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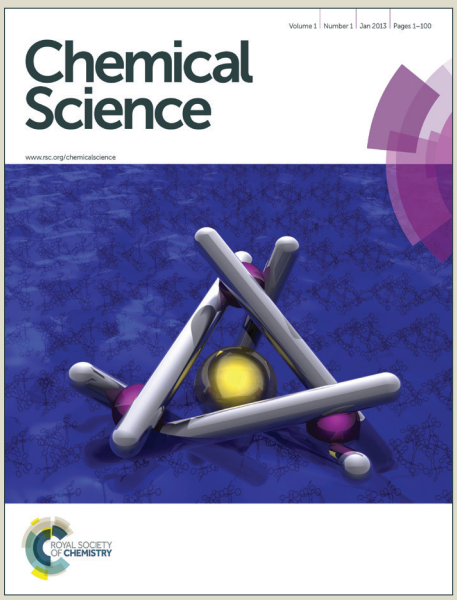

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Activation of group 15 based cage compounds by $[Cp^{BIG}Fe(CO)_2]$ radicals

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The sterically encumbered dimer $[Cp^{BIG}Fe(CO)_2]_2$ (**1**) (Cp^{BIG} = $C_5(4\text{-}n\text{Bu}C_6H_4)_5$) is able to activate small tetrahedral molecules like P_4 and As_4 as well as the less reactive cage compounds P_4S_3 and P_4Se_3 at room temperature to give the products $[\{Cp^{BIG}Fe(CO)_2\}_2(\mu,\eta^{1:1}\text{-cage})]$ (**cage** = P_4 (**2a**), As_4 (**2b**), P_4S_3 (**2c**), P_4Se_3 (**2d**) in a quantitative manner. The reaction proceeds via selective cleavage of one E–E bond (E = P, As) of the starting material. Complex **1** also reacts with CS_2 forming the binuclear compound $[\{Cp^{BIG}Fe(CO)_2\}\{Cp^{BIG}FeCO)(\mu,\eta^{1:2}\text{-}CS_2)]$ (**3**).

Introduction

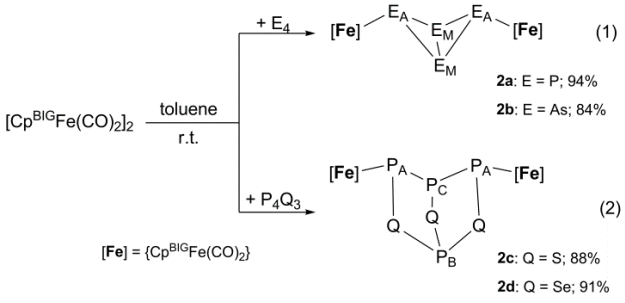
The activation of white phosphorus with transition metal complexes[1] and main group elements[2] is of current research interest. In recent decades, a large variety of transition-metal complexes with P_n units have been synthesized. In general, the reactions are thermolytically or photolytically induced to generate reactive complex fragments. Under these rather severe conditions, a substantial fragmentation and reaggregation of the P_4 tetrahedron is typically found, which often is accompanied with mixtures of products. Exemplifying the situation for P_4, Scherer et al. reacted $[Cp'''Fe(CO)_2]_2$ with white phosphorus for a short thermolysis (5 min) in toluene,[3] and detected the butterfly complex $[\{Cp'''Fe(CO)_2\}_2(\mu,\eta^{1:1}\text{-}P_4)]$ as the main product. However, due to the high temperatures further decarbonylation takes place leading to by-products, which had to be removed by low temperature column chromatography that led to reduced isolated yields. The situation for the mixed cage compounds P_4S_3 and P_4Se_3, is even more problematic.[4] The presence of two different types of atoms complicated the separation and characterization of the obtained products. Thus, e.g. Wachter et al. described the reaction of P_4S_3 with $[Cp^*Mo(CO)_2]_2$ in boiling toluene to give triple-decker sandwich complexes with five-membered rings as a middle deck. Both products, $[(Cp^*Mo)_2(P_2S_3)]$ and $[(Cp^*Mo)_2(P_4S)]$, have almost the same molecular structure, only the middle deck is different (P_4S vs. P_2S_3).[5] The separation was only possible after the coordination of $M(CO)_5$ fragments (M = Cr, W) to these products.

To avoid high temperatures or UV irradiation for triggering a reaction, isolable complexes with reactive metal centers are needed. The dimeric compounds $[(Cp^{Aryl})Fe(CO)_2]_2$ (Cp^{Aryl} = C_5Ph_5, C_5Ph_4(*p*-tolyl)) readily dissociate in solution into two 17-VE radical fragments at room temperature and, therefore, should be capable for this mission.[6] However, their low solubility is a disadvantage for reactivity studies. Therefore, we synthesized the analogous complex $[Cp^{BIG}Fe(CO)_2]_2$ (**1**) (Cp^{BIG} = pentakis(4-*n*-butylphenyl)cyclopentadienyl),[7] whose additional n-butyl groups lead to a good solubility. The general goal of **1** is to activate small molecules under mild condition in a selective and complete manner.

