Electronic Supplementary Information for:

The Potential of a *cyclo*-As_5 Ligand Complex in Coordination Chemistry

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1. Experimental details

General remarks:

All experiments were carried out under an atmosphere of dry argon using glovebox and schlenk techniques. Solvents were purified, dried, and degassed prior to use. [Cp*Fe(η^5-As_5)] (**1**) was prepared according to a literature procedure.[1] CuCl, CuBr, CuI were used as received from Merck. ESI-MS spectra were measured on a Finnigan Thermoquest TSQ 7000 mass spectrometer. The C, H, N analyses were determined on an Elementar Vario EL III apparatus.

Synthesis of $[\{Cu(\mu\text{-}Cl)\}_3(CH_3CN)\{Cp^*Fe(\eta^5{:}\eta^2{:}\eta^2{:}\eta^2\text{-}As_5)\}]_n$ (2):

A solution of 11 mg (0.106 mmol) CuCl in 5 ml CH_3CN was carefully layered over a solution of 60 mg (0.106 mmol) of **1** in 10 ml CH_2Cl_2. After five days at room temperature, black block-like crystals of **2** were obtained. The supernatant solvent was removed, the crystals were washed with hexane and subsequently dried in vacuum to give pure **2** (25 mg, 59%). Found: C, 15.67; H, 2.02; N, 1.48. Calc. for $C_{12}H_{18}Cl_3Cu_3As_5FeN$: C, 15.95; H, 2.01; N, 1.55%; *m/z* (ESI) 1294 (2%, $[2M - Cu_4Cl_5 - 2\ CH_3CN]^+$), 1195 (27, $[2M - Cu_5Cl_6 - 2\ CH_3CN]^+$), 670 (100, $[M - Cu_2Cl_3]^+$), 629 (56, $[M - Cu_2Cl_3 - CH_3CN]^+$).

Synthesis of $[\{Cu(\mu\text{-}Br)\}_3(CH_3CN)\{Cp^*Fe(\eta^5{:}\eta^2{:}\eta^2{:}\eta^2\text{-}As_5)\}]_n$ (3):

A solution of 30 mg (0.212 mmol) CuBr in 5 ml CH_3CN was carefully layered over a solution of 60 mg (0.106 mmol) of **1** in 10 ml CH_2Cl_2. After five days at room temperature, brown crystals of **3** were obtained. The supernatant solvent was removed, the crystals were washed with hexane and subsequently dried in vacuum to give **3** (53 mg, 73%). Found: C, 13.82; H, 1.61; N, 1.32. Calc. for $C_{12}H_{18}NAs_5Cu_3Br_3Fe$: C, 13.90; H, 1.75; N, 1.35%; *m/z* (ESI) 1338 (3%, $[2M - Cu_4Br_5 - 2\ CH_3CN]^+$), 1194 (10, $[2M - Cu_5Br_6 - 2\ CH_3CN]^+$), 670 (13, $[M - Cu_2Br_3]^+$).

Synthesis of $[\{Cu(\mu_3\text{-}I)\}_2\{Cp^*Fe(\eta^5{:}\eta^2{:}\eta^2\text{-}As_5)\}]_n$ (4) and $[\{Cu(\mu\text{-}I)\}_3\{CuI\}\{Cp^*Fe(\eta^5{:}\eta^2{:}\eta^2{:}\eta^1{:}\eta^1\text{-}As_5)\}\{Cp^*Fe(\eta^5{:}\eta^5{:}\eta^2\text{-}As_5)\}]_n$ (5):

