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A tetradentate metalloligand: synthesis and coordination behaviour of a 2-pyridyl-substituted cyclobutadiene iron complex†

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The salt [K([18]crown-6){Cp*Fe(η^4-C_4py_4)}] (K1, py = 2-pyridyl, Cp* = C_5Me_5) is accessible by the reaction of an iron(0) naphthalene precursor and bis(2-pyridyl)acetylene. Cyclic voltammetry and preparative investigations demonstrate the electron-rich nature of K1, which is reversibly oxidized to neutral [Cp*Fe(η^4-C_4py_4)] (1) at a low potential. The first coordination studies with iron(II) and zinc(II) chloride show that all four 2-pyridyl units may be employed for metal coordination.

There is much interest in the preparation of novel multitopic ligands which may serve as building units for coordination-driven supramolecular assemblies.[1] Ligands with redox-active cores are particularly attractive targets, because they potentially allow one to switch functional properties such as catalytic activity, molecular recognition and cavity-directed synthesis by changing the redox state of the ligand.[2] Known examples incorporate electron-acceptor ligands (typically of the 1,3,5-triazine or quinone family), while ligands with π-electron-donating cores are scarce, although recently reported electroactive cages self-assembled from highly π-electron-donating tetrathiafulvalene-based linkers are promising.[3]

In the course of our investigations into the chemistry of low-valent polyarene metalates,[4,5] we recently studied the reactions of naphthalene and anthracene ferrates with alkynes and phosphaalkynes.[6] The reaction of [Fe(η^4-anthracene)$_2$]$^-$ with diphenylacetylene afforded the hexaphenylbenzene complex **A** (Fig. 1),[7] while the analogous reaction with [K([18]crown-6) Cp*Fe-(η^4-naphthalene)] gave the tetraphenylcyclobutadiene compound **B** as a result of the cyclodimerisation of the alkyne in the coordination sphere of iron.[8]

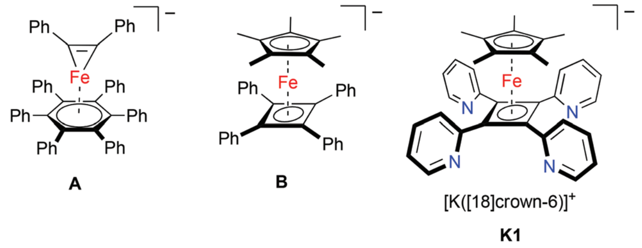

Fig. 1 Products arising from the metal-mediated cyclooligomerisation of diphenylacetylene and bis(2-pyridyl)acetylene.

Considering that the 2-pyridyl substituent is one of the most popular donor moieties in coordination chemistry,[9] we were intrigued by the possibility that this methodology might provide a convenient route to redox-active and electron-rich polypyridyl-substituted anions that can be applied as ligands in oligonuclear complexes or supramolecular assemblies.[10] Here, we report the synthesis and characterization of the first cyclobutadiene complex that is substituted by four 2-pyridyl units, [K([18]crown-6){Cp*Fe(η^4-C_4py_4)}] (**K1**). Cyclic voltammetry demonstrates the electron-rich nature of this complex, while coordination studies show that the [Cp*Fe(η^4-C_4py_4)]$^-$ anion is able to act as a bidentate chelate ligand to zinc(II) and iron(II) cations.