In the following, we report the room temperature activation of P_4, As_4, P_4S_3 or P_4Se_3 by $[Cp^{BIG}Fe(CO)_2]_2$ (**1**) resulting in a selective E-E bond cleavage to give exclusively the corresponding cage complexes in high yields. In addition, this complex also activates small organic molecule like CS_2. Note, some examples for the functionalization of P_4 by main group-based radicals have been reported.[8]

Results and discussion

Addition of **1** to toluene solutions of P_4, As_4, P_4S_3 or P_4Se_3, respectively, gives an immediate color change from green to intensive orange (P_4, As_4) or pink (P_4S_3, P_4Se_3), respectively. The IR spectra indicate a complete conversion of the starting material by showing two new CO stretching frequencies (Table 1, 4 CO bands for **1**). Also, the NMR spectra of the reaction mixtures illustrate a clean and complete reaction. The products $[\{Cp^{BIG}Fe(CO)_2\}_2(\mu,\eta^{1:1}\text{-cage})]$ (**cage** = P_4 (**2a**), As_4 (**2b**), P_4S_3 (**2c**), P_4Se_3 (**2d**)) are isolated in almost quantitative yields (Eqs. 1 and 2) and reveal that selectively only one homolytic E-E bond (E = P, As) was cleaved.



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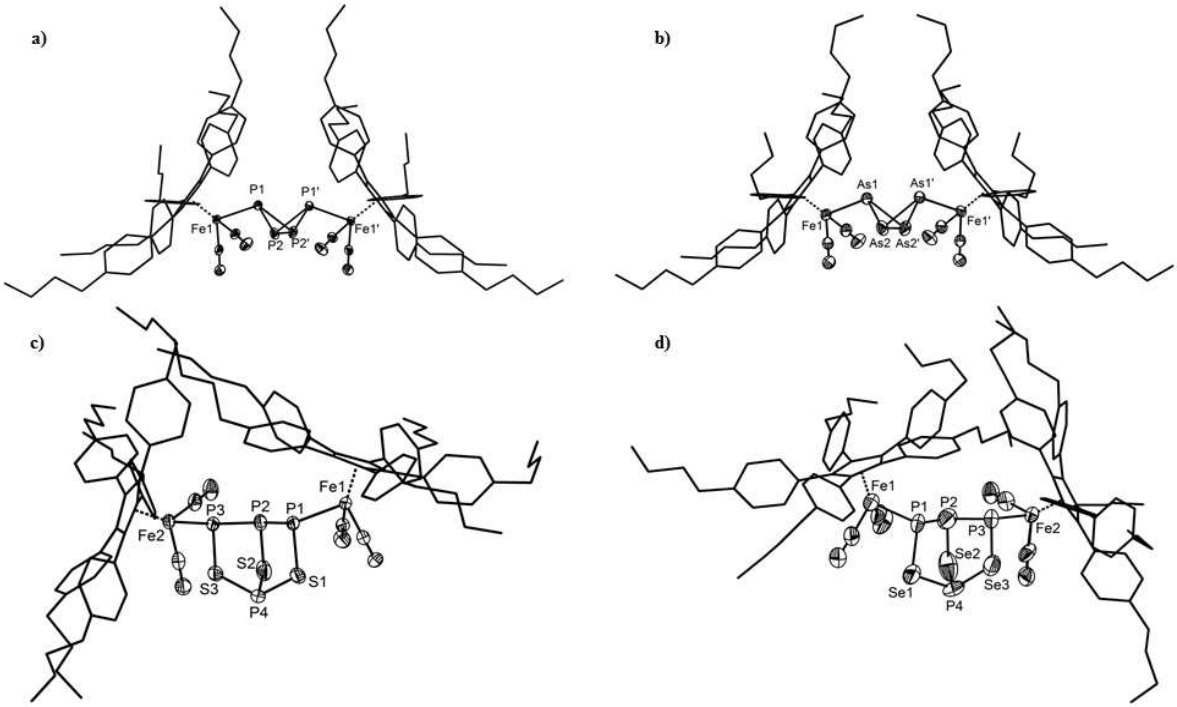