A solution of 51 mg (0.256 mmol) CuI in 10 ml CH_3CN was carefully layered over a solution of 50 mg (0.088 mmol) of **1** in 10 ml CH_2Cl_2. After eight days at room temperature, dark brown crystals of **4** (70 mg, 84%) precipitate. The supernatant solution was stored at -30 °C. After five days brownish black crystals were isolated to give **5** · n CH_2Cl_2 (11 mg, 12%). The selection of several crystals of both crops for X-ray analysis revealed unique unit cells within the charges of the crystalline products. It can not be excluded, that **5** is contaminated with small amounts of **4**. As both products comprise the same stoichiometric compositions (besides the solvent molecule in the crystal lattice), elemental analysis is not useful to distinguish between both compounds. Also, both products show the similar fragment peaks in the ESI mass spectra. **4**: Found: C, 12.02; H, 1.41. Calc. for $C_{10}H_{15}As_5Cu_2FeI_2$: C, 12.69; H, 1.60%; *m/z* (ESI) 1384 (6%, $[2M - Cu_2I_3]^+$), 1194 (30, $[2M - Cu_3I_4]^+$), 670 (100, $[M - CuI_2 + CH_3CN]^+$), 629 (8, $[M - CuI_2]^+$); **5**: Found: C, 12.30; H, 1.22. Calc. for $C_{10}H_{15}As_5Cu_2FeI_2$: C, 12.69; H, 1.60%; *m/z* (ESI) 1384 (3%, $[M - Cu_2I_3]^+$), 1194 (30, $[M - Cu_3I_4]^+$), 670 (100, $[½M - CuI_2 + CH_3CN]^+$), 629 (32, $[½M - CuI_2]^+$).

2. Crystallographic details

Crystal structure analysis: The crystal structure analyses were performed on an Oxford Diffraction Gemini R Ultra CCD. Semi-empirical absorption corrections from equivalents (multi-scan) were applied for **2**, **4** and **5**.[2] For **3** an analytical absorption correction from crystal faces was carried out.[3] The structures were solved by direct methods with the program SIR-97,[4] and full matrix least-square refinement on F^2 in SHELXL-97[5] was performed with anisotropic displacements for non-H atoms. Hydrogen atoms were located in idealized positions and refined isotropically according to the riding model. **2** was identified as a pseudo-merohedral twin and was detwinned using PLATON.[6]

Crystal data for **2**: $C_{12}H_{18}As_5Cl_3Cu_3FeN$, $M = 903.72$, monoclinic, space group $P2_1/c$ (no. 14), $a = 11.660(3)$ Å, $b = 21.626(6)$ Å, $c = 8.490(2)$ Å, $\beta = 90.00(2)°$, $V = 2140.8(10)$ Å^3, $Z = 4$, $\mu = 11.647$ mm^{-1}, $F(000) = 1704$, $T = 123(1)$ K, 24053 reflections measured, 6531 unique ($R_{\text{int}} = 0.0929$), $R_1 = 0.0427$, $wR_2 = 0.1015$ for $I > 2\sigma(I)$. CCDC XXXXXX. Crystal data for **3**: $C_{12}H_{18}As_5Br_3Cu_3FeN$, $M = 1037.07$, monoclinic, space group $P2_1/c$ (no. 14), $a = 11.8229(4)$ Å, $b = 21.7908(8)$ Å, $c = 8.6497(2)$ Å, $\beta = 90.118(2)°$, $V = 2228.42(12)$ Å^3, $Z = 4$, $\mu = 22.890$ mm^{-1}, $F(000) = 1920$, $T = 123(1)$ K, 15185 reflections measured, 3774 unique ($R_{\text{int}} = 0.0816$), $R_1 = 0.0381$, $wR_2 = 0.0840$ for $I > 2\sigma(I)$. CCDC XXXXXX. Crystal data for **4**: $C_{10}H_{15}As_5Cu_2FeI_2$, $M = 946.57$, triclinic, space group $P\bar{1}$ (no. 2), $a = 8.4256(6)$ Å, $b = 10.9119(8)$ Å, $c = 11.4820(9)$ Å, $\alpha = 71.256(7)°$, $\beta = 81.825(6)°$, $\gamma = 78.273(6)°$, $V = 975.42(13)$ Å^3, $Z = 2$, $\mu = 42.587$ mm^{-1}, $F(000) = 860$, $T = 123(1)$ K, 4805 reflections measured, 2111 unique ($R_{\text{int}} = 0.0375$), $R_1 = 0.0337$, $wR_2 = 0.0711$ for $I > 2\sigma(I)$. CCDC

