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The influence of differently substituted cyclopentadienyl Cp^R ligands on the reactivity of [Cp^{R}Fe(CO)$_2$]$_2$ with yellow arsenic

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General considerations

All manipulations were carried out using standard Schlenk techniques at a Stock apparatus under N_2 as an inert gas or in a glove box with Ar atmosphere. All glassware was dried with a heat gun (600 °C) for at least 1 h prior to use. CD_2Cl_2 was distilled from CaH_2, decaline and C_6D_6 over sodium. The other solvents were directly taken from an MBraun SPS-800 solvent purification system and degassed at room temperature. Solution ^{1}H (400.130 MHz), ^{13}C (100.627 MHz), ^{19}F (376.498 MHz) NMR spectra were recorded at an Avance400 (Bruker) spectrometer using $(H_3C)_4Si$ (^{1}H, ^{13}C), $CFCl_3$ (^{19}F), respectively, as external standards. Chemical shifts (δ) are provided in parts per million (ppm). ESI mass spectra were recorded at the internal mass spectrometry department using a ThermoQuest Finnigan TSQ 7000 mass spectrometer. Elemental analysis of the products was conducted by the elemental analysis department at the University of Regensburg using an Elementar Vario EL. The compounds [Cp^{R}Fe(CO)$_2$]$_2$ (Cp^R = Cp* (**1a**), Cp$^+$ (**1b**), Cp'' (**1c**)))[S1] and Tl[Al(OC(CF$_3$)$_3$)$_4$][S2] were available or were synthesized according to the literature procedures. All other chemicals were purchased from commercial vendors.

Synthesis of [(Cp"Fe)$_3$As$_6$] (3c)

Starting from grey arsenic (6 g), a solution of yellow arsenic in decalin (~300 ml) is prepared. Complex [Cp"Fe(CO)$_2$]$_2$ **1c** (800 mg, 1.38 mmol) was suspended in decalin in a 500 ml two-necked flask with a reflux condenser attached. The still hot As_4 solution is added to this suspension under strict exclusion of light and the mixture is refluxed for 90 min. The solvent was removed in vacuum. The black residue was suspended in toluene (~20 ml) and subjected to column chromatography (SiO_2, toluene, approx. 2 x 8 cm). A brown band was eluted with toluene. From the concentrated solution, product **3c** was obtained as a crystalline solid at −30°C.

Yield: 176 mg (0.153 mmol) = 17% based on **1c**.

Analytical data for $[(Cp''Fe)_3As_6]$ (**3c**):

^{1}H NMR (CH_2Cl_2)	δ/ppm = 1.13 (br, $\omega_{/2}$ = 10 Hz, $C_5H_3(C_4\mathbf{H}_9)_2$), 10.19 (br, $\omega_{/2}$ = 55 Hz, $C_5\mathbf{H}_3(C_4H_9)_2$)		
MS (EI, CH_2Cl_2)	*m/z*: 1149 ($[\{Cp''Fe\}_3As_6]^{\cdot+}$, 17%), 1074 ($[\{Cp''Fe\}_3As_5]^{\cdot+}$, 2 %), 999 ($[\{Cp''Fe\}_3As_4]^{\cdot+}$, 1 %), 766 ($[\{Cp''Fe\}_2As_4]^{\cdot+}$, 100 %), 691 ($[\{Cp''Fe\}_2As_3]^{\cdot+}$, 8 %), 608 ($[\{Cp''Fe\}As_5]^{\cdot+}$, 32 %), 458 ($[\{Cp''Fe\}As_3]^{\cdot+}$, 41 %), 300 ($[As_4]^{\cdot+}$, 52 %)		
elemental analyses	calculated:	C: 40.77 %	H: 5.53 %
$As_6C_{39}Fe_3H_{63}$	found:	C: 37.17 %	H: 5.27 %
M = 1149 g/mol			

Synthesis of $[(Cp^+Fe)_3As_6\{(\eta^3\text{-}As_3)Fe\}]$ (4b)

Starting from grey arsenic (4 g), a solution of yellow arsenic in decalin (~300 ml) is prepared. Complex $[Cp^+Fe(CO)_2]_2$ **1b** (810 mg, 1.56 mmol) was suspended in decalin in a 500 ml two-necked flask with an attached reflux condenser. The still hot As_4 solution was added to this suspension under strict exclusion of light, and the mixture was refluxed for 90 min. The solvent was removed in vacuum, the black residue was suspended in hexane (~20 ml) and subjected to column chromatography (SiO_2, hexane, approx. 2 x 15 cm). A green band of $[Cp^+Fe(\eta^5\text{-}As_5)]$ **2b** was eluted with hexane (98 mg, 0.17 mmol, approx. 5% yield). With toluene, a brown band was eluted. The solvent of the brown fraction was removed in vacuo, the residue taken up in a 1:3 mixture of toluene/hexane. A brown microcrystalline solid containing a 1:1 mixture of $[(Cp^+Fe)_3As_6]$ **3b** and **4b** (311 mg, each approx. 0.13 mmol, approx. 13% **3b** and 17% **4b** yield) was isolated by cooling the solution to −30°C. In order to purify **4b** further, the solid was again dissolved in toluene and purified over a long chromatography column (SiO_2, toluene, 1.5 × 25 cm) using toluene as the mobile phase. Compound **3b** decomposes on the column, and a brown solution is eluted. From this solution compound **4b** can be isolated after concentration and storage at −30°C as a crystalline solid.