Fig. 1 Molecular structures of **2a-d** in the crystal (a: **2a**; b: **2b**; c: **2c**; d **2d**). Ellipsoids are drawn at 50% probability level. In case of **2c** only one of the two molecules of the asymmetric unit is depicted. In case of disorder only the main part is shown. For clarity H atoms and solvent molecules are omitted. Cp^{BIG} ligands are drawn in 'wires or sticks' model. Selected bond distances [Å] and angles [°] in **2a**: P1-P2 2.2343(5), P1-P2' 2.2094(6), P1···P1' 2.7749(4), P2-P2' 2.1717(7), Fe1-P1 2.3397(4), P1-P2-P1' 77.28(2), P1-P2-P2' 60.17(2), P2-P2'-P1 61.32(2), P2-P1-P2' 58.51(2). Selected bond distances [Å] and angles [°] in **2b**: As1-As2 2.4639(6), As1-As2' 2.4357(7), As1···As1' 2.9958(4), As2-As2' 2.3976(9), Fe1-As1 2.4315(7), As1-As2-As1' 75.39(2), As1-As2-As2' 60.12(2), As2-As2'-As1 61.29(2), As2-As1-As2' 58.59(2). Selected bond distances [Å] and angles [°] in **2c** from both molecules in the asymmetric unit: P1-P2/P6-P7 2.227(2)/2.190(1), P2-P3/P5-P6 2.185(1)/2.194(1), P1···P3/P5···P7 3.268(1)/3.318(1), P1-S1/P7-S6 2.156(1)/2.172(1), P2-S2/P6-S5 2.108(2)/2.114(1), P3-S3/P5-S4 2.157(1)/2.161(1), P4-S1/P8-S6 2.074(2)/2.099(2), P4-S2/P8-S5 2.107(2)/2.100(1), P4-S3/P8-S4 2.097(2)/2.094(2), Fe1-P1/Fe4-P7 2.314(1)/2.313(1), Fe2-P3/Fe3-P5 2.309(1)/2.314(1), P1-P2-P3/P5-P6-P7 95.60(5)/98.38(5), P1-S1-P4/P7-S6-P8 105.34(6)/107.52(5), P2-S2-P4/P6-S5-P8 97.51(7)/97.46(5), P3-S3-P4/P5-S4-P8 108.02(6)/106.27(6). Selected bond distances [Å] and angles [°] in **2d** (in case of disordered atoms both values are given, signed by postfixes A and B): P1-P2A/P1-P2B 2.12(1)/2.247(8), P2A-P3/P2B-P3 2.18(1)/2.148(10), P1···P3 3.260(3), P1-Se1 2.299(2), P2A-Se2A/P2B-Se2B 2.32(2)/2.14(1), P3-Se3 2.304(2), P4A-Se1/P4B-Se1 2.25(2)/2.23(1), P4A-Se2A/P4B-Se2B 2.09(2)/2.36(2), P4A-Se3/P4B-Se3 2.30(1)/2.23(1), Fe1-P1 2.321(2), Fe2-P3 2.298(2), P1-P2A-P3/P1-P2B-P3 98.6(5)/95.7(3), P1-Se1-P4A/P1-Se1-P4B 96.1(3)/104.4(4), P2A-Se2A-P4A/P2B-Se2B-P4B 93.5(5)/97.1(5), P3-Se3-P4A/P3-Se3-P4B 98.9(3)/110.0(4).

Table 1 IR and $^{31}P\{^{1}H\}$ NMR data of **2a**, **2c** in C_6D_6, **2d** in CD_2Cl_2 and ν_{CO} in toluene of **2a-d**. For P labeling cf. Figure 1. (δ in ppm, J_{PP} in Hz, ν_{CO} in cm^{-1})

Complex	δ (P_A)	δ ($P_{M/B}$)	δ (P_C)	J_{PP}	ν_{CO}
2a	-53.9	-317.1	-	187 (P_AP_M)	2002, 1955
2b	-	-	-	-	1993, 1948
2c	169.4	153.5	91.5	296 (P_AP_C), 63 (P_BP_C), 45 (P_AP_B)	2011, 1967
2d	181.3	123.5	101.8	305 (P_AP_C), 66 (P_BP_C), 45 (P_AP_B)	2011, 1967

Compounds **2a-d** are soluble in CH_2Cl_2, toluene, thf, and hexane but insoluble in CH_3CN. The ESI mass spectra of **2a** and **2b** show the molecular ion peaks. In the case of **2c** and **2d** characteristic fragments could be detected. The $^{31}P\{^{1}H\}$ NMR spectrum of **2a** show two triplets at δ = -54.0 ppm and δ = -317.1 ppm ($^{1}J_{PP}$ = 187 Hz), which is typical for P_4 butterfly complexes.[9] For **2c** and **2d** the $^{31}P\{^{1}H\}$ NMR spectra show A_2BC spin systems (Table 1), which clearly indicate the suggested molecular structures.

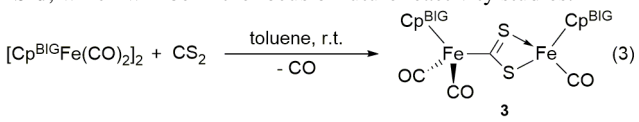
Single crystal X-ray structure analyses of **2a-d** (Fig. 1) reveal the selective cleavage of one single E–E bond (E = P, As) and two $\{Cp^{BIG}Fe(CO)_2\}$ fragments are now coordinated at these atoms. Compounds **2a** and **2b** show a central tetraphospha/tetraarsa-bicyclo[1.1.0]butane (butterfly) structural motif, whereas for **2c** and **2d** a tetraphospha-trithio/triseleno-bicyclo[2.2.1]heptane core is found. The P_4 butterfly complex **2a** follow the same trend for P–P bond lengths like other derivatives, e.g. $[\{Cp'''Fe(CO)_2\}_2(\mu,\eta^{1:1}\text{-}P_4)]$.[3] The bond between P1 and P2/P2' (2.2094(6) Å and 2.2343(5) Å) are similar to a single bond like in P_4 (2.21 Å)[2a,10], however the bond P2-P2' is slightly shortened (2.1717(7) Å).