XXXXXX. Crystal data for **5** · n CH_2Cl_2: $C_{11}H_{17}As_5Cl_2Cu_2FeI_2$, $M = 1031.50$, orthorhombic, space group *P*nma (no. 62), $a = 15.6513(1)$ Å, $b = 11.7371(3)$ Å, $c = 24.5300(5)$ Å, $V = 4506.18(16)$ Å^3, $Z = 8$, $\mu = 39.105$ mm^{-1}, $F(000) = 3776$, $T = 123(1)$ K, 10949 reflections measured, 3650 unique ($R_{\mathrm{int}} = 0.0367$), $R_1 = 0.0322$, $wR_2 = 0.0741$ for I > 2σ(I). CCDC XXXXXX.

3. Computational details

The DFT calculations were performed with the Gaussian03[7] program package using the B3LYP[8] functional with the 6-31G[9] basis sets to which two additional polarisation and three sets of diffuse functions were added. The geometries of **1** and [Cp*Fe(η^5-P_5)] (**1a**) were optimised in the staggered conformation in the C_{5v} symmetry. The cartesian coordinates of the optimised structures of **1** and **1a** are given in table S1 and S2, respectively. The isosurfaces of the selected molecular orbitals were visualised using the MOLEKEL program[10] and are depicted in Fig. S1. A comparative molecular orbital energy level diagram for **1** and **1a** is given in Fig. S2.

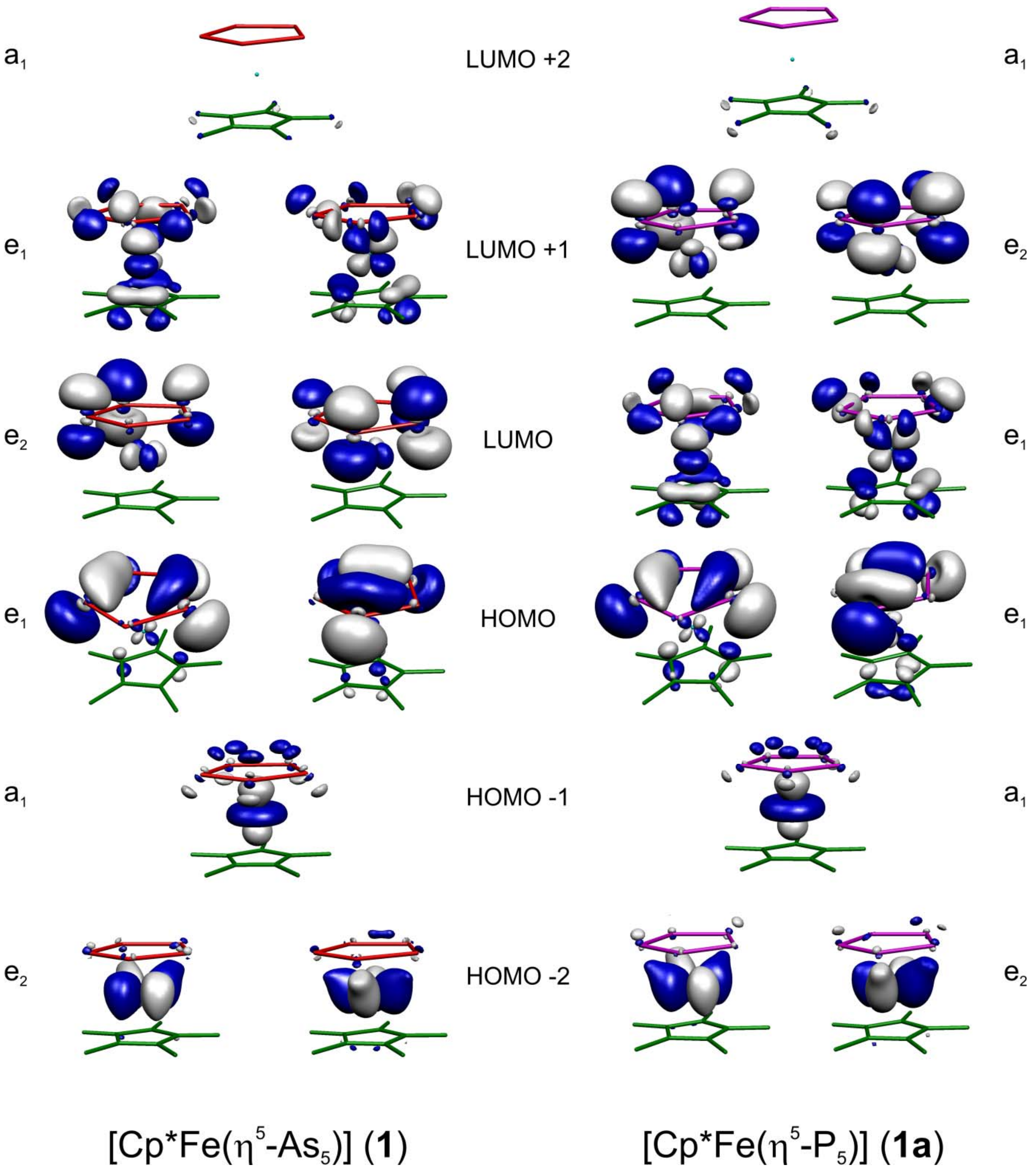

Figure S1 Isosurfaces of the frontier molecular orbitals in **1** and **1a**.

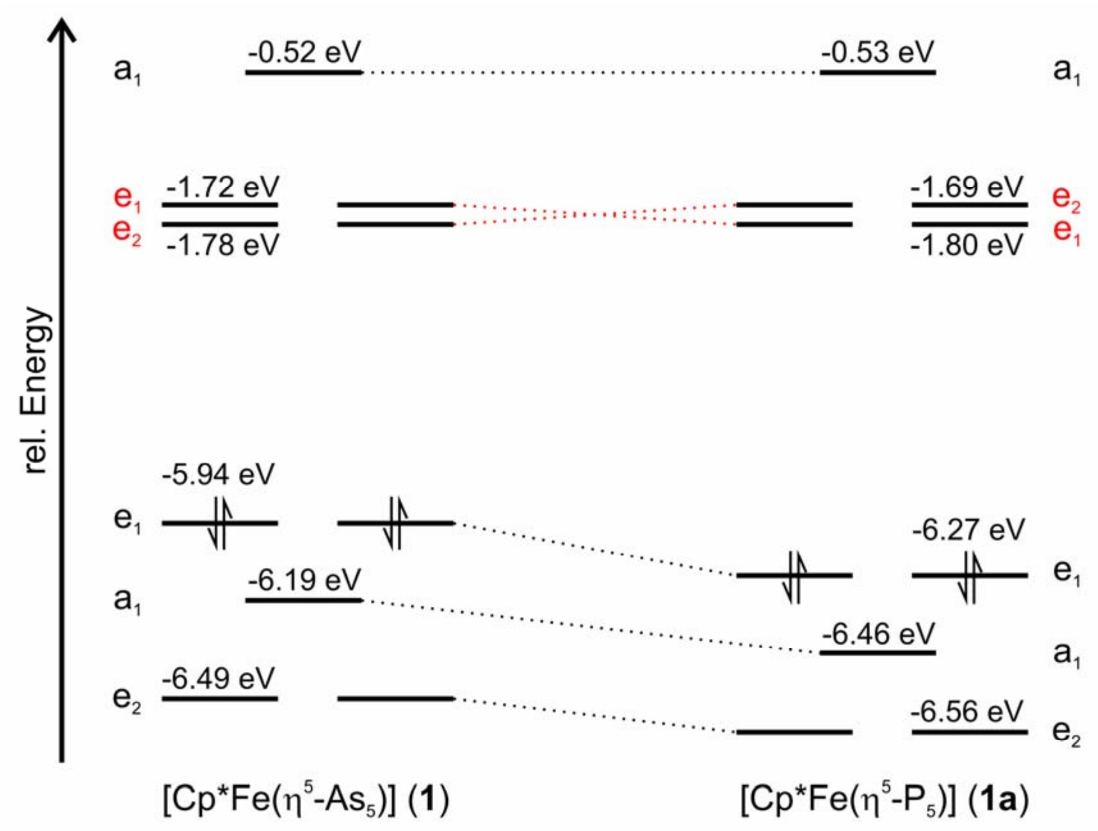

Figure S2 Comparative molecular orbital energy level diagram for **1** and **1a**.

Table S1 Cartesian coordinates for the optimised structure of **1** at the B3LYP/6-31++G(3df,3pd) level of theory.

Atom	x	y	z
Fe	-0.000452	-0.001366	0.003842
As	-1.860382	-0.631142	1.506046
As	0.014005	-1.965046	1.504002
As	-1.166740	1.564059	1.510595
As	1.867487	-0.599298	1.507649
As	1.134963	1.584105	1.516263
C	-0.715684	-0.987077	-1.708244
C	-1.158356	0.375029	-1.706729
C	0.000212	1.216868	-1.706317
C	1.158594	0.374891	-1.705839
C	0.715765	-0.986908	-1.710046
C	-2.582068	0.836852	-1.770154
C	-0.000401	2.713515	-1.774913
C	-1.593906	-2.198985	-1.775490
C	2.583250	0.835585	-1.768484
C	1.595388	-2.197483	-1.782145
H	0.883868	3.137477	-1.298439
H	2.712223	1.803431	-1.283337
H	-2.902435	0.952361	-2.810748

H	-3.254100	0.126101	-1.288755
H	-0.013742	3.048315	-2.817372
H	-1.785306	-2.475434	-2.817574
H	-1.132978	-3.054467	-1.280915
H	-2.555721	-2.024183	-1.292942
H	3.252612	0.133081	-1.271356
H	1.789982	-2.466912	-2.825500
H	2.555468	-2.024155	-1.295676
H	1.134856	-3.056939	-1.294599
H	2.909246	0.934135	-2.809103
H	-2.713305	1.796674	-1.270075
H	-0.872346	3.136926	-1.275872

Table S2 Cartesian coordinates for the optimised structure of **1a** at the B3LYP/6-31++G(3df,3pd) level of theory.

Atom	x	y	z
Fe	0.000000	0.000000	-0.006026
P	-1.718954	-0.558522	1.576667
P	0.000000	-1.807415	1.576667
P	-1.062372	1.462229	1.576667
P	1.718954	-0.558522	1.576667
P	1.062372	1.462229	1.576667
C	-0.715982	-0.985464	-1.731074
C	-1.158483	0.376414	-1.731074
C	0.000000	1.218101	-1.731074
C	1.158483	0.376414	-1.731074
C	0.715982	-0.985464	-1.731074
C	-2.581362	0.838735	-1.806426
C	0.000000	2.714205	-1.806426
C	-1.595370	-2.195838	-1.806426
C	2.581362	0.838735	-1.806426
C	1.595370	-2.195838	-1.806426
H	0.880441	3.144424	-1.328424
H	2.718454	1.809030	-1.328424
H	-2.893135	0.940037	-2.851701
H	-3.262597	0.134331	-1.328424
H	0.000000	3.042022	-2.851701
H	-1.788056	-2.461048	-2.851701
H	-1.135955	-3.061403	-1.328424
H	-2.560538	-2.026383	-1.328424
H	3.262597	0.134331	-1.328424
H	1.788056	-2.461048	-2.851701
H	2.560538	-2.026383	-1.328424

H	1.135955	-3.061403	-1.328424
H	2.893135	0.940037	-2.851701
H	-2.718454	1.809030	-1.328424
H	-0.880441	3.144424	-1.328424

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