the dimerization of **3a**, a step that is suggested by the same Fe/As ratio and the same coordination modes of the iron moieties. Additionally, **3b** crystallizes from solutions of pure **3a**. An analogous reaction pattern may also be assumed for the above mentioned photolytic reaction of $[\{Cp^{Me}Fe(CO)_2\}_2]$ with P_4 to yield the P_8 cuneane complex **D**.[7] In both cases, the steric bulk of the Cp^R ligand seems to play an important role for the formation of the E_8 cuneane (E = P, As) framework. While in the case of **1a** the bulky Cp‴ ligand prevents any P−P interactions and therefore inhibits aggregation processes, the small Cp^{Me} ligand is not bulky enough to shield the corresponding butterfly complex and/or the mono-decarbonylated species. Hence the formation of the P_8 cuneane **D** is observed. In the case of arsenic, the Cp‴ ligand provides enough steric shielding to stabilize the As_4 butterfly complex **1b**. The loss of one carbonyl ligand leads to the bridged butterfly complex **3a** in which the As_4 butterfly framework is not sufficiently shielded by the two $[Cp'''Fe(CO)_n]$ ($n = 1$ or 2) fragments. Hence, intermolecular As–As interactions are possible, which lead to the dimerization product **3b**. In contrast, **2b** shows a dimerization to the corresponding As_8 cuneane complex at room temperature. The reason for the enhanced dimerization tendency might be the small steric bulk of the $[Cp^*Cr(CO)_3]$ fragment compared to the large $[Cp'''Fe(CO)_2]$ unit. Hence, intermolecular As–As interactions are possible for the butterfly complex **2b** and no initial decarbonylation is necessary.

To obtain a deeper insight into the experimental observations, DFT calculations at the B3LYP/def2-SVP level of theory have been carried out that focused on the dimerization tendency of the butterfly complexes, the influence of the Cp^R ligand, as well as the different reaction behavior of arsenic and phosphorus derivatives.

While the direct dimerization of the E_4 butterfly complex is predicted to be highly endothermic for the iron derivatives **1**, it is exothermic for both Cr compounds **2**. However, taking entropic effects into account, the hypothetical dimerization of **2a** ($23\,kJ\,mol^{-1}$) is higher in energy than that for **2b** ($7\,kJ\,mol^{-1}$), which confirms the experimental observation of the formation of **4** but not the dimerization of **2a**. Kinetic reasons, such as the E−E bond strength, might also play an important role.

In general, the decarbonylation of both **1a** and **1b**, are highly endothermic. However, a closer look at the decarbonylated species and their reaction behavior rationalizes the experimental observations. To determine the influence of the Cp^R ligand, the decarbonylated species $[\{Cp^RFe(CO)_2\}\{Cp^RFe(CO)\}(\mu,\eta^{1:2}\text{-}E_4)]$ ($Cp^R = Cp^*$, E = P (**I**), As (**II**); $Cp^R = Cp'''$, E = P (**III**), As (**IV** = **3a**)) were chosen as model systems. While for the Cp* derivatives **I** and **II** the dimerization reactions are exergonic, they are endergonic for **III** and **IV** with the large Cp‴ substituents. This result is consistent with the findings of Dahl et al. who observed the formation of the P_8 cuneane complex with the small Cp^{Me} substituent.[7] Furthermore, the stabilizing effect of the large Cp‴ ligand is indicated.

Calculations also predict that dimerization of the P derivatives **I** and **III** is energetically more favored compared to the As derivatives **II** and **IV** (by 20 and $33\,kJ\,mol^{-1}$). At first glance, this finding is contrary to the experimentally observed dimerization of **IV**, but not **III**. However, possibility of the second decarbonylation reaction has to be taken into account. The loss of an additional CO group from **III** is predicted to be less endergonic than for **IV** ($5.5\,kJ\,mol^{-1}$ vs $42.3\,kJ\,mol^{-1}$ in the gas phase). Hence, in solution, **III** is more likely to lose the second CO ligand to form **5**, while **IV** dimerizes to form the As_8 cuneane complex **3b**.

In conclusion, we reported the mild and selective formation of the dinuclear butterfly complexes $[\{L_nM\}_2(\mu,\eta^{1:1}\text{-}E_4)]$ (E = P, As; $L_nM = Cp'''Fe(CO)_2$, $Cp^*Cr(CO)_3$) as new representatives of that scarcely known class of compounds. Complexes **1b** and **2b** are the first As_4 butterfly compounds with a bridging coordination mode. Moreover, initial studies regarding the reactivity of **1b** and **2b** are presented, revealing the formation of the unprecedented As_8 cuneane complexes **3b** and **4**. Theoretical calculations rationalize the spontaneous formation of the Cr_4As_8 cuneane complex, while the Fe_4As_8 cuneane complex is only formed after photolytic activation. Moreover, it is shown that the steric bulk of the used Cp^R ligand and a potential second decarbonylation step play an important role for the formation of these complexes and their structural differences.

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[13] Note, the IR data of **3a** fit very well with those of the P analogue $[\{Cp''Fe(CO)_2\}(\mu,\eta^{1:2}\text{-}P_4)\{Cp''Fe(CO)\}]$, which was synthesized and structurally characterized by Scherer et al.[4b]