While for P_4 ligands the butterfly structural motif is known, it is particularly rare for As_4 ligands. The only structurally

characterized compound in literature is [Cp*Co(CO)($\eta^{1:1}$-As_4)] in which the As_4 unit is bound to only one metal atom.[11] Recently in our group, two other arsenic containing butterfly complexes were obtained, [{Cp'''Fe(CO)$_2$}$_2$(μ,$\eta^{1:1}$-As_4)] and [{Cp*Cr(CO)$_3$}$_2$(μ,$\eta^{1:1}$-As_4)].[12] In **2b** the bonds between the coordinated atom As1 and the non-coordinated As2 are also longer (2.4357(7) Å and 2.4639(6) Å) than the bridgehead bond (2.3976(9) Å) and agree well with the above mentioned examples. In addition, **2b** shows the same distortion after conversion as compared with As_4 (As–As 2.44 Å),[13] as with **2a** and P_4.

For the cleavage of one P–P bond of the P_3 ring in P_4S_3 only three examples are known. They all reveal an oligomeric metal bridged structure; dimeric for the iridium complexes *cis*/*trans*-[Ir(μ-P_4S_3)(PPh$_3$)Cl(CO)]$_2$[14] and trimeric for [Pt(μ-P_4S_3)(PPh$_3$)]$_3$.[15] In contrast for **2c-d**, a monomeric structural motif is observed without an oligomerization because of the steric protection of the {Cp^{BIG}Fe(CO)$_2$} fragments compared to PPh$_3$ ligands in the complexes mentioned above. Despite the different structures, the distances in the P_4S_3 core in **2c** are similar except of the average P–P bond length of 2.20 Å which is about 0.05-0.10 Å shorter than those of the Ir and Pt complexes, respectively. Compound **2d** represents the unprecedented example, in which the first step of the degradation of the P_4Se_3 cage is observed. The P–P bond lengths are (average of 2.17 Å) shorter than in the P_4Se_3 molecule (2.22 Å – 2.26 Å),[16] while the other bonds of the cage are rather unaffected.

The activation of a second bond of the cages in **2a-d** by **1** was not observed regardless of the stoichiometry used and increased reaction times. However, if solutions of **2a** are heated, formation of [Cp^{BIG}Fe(η^5-P_5)] and [(Cp^{BIG}Fe)$_2$(μ,$\eta^{4:4}$-P_4)] is observed. We recently reported on the thermolysis of **1** with P_4, resulting in complete degradation of the tetrahedral structure of P_4 resulting in the two products [Cp^{BIG}Fe(η^5-P_5)] and [(Cp^{BIG}Fe)$_2$(μ,$\eta^{4:4}$-P_4)].[7] Furthermore, if white phosphorus is added to **2a** before heating, the same ratio of products and yields are obtained as was found before.[7] This indicates that **2a** is the initial activation step for the complete conversion of P_4 by Cp^RFe fragments. A higher grade of degradation at elevate temperatures can also be assumed for **2b-d**, which will be in the focus of future reactivity studies.



In addition, the reaction of **1** with an excess of CS_2 at ambient temperature results in the quantitative formation of the binuclear complex [{Cp^{BIG}Fe(CO)$_2$}{Cp^{BIG}Fe(CO)}(μ,$\eta^{1:2}$-CS_2)] (**3**) accompanied by instant change of color from green to brown (Eq. 3). Three new CO absorption bands for **3** are observed in both, solution (CH_2Cl_2: 2023 cm^{-1}, 1979 cm^{-1}, 1928 cm^{-1}) and solid state (KBr: 2022 cm^{-1}, 1979 cm^{-1}, 1936 cm^{-1}). The ^{1}H NMR and the ^{13}C NMR spectra of **3** in CH_2Cl_2 show multiple superimposed signals, indicating magnetic different Cp^{BIG} ligands due to the hindered rotation.[9,17] The X-ray structure analysis of **3** (Fig. 2) shows two different iron fragments are bridged by a CS_2 ligand. The molecule can be described as a ferradithiocarboxylate [Cp^{BIG}(CO)$_2$Fe-CS_2]$^-$ coordinating as a chelate ligand to a {Cp^{BIG}FeCO}$^+$ fragment. The bond lengths within the dithiocarboxylate ligand show large differences. The C99-S1 bond is with 1.762(6) Å by about 0.1 Å longer than the one between C99 and S2 (1.660(6) Å), indicating localized single and double bonds. Also the IR spectrum of **3** is consistent with the observation of a non-symmetric CS_2 ligand, where two bands in the appropriate region can be found at 1082 cm^{-1} and 1030 cm^{-1}. These values are in a comparable range with other CS_2 complexes.[18]

A possible reaction pathway starts from the addition of two [Cp^{BIG}Fe(CO)$_2$] units onto a CS_2 molecule, one on the carbon atom the other on one S atom. The not to iron bound S atom than attacks the iron fragment bound to sulfur with CO elimination and formation of **3**.

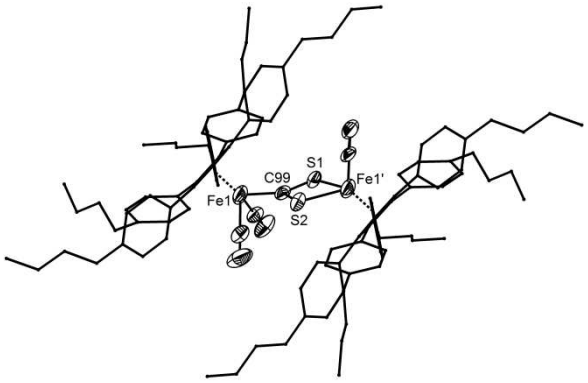


Fig. 2 Molecular structure of **3** in the crystal. Ellipsoids are drawn at a 50% probability level. For clarity H atoms are omitted and Cp^{BIG} ligands are drawn in 'wires or sticks' model. Selected bond distances [Å] and angles [°] in **3**: Fe1-C99 1.893(5), C99-S1 1.762(6), C99-S2 1.660(6), S1-Fe1' 2.396(2), S2-Fe1' 2.302(2), S1-C99-S2 104.9(3), Fe1'-S1-C99 89.4(2), Fe1'-S2-C99 95.3(3), S1-Fe1'-S2 70.51(5).

Conclusions

The spontaneous formation of metal centred radicals from the sterically encumbered complex **1** enables the selective cleavage of a single E–E bond (E = P, As) in the cage molecules P_4, As_4, P_4S_3 and P_4Se_3, respectively, already at room temperature. The quantitatively obtained products [{Cp^{BIG}Fe(CO)$_2$}$_2$(μ,$\eta^{1:1}$-**cage**)] (**cage** = P_4 (**2a**), As_4 (**2b**), P_4S_3 (**2c**), P_4Se_3 (**2d**)) exhibit bicyclic structural motifs. Regardless of stoichiometry and reaction time applied, no further degradation of the molecules could be observed. Thermolysis of **2a** leads to *cyclo*-P_5 and P_4-butadiene containing products, which are also formed by the direct reaction of **1** with P_4 under elevated temperatures. Furthermore we have shown that **1** readily reacts with CS_2 to form a binuclear complex with a dithiocarboxylate ligand.

Further studies will be focus on the use of the dimeric complex **1** to activate other small (organic) molecules, also in a catalytically manner.

Acknowledgments

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Experimental details

General remarks

All experiments were carried out under an atmosphere of dry argon or nitrogen using glovebox and Schlenk techniques. Solvents were purified, dried, and degassed prior to use. P_4, P_4S_3 and P_4Se_3 were available and solutions of As_4[19] and $[Cp^{BIG}Fe(CO)_2]_2$ (**1**)7 were prepared according to literature procedures. The NMR spectra were measured on a Bruker Avance 300, 400, or 600 MHz spectrometer. ESI-MS spectra were measured on a ThermoQuest Finnigan TSG 7000 mass spectrometer and FD-MS spectra on a Finnigan MAT 95 mass spectrometer. The elemental analyses were determined on a Vario EL III apparatus. The IR spectra were measured on a VARIAN FTS-800 FT-IR spectrometer.

Preparation of $[\{Cp^{BIG}Fe(CO)_2\}_2(\mu,\eta^{1:1}\text{-}P_4)]$ (2a). A solution of $[Cp^{BIG}Fe(CO)_2]_2$ (**1**) (1.3 g, 0.78 mmol) in 100 mL toluene is added to a solution of P_4 (96 mg, 0.78 mmol) in 50 mL toluene. The orange solution is stirred for 30 min, and the solvent is removed in vacuum. The residue is dissolved in ca. 15 mL CH_2Cl_2, transferred into a Schlenk-tube and 50 mL CH_3CN is layered over it. After complete diffusion, red crystals of **2a** are obtained. Yield: 1.30 g (94%).

$[C_{114}H_{130}Fe_2O_4P_4]$ calc.: C, 76.08; H, 7.28. found: C, 75.82; H, 7.13. *m/z* (ESI, toluene/CH_3CN/CH_2Cl_2) 1884.7 (65%, $[M+CH_2Cl_2]^+$), 1718.7 (20%, $[Cp^{BIG}{}_2Fe_2P_5]^+$), 1508.3 (20%, $[Cp^{BIG}{}_2Fe_2]^+$), 1718.7 (100%, $[Cp^{BIG}Fe(toluene)]^+$), 741.5 (80%, $[Cp^{BIG}OH]^+$). IR (toluene, cm^{-1}): ν_{CO} 2002 (s), 1955 (s). ^1H NMR (C_6D_6): δ 0.81 (t, $^3J_{HH}$ = 7.3 Hz, 30H, CH_3), 1.16 (m, 10H, CH_2), 1.35 (m, 10H, CH_2), 2.29 (t, $^3J_{HH}$ = 7.7 Hz, 10H, CH_2), 6.73 (d, $^3J_{HH}$ = 7.9 Hz, 10H, C_6H_4), 7.34 (d, $^3J_{HH}$ = 7.9 Hz, 10H, C_6H_4). $^{31}P\{^1H\}$ NMR (C_6D_6): δ -317.1 (t, $^1J_{PP}$ = 187 Hz, 2P, P_M), -53.9 (t, $^1J_{PP}$ = 187 Hz, 2P, P_A).

Preparation of $[\{Cp^{BIG}Fe(CO)_2\}_2(\mu,\eta^{1:1}\text{-}As_4)]$ (2b). A solution of $[Cp^{BIG}Fe(CO)_2]_2$ (**1**) (0.75 g, 0.44 mmol) in 50 mL toluene is added at room temperature to a freshly prepared solution of As_4 (from 5 g As_{gray} in 300 mL toluene). The orange solution is stirred for 30 min and the solvent is removed in vacuum. The residue is solved in ca. 10 mL CH_2Cl_2, filtered into a Schlenk-tube and 30 mL CH_3CN is layered over it. After complete diffusion, red crystals of **2b** are obtained. Yield: 0.73 g (84%).

$[C_{114}H_{130}Fe_2O_4As_4{*}CH_2Cl_2]$ calc.: C, 67.03; H, 6.46. found: C, 66.64; H, 6.44. *m/z* (ESI, CH_2Cl_2) 1976.2 (100%, $[M]^+$). IR (toluene, cm^{-1}): ν_{CO} 1993 (s), 1948 (s). ^1H NMR (C_6D_6): δ 0.80 (t, $^3J_{HH}$ = 7.2 Hz, 30H, CH_3), 1.16 (m, 10H, CH_2), 1.34 (m, 10H, CH_2), 2.27 (t, $^3J_{HH}$ = 7.6 Hz, 10H, CH_2), 6.72 (d, $^3J_{HH}$ = 8.0 Hz, 10H, C_6H_4), 7.34 (d, $^3J_{HH}$ = 8.0 Hz, 10H, C_6H_4).

Preparation of $[\{Cp^{BIG}Fe(CO)_2\}_2(\mu,\eta^{1:1}\text{-}P_4S_3)]$ (2c) and $[\{Cp^{BIG}Fe(CO)_2\}_2(\mu,\eta^{1:1}\text{-}P_4Se_3)]$ (2d). A solution of $[Cp^{BIG}Fe(CO)_2]_2$ (**1**) (0.20 g, 0.11 mmol) in 5 mL toluene is added to a solution of P_4Q_3 (P_4S_3: 25 mg, 0.11 mmol; P_4Se_3: 40 mg, 0.11 mmol) in 5 mL toluene. The pink solution is stirred for 30 min, filtered via cannula and the solvent is removed in vacuum. According to the NMR spectroscopy the isolated solids are pure. Yield: 100 mg (88%) of **2c**; 110 mg (91%) of **2d**.

2c: An analytically pure crystalline sample can be obtained by the diffusion of CH_3CN in CH_2Cl_2 solutions of **2c**. Crystalline yield: 99 mg (47%). $[C_{114}H_{130}Fe_2O_4P_4S_3{*}CH_2Cl_2]$ calc.: C, 69.73; H, 6.72; S, 4.86. found: C, 70.03; H, 6.54; S, 4.86. *m/z* (ESI, toluene/CH_3OH) 1839.1 (100%, $[M\text{-}2CO]^+$). IR (toluene, cm^{-1}): ν_{CO} 2011 (s), 1967 (s). ^1H NMR (C_6D_6): δ 0.82 (t, $^3J_{HH}$ = 7.3 Hz, 30H, CH_3), 1.18 (m, 10H, CH_2), 1.38 (m, 10H, CH_2), 2.32 (t, $^3J_{HH}$ = 7.8 Hz, 10H, CH_2), 6.75 (d, $^3J_{HH}$ = 8.2 Hz, 10H, C_6H_4), 7.30 (d, $^3J_{HH}$ = 8.2 Hz, 10H, C_6H_4). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 91.5 (td, $^1J(P_AP_C)$ = 296 Hz, $^2J(P_BP_C)$ = 63 Hz, 1P, P_C), 153.5 (dt, $^2J(P_BP_C)$ = 63 Hz, $^2J(P_AP_B)$ = 45 Hz, 1P, P_B), 169.4 (dd, $^2J(P_AP_B)$ = 45 Hz, $^1J(P_AP_C)$ = 296 Hz, 2P, P_A). $^{13}C\{^1H\}$ NMR (C_6D_6): 14.1 (CH_3), 22.7 (CH_2), 33.1 (CH_2), 35.5 (CH_2), 103.5 (Cp), 128.4 (C_6H_4), 133.1 (C_6H_4), 142.6 (C_6H_4), 215.0 (CO), one Ph C atom is obscured by solvent signal.

2d: $[C_{114}H_{130}Fe_2O_4P_4S_3{*}CH_2Cl_2]$ calc.: C, 67.23; H, 6.43. found: C, 66.06; H, 6.47. *m/z* (FD, toluene) 1786.1 (100%, $[M\text{-}P_3Se_2]^+$). IR (toluene, cm^{-1}): ν_{CO} 2011 (s), 1967 (s). ^1H NMR (CD_2Cl_2): δ 0.91 (t, $^3J_{HH}$ = 7.2 Hz, 30H, CH_3), 1.30 (m, 10H, CH_2), 1.53 (m, 10H, CH_2), 2.49 (t, $^3J_{HH}$ = 7.2 Hz, 10H, CH_2), 6.84 (d, $^3J_{HH}$ = 7.7 Hz, 10H, C_6H_4), 6.92 (d, $^3J_{HH}$ = 7.7 Hz, 10H, C_6H_4). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 101.8 (td, $^1J(P_AP_C)$ = 305 Hz, $^2J(P_BP_C)$ = 66 Hz, 1P, P_C), 123.5 (dt, $^2J(P_BP_C)$ = 66 Hz, $^2J(P_AP_B)$ = 45 Hz, 1P, P_B), 181.3 (dd, $^2J(P_AP_B)$ = 45 Hz, $^1J(P_AP_C)$ = 305 Hz, 2P, P_A). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 14.1 (CH_3), 22.7 (CH_2), 33.5 (CH_2), 35.6 (CH_2), 103.4 (Cp), 127.9 (C_6H_4), 127.9 (C_6H_4), 132.8 (C_6H_4), 143.0 (C_6H_4), 215.4 (CO).

Preparation of $[\{Cp^{BIG}Fe(CO)_2\}\{Cp^{BIG}Fe(CO)\}(\mu,\eta^{1:2}\text{-}CS_2)]$ (3). To a solution of $[Cp^{BIG}Fe(CO)_2]_2$ (**1**) (100 mg, 0.06 mmol) in 5 mL toluene 1 mL CS_2 is added. The solution immediately becomes brown. The reaction mixture is stirred for 30 min, filtered, and the solvent is removed in vacuum. **3** is obtained as brown powder. Yield: 93 mg (91%)

To obtain single crystals, the residue is dissolved in ca. 5 mL CH_2Cl_2, transferred into a Schlenk-tube and 10 mL CH_3CN is layered over it. After complete diffusion, red needle shaped crystals of **2a** are obtained.

3: $[\{Cp^{BIG}Fe(CO)_2\}\{Cp^{BIG}Fe(CO)\}(\mu,\eta^{1:2}\text{-}CS_2)]$: *m/z* (FD, toluene) 1724.0 (45%, $[M]^+$), 1696.1 (100%, $[M - CO]^+$), 1640.2 (55%, $[M - 3CO]^+$). IR (CH_2Cl_2, cm^{-1}): ν_{CO} 2023 (s), 1979 (s), 1928 (s). IR (KBr, cm^{-1}): ν_{CO} 2022 (s), 1979 (s), 1936 (s). ^1H NMR (CD_2Cl_2): δ 0.91 (m, 30H, CH_3), 1.32 (m, 20H, CH_2), 1.53 (m, 20H, CH_2), 2.52 (m, 20H, CH_2), 6.7 – 7.0 (m, 40H, C_6H_4). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 14.14, 14.17, 22.70, 22.76, 22.80, 22.84, 33.56, 33.59, 33.61, 33.72, 33.78, 35.68, 96.29, 98.27, 102.00, 102.50, 103.49, 103.60, 127.24. 127.44, 127.49, 127.58, 127.88, 127.96, 128.08, 128.12, 128.20, 128.24, 129.0, 131.69, 132.23, 132.43, 132.55, 132.92, 141.14, 141.64, 142.21, 142.91, 142.97, 143.59, 214.87, 216.10.

Notes and references

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† Electronic Supplementary Information (ESI) available: Full crystallographic data, NMR spectra. See DOI: 10.1039/b000000x/

1 a) B. M. Cossairt, N. A. Piro, C. C. Cummins, *Chem. Rev.*, 2010, **110**, 4164-4177; b) M. Caporali, L. Gonsalvi, A. Rossin, M. Peruzzini, *Chem. Rev.*, 2010, **110**, 4178-4235.

2 a) M. Scheer, G. Balázs, A. Seitz, *Chem. Rev.*, 2010, **110**, 4236-4256. b) N. A. Giffin, J. D. Masuda, *Coord. Chem. Rev.*, 2011, **255**, 1342-1359.

3 O. J. Scherer, T. Hilt, G. Wolmershäuser, *Organometallics* 1998, **17**, 4110-4112.

4 a) J. Wachter, *Angew. Chem., Int. Ed.*, 1998, **37**, 751-768. b) M. Di Vaira, P. Stoppioni, *Coord. Chem. Rev.* 1992, **120**, 259-279.

5 H. Brunner, U. Klement, W. Meier, J. Wachter, O. Serhadle, M. L. Ziegler, *J. Organomet. Chem.*, 1987, **335**, 339-352.

6 a) I. Kuksis, M. C. Baird, *Organometallics*, 1994, **13**, 1551-1553. b) I. Kuksis, M. C. Baird, *Organometallics*, 1996, **15**, 4755-4762.

7 S. Heinl, G. Balázs, M. Scheer, *Phosphorus, Sulfur Silicon Relat. Elem.*, **2014,** accepted. http://dx.doi.org/10.1080/10426507.2014.903489

8 a) D. H. R. Barton, J. Zhu, *J. Am. Chem. Soc.* **1993**, *115*, 2071-2072. b) D. H. R. Barton, R. A. Vonder Embse, *Tetrahedron* **1998**, *54*, 12475-12496; c) B. M. Cossairt, C. C. Cummins, *New J. Chem.* **2010**, *34*, 1533-1536; d) J.-P. Bezombes, P. B. Hitchcock, M. F. Lappert, J. E. Nycz, *Dalton Trans.* **2004**, 499-501.

9 S. Heinl, S. Reisinger, C. Schwarzmaier, M. Bodensteiner, M. Scheer, *Angew. Chem. Int. Ed.*, 2014**, 53,** accepted. http://dx.do.org/10.1002/anie.201403295.

10 a) C. Schwarzmaier, A. Schindler, C. Heindl, S. Scheuermayer, E. V. Peresypkina, A. V. Virovets, M. Neumeier, R. Gschwind, M. Scheer, *Angew. Chem., Int. Ed.* **2013**, *52*, 10896-10899. b) A. Simon, H. Borrmann, H. Craubner, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1987, **30**, 507-510. c) B. M. Cossairt, C. C. Cummins, A. R. Head, D. L. Lichtenberger, R. J. F. Berger, S. A. Hayes, N. W. Mitzel, G. Wu, *J. Am. Chem. Soc.*, 2010, **132**, 8459-8465.

11 O. J. Scherer, K. Pfeiffer, G. Wolmershäuser, *Chem. Ber.* **1992**, *125*, 2367-2372.

12 C. Schwarzmaier, PhD thesis, University of Regensburg (Regensburg, Germany), 2012.

13 a) Y. Morino, T. Ukaji, T. Ito, *Bull. Chem. Soc. Jpn.* **1966**, *39*, 64-71.b) H. A. Spinney, N. A. Piro, C. C. Cummins, *J. Am. Chem. Soc.* **2009**, *131*, 16233-16243.

14 a) C. A. Ghilardi, S. Midollini, A. Orlandini, *Angew. Chem., Int. Ed.*, 1983, **22**, 790-791. b) E. Kuwabara, R. Bau, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1994, **50**, 64-67.

15 M. Di Vaira, M. Peruzzini, P. Stoppioni, *J. Chem. Soc., Dalton Trans.*, 1985, 291-295.

16 E. Keulen, A. Vos, *Acta Crystallogr.*, 1959, **12**, 323-329.

17 a) S. Heinl, E. V. Peresypkina, A. Y. Timoshkin, P. Mastrorilli, V. Gallo, M. Scheer, *Angew. Chem., Int. Ed.*, 2013, **52**, 10887-10891. b) S. Heinl, E. V. Peresypkina, A. Y. Timoshkin, P. Mastrorilli, V. Gallo, M. Scheer, *Angew. Chem.*, 2013, **125**, 11087-11091.

18 a) W. Uhl, A. Vester, W. Hiller, *J. Organomet. Chem.* **1993**, *443*, 9-17. b) C. Bianchini, C. Mealli, A. Meli, A. Orlandini, L. Sacconi, *Inorg. Chem.* **1980**, *19*, 2968-2975. c) M. Herberhold, M. Süß-Fink, *Chem. Ber.* **1978**, *111*, 2273-2281. d) U. Oehmichen, T. G. Southern, H. Le Bozec, P. Dixneuf, *J. Organomet. Chem.* **1978**, *156*, C29-C32.

19 O. J. Scherer, H. Sitzmann, G. Wolmershäuser, *J. Organomet. Chem.*, 1986, **309**, 77-86.

Table of Contents entry:

The sterically encumbered complex $[Cp^{BIG}Fe(CO)_2]_2$ (**1**) (Cp^{BIG} = pentakis(4-*n*-butylphenyl)cyclopentadienyl) forms in solution radicals, which enable the selective cleavage of a E–E single bond (E = P, As) in the cage molecules P_4, As_4, P_4S_3 and P_4Se_3, respectively, already at room temperature.