Complex **K1** was prepared in 30% isolated yield as dark purple crystals by treatment of a THF solution of [K(18-crown-6)-{Cp*Fe(η^4-naphthalene)}] with two equiv. of bis(2-pyridyl)-acetylene (Fig. 2).‡ The complex dissolves well in polar solvents such as THF, acetonitrile and difluorobenzene, but is less soluble in more apolar solvents. A single-crystal X-ray structure analysis§ confirmed the formation of the desired sandwich complex (Fig. 1) with an η^4-coordinated cyclo-butadiene moiety and an η^5-coordinated Cp* ligand. A striking aspect of the structure of **K1** is the coordination of one of the pyridyl groups to potassium (K1–N4 2.749(4) Å). This interaction results in a distinct conformation for this substituent, which encloses a dihedral angle of 55.3° with the C_4 ring of the

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† Electronic supplementary information (ESI) available: Full synthetic and experimental details, UV-vis spectra of complexes **K1** and **1–4** (Fig. S1), cyclic voltammograms of **K1** and **2–4** (Fig. S2–S5), and crystallographic data for **K1** and **1–4**. Q3 CCDC 962751–962755. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt52699b

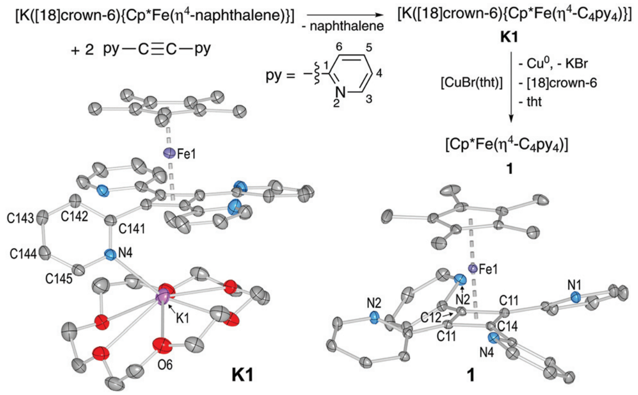
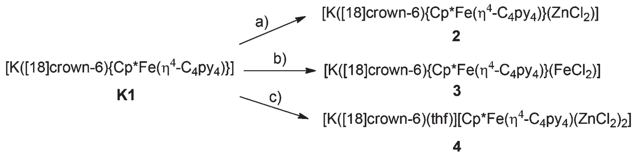


Fig. 2 Synthesis and molecular structures of complexes **K1** and **1**, displacement ellipsoids are drawn at the 35% probability level, H atoms and disorder in one of the 2-pyridyl substituents of **K1** are omitted for clarity, important bond lengths (Å) and angles (°) of **K1**: av. Fe1–C(Cp*) 2.046, av. Fe1–C(C_4py_4) 2.012, K1–N3 2.741(4), dihedral C11–C14/N3,C131–C135 53.6°, C11–C14/N1,C111–C115 9.0°, C11–C14/N2,C121–C125 4.6°, C11–C14/N3,C131–C135 5.5°; important bond lengths (Å) and angles (°) of **1**: av. Fe1–C(Cp*) 2.119, av. Fe1–C(C_4py_4) 2.003, dihedral C11–C14/N1,C111–C115 18.4, C11–C14/N2,C121–C125 32.6, C11–C14/N3,C131–C135 23.9, C11–C14/N4,C141–C145 32.2.

cyclobutadiene ligand, while the remaining three pyridyl moieties are almost coplanar with that ring.

The ^1H and $^{13}C\{^1H\}$ NMR data of **K1** recorded in C_6D_6 support the crystallographically-determined composition. Only one set of 2-pyridyl resonances was observed, which indicates that the potassium cation is not statically bound to one of the 2-pyridyl substituents in solution. Instead, the cation either rapidly fluctuates between the substituents or an ion-separated structure is formed. The UV-vis spectrum (THF, Fig. S1†) shows two intense absorptions in the UV at 333 and 371 nm in addition to a broad absorption in the visible at 518 nm. The cyclic voltammogram of **K1** (CH_3CN–TBAH, Fig. S2a†) features a reversible redox wave at −1.57 V *vs.* Fc/Fc$^+$, which corresponds to the one-electron oxidation of **K1** to form neutral, 17*e* [Cp*Fe(η^4-C_4py_4)] (**1**). A second, irreversible redox process at a peak potential of −0.07 V *vs.* Fc/Fc$^+$ might presumably correspond to the oxidation of **1** to the unstable 16*e* cation [Cp*Fe(η^4-C_4py_4)]$^+$ (**1**$^+$).¶