Yield: 95 mg (0.071 mmol) = 9% based on **1b**.

Analytical data for $[(Cp^+Fe)_3As_6]$ (**3b**):

^{1}H NMR (C_6D_6)	δ/ppm = 1,14 (br, $-CH_2-C\mathbf{H}_3$), 2,63 (br, $-C\mathbf{H}_2-CH_3$), 3.15 (br, $C_5(C\mathbf{H}_3)_2(CH_3)_2(C_2H_5)$), 4,16 (br, $C_5(CH_3)_2(C\mathbf{H}_3)_2(C_2H_5)$),

Analytical data for $[(Cp^+Fe)_3As_6(FeAs_3)]$ (**4b**):

^{1}H NMR (C_6D_6)	δ/ppm = 0.89 (t, $^3J_{H,H}$ = 7.5 Hz, $-CH_2-C\mathbf{H_3}$), 1.76 (s, $C_5(C\mathbf{H_3})_2(CH_3)_2(C_2H_5)$), 1.79 (s, $C_5(CH_3)_2(C\mathbf{H_3})_2(C_2H_5)$), 2.41 (q, $^3J_{H,H}$ = 7.5 Hz, $-C\mathbf{H_2}-CH_3$)		
MS (EI, CH_2Cl_2)	*m/z*: 1345 ($[\{Cp^+Fe\}_3FeAs_9]^{\cdot+}$, 10 %), 1195 ($[\{Cp^+Fe\}_3FeAs_7]^{\cdot+}$, 7 %), 1065 ($[\{Cp^+Fe\}_3As_6]^{\cdot+}$, 34 %), 710 ($[\{Cp^+Fe\}_2As_4]^{\cdot+}$, 9 %), 580 ($[\{Cp^+Fe\}As_5]^{\cdot+}$, 15 %), 300 ($[As_4]^{\cdot+}$, 100 %), 225 ($[As_3]^{\cdot+}$, 7 %)		
Elemental analyses	calculated:	C: 29.46 %	H: 3.82 %
$As_9C_{33}Fe_4H_{51}$	found[a]:	C: 32.24 %	H: 4.36 %
M = 1345 g/mol			

[a] The deviation of the C and H content is probably due to the presence of impurities of **3b** in the samples. All attempts to obtained more accurate elemental analyses for **4b** failed.

Synthesis of $[\{(Cp^*Fe)_3As_6Fe\}_2(\mu,\eta^3:\eta^3-As_3)][Al(OC(CF_3)_3)_4]_2$ (5)

A solution of $Tl[Al(OC(CF_3)_3)_4]$ (11 mg, 10 µmol) in CH_2Cl_2 (10 ml) was carefully over-layered with a solution of $[(Cp^*Fe)_3As_6\{(\eta^3-As_3)Fe\}]$ **4a** (37 mg, 28 µmol) in toluene (15 ml), and this was stored at room temperature. After complete mixing of the phases, black crystals of compound **5**·(2 CH_2Cl_2)·(toluene) are formed. The mother liquor was decanted off together with a yellowish white amorphous precipitate which was also formed. The remaining crystalline solid was washed several times with hexane. Another batch of the crystalline solid can be obtained from the mother liquor by over-layering it with hexane. The batches are combined and dried extensively *in vacuo* to obtain pure **5**.

Yield: 23 mg (4.9 µmol) = 98% based on Tl[TEF].

Analytical data for $[\{(Cp^*Fe)_3As_6Fe\}_2(\mu,\eta^3:\eta^3-As_3)][Al(OC(CF_3)_3)_4]_2$ (**5**)

^{1}H NMR (THF-d_8)	δ/ppm = 4.36 (br, $\omega_{/2}$ = 50 Hz, $C_{10}\mathbf{H_{15}}$)		
^{19}F{^{1}H} NMR (THF-d_8)	δ/ppm = –74.9 (s, $[Al(OC(C\mathbf{F_3})_3)_4]$)		
MS (ESI, CH_2Cl_2)	*m/z*: 1304 ($[\{Cp^*Fe\}_3As_6FeAs_3\}]^+$, 15 %), 1191 $[\{(Cp^*Fe)_3As_6Fe\}_2As_3]^{2+}$, 67 %), 1023 ($[\{Cp^*Fe\}_3As_6]^+$, 100 %)		
Elemental analyses	calculated:	C: 25.60 %	H: 2.10 %
$Al_2As_{15}C_{92}F_{72}Fe_8H_{90}O_8$	found:	C: 25.71 %	H: 3.03 %
M = 4315 g/mol			

Crystallographic Details

The crystals were selected and measured on a Xcalibur Gemini Ultra diffractometer equipped with a Ruby CCD detector. The crystals were kept at T = 123(1) K (**3c**, **4a**, **4b**) or 100(1) K (**5**) during data collection. Data collection and reduction were performed with **CrysAlisPro**.[S3] Using **Olex2**,[S4] the structures were solved with **ShelXT**,[S5] **Superflip**[S6] or **SIR-97**[S7] and a least-square refinement on F^2 was carried out with **ShelXL**.[S8] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms at the carbon atoms were located in idealized positions and refined isotropically according to the riding model.

Figures were created with **Olex2**.[S4]

Compound 3c: The asymmetric unit contains two molecules of **3**.

Compound 4a: The asymmetric unit contains one molecule of **4a**.

Compound 4b: The asymmetric unit contains one molecule of **4b**. The *cyclo*-As_3 ligand is disordered over two positions (93:7). The restraints SADI and SIMU were applied to describe the disordered *cyclo*-As_3 ligand.

Compound 5: The asymmetric unit contains one $[Al\{OC(CF_3)_3\}_4]^-$ anion, one half of the dication $[\{(Cp^*Fe)_3As_6Fe\}_2(\mu,\eta^3:\eta^3\text{-}As_3)]^{2+}$, half a toluene molecule and one CH_2Cl_2 molecule. All four $\{OC(CF_3)_3\}$ groups of the anion are disordered over two positions with distributions of 75:25, 73:27, 70:30 and 67:33. Further, the CH_2Cl_2 molecule is disordered over two positions with distributions of 82 to 18. The restraints DFIX, SADI and SIMU were applied to describe these disorders.

CCDC-2104962 (**3c**), CCDC-2104963 (**4a**), CCDC-2104964 (**4b**) and CCDC-2104965 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Table S1. Crystallographic data for compounds **3c**, **4a, 4b** and **5**.

Compound	**3c**	**4a**	**4b**	**5**
Data set (internal naming)	**hfk167**	**hfk179_2**	**hfk210_2**	**hfk236**
CCDC number	2104962	2104963	2104964	2104965
Formula	$C_{39}H_{63}As_6Fe_3$	$C_{30}H_{45}As_9Fe_4$	$C_{33}H_{51}As_9Fe_4$	$C_{101}H_{102}Al_2As_{15}Cl_4F_{72}Fe_8O_8$
Dcalc	1.750	2.299	2.215	2.134
μ/mm^{-1}	13.141	21.065	19.695	12.358
Formula Weight	1148.96	1303.34	1345.41	4578.18
Colour	black	brown	black	dark brown
Shape	plate-shaped	rod-shaped	platelet-shaped	plate-shaped
Size/mm^3	0.23×0.15×0.05	0.25×0.06×0.05	0.20×0.18×0.07	0.24×0.21×0.05
T/K	123(1)	123(1)	123(1)	100(2)
Crystal System	monoclinic	monoclinic	triclinic	triclinic
Space Group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a/Å	12.41380(10)	17.5235(2)	9.8819(3)	15.8190(5)
b/Å	24.0436(2)	14.0195(2)	11.8419(4)	16.4245(6)
c/Å	29.2262(3)	15.4107(2)	17.4558(6)	16.4417(6)
α/°	90	90	93.909(3)	60.077(4)
β/°	90.3100(10)	95.8610(10)	94.778(3)	75.683(3)
γ/°	90	90	96.367(3)	77.099(3)
V/Å^3	8723.09(13)	3766.17(8)	2016.84(12)	3561.9(3)
Z	8	4	2	1
Z'	2	1	1	0.5
Wavelength/Å	1.54178	1.54178	1.54178	1.54184
Radiation type	CuK$_\alpha$	CuK$_\alpha$	CuK$_\alpha$	CuK$_\alpha$
θ_{min}/°	3.539	4.046	3.767	3.127
θ_{max}/°	66.763	62.152	66.545	66.532
Measured Refl's.	39679	15529	17613	23890
Indep't Refl's	15129	5847	6904	12217
Refl's I≥2 σ(I)	12423	5017	6450	11165
R_{int}	0.0337	0.0467	0.0406	0.0328
Parameters	901	403	458	1457
Restraints	0	0	51	872
Largest Peak	1.505	1.062	2.264	1.006
Deepest Hole	-0.890	-0.775	-0.939	-0.947
GooF	0.952	0.981	1.046	1.028
wR_2 (all data)	0.0844	0.0750	0.1035	0.1094
wR_2	0.0817	0.0728	0.1014	0.1062
R_1 (all data)	0.0432	0.0376	0.0406	0.0466
R_1	0.0348	0.0311	0.0381	0.0424

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