Due to its low oxidation potential, **K1** was oxidized when it was reacted with various copper(I) and silver(I) salts.[11] The formation of the desired coinage metal complexes could not be verified. Instead, neutral **1** was isolated as red-brown crystals in 53% yield from the reaction of **K1** with one equiv. [CuBr(tht)] (tht = tetrahydrothiophene, see Fig. 2), confirming that **1** is accessible on a preparative scale.‡ The molecular structure (Fig. 2) is similar to the [Cp*Fe(η^4-$C_{10}H_8$)]$^-$ anion of **K1**.§ The 2-pyridyl substituents adopt a “propeller-like” orientation in this case. Complex **1** displays a distinct UV-vis spectrum with a strong UV band at 332 nm and a weaker shoulder at 420 nm. The complex is paramagnetic with a solution magnetic moment of 1.8(1)μ_B in C_6D_6 (Evans method), which agrees well with the presence of one unpaired electron per molecule.



Scheme 1 Synthesis of **2–4**, reagents: (a) one equiv. $ZnCl_2$; (b) $FeCl_2(thf)_{1.5}$; (c) two equiv. $ZnCl_2$.

Coordination compounds of **K1** can be obtained with metal halides that are less prone to reduction. The reaction of **K1** with one equiv. $ZnCl_2$ and $FeCl_2(thf)_{1.5}$ in THF gave [K([18]-crown-6)Cp*Fe(η^4-C_4py_4)($ZnCl_2$)] (**2**) and [K([18]crown-6)Cp*Fe(η^4-C_4py_4)($FeCl_2$)] (**3**, see Scheme 1a and b). Both compounds were isolated in moderate yields (55% and 58%, respectively) as air-sensitive, dark purple solids by crystallisation from THF–*n*-hexane.‡ Single-crystal X-ray analyses§ of the isostructural complexes **2** and **3** (Fig. 3) revealed 1 : 1 chelates of the [Cp*Fe(η^4-C_4py_4)]$^-$ anion with the metal halide. Two nitrogen atoms from adjacent 2-pyridyl units and the two chlorines form a distorted tetrahedral coordination geometry around the Zn^{2+} or Fe^{2+} cation.[12,13] The N1–M–N2 “bite angles” (**2**: N1–Zn1–N2 106.88(7)°, **3**: N2–Fe2–N1 103.06(8)°) are slightly smaller than the Cl–M–Cl and N–M–Cl angles (**2**: Cl1–Zn1–Cl2 113.20(2)°, N–Zn1–Cl range 108.86(5)–109.52(5)°, **3**: Cl1–Fe2–Cl2 113.60(3)°, N–Fe2–Cl range 103.06(8)–111.52(6)°) probably due to steric reasons. One of the chlorides acts as a bridging ligand to the potassium cation (**2**: K1–Cl2 3.0306(7) Å, **3**: 3.0243(9) Å), which is additionally coordinated by an [18]crown-6 molecule.

The reaction of **K1** with two equiv. $ZnCl_2$ (Scheme 1c) afforded the dizinc complex [K([18]crown-6)(thf)][Cp*Fe(η^4-C_4py_4)($ZnCl_2$)$_2$] (**4**) in 26% yield.‡ Dark purple **4** crystallized from THF–acetonitrile–diethyl ether, allowing for its X-ray crystallographic characterization.§ The molecular structure (Fig. 3) shows the formation of a bis(chelate) of the [Cp*Fe(η^4-C_4py_4)]$^-$ ligand with two $ZnCl_2$ fragments. The [Cp*Fe(η^4-C_4py_4)($ZnCl_2$)$_2$]$^-$ molecule resides on a crystallographic mirror plane formed by iron, the two zinc cations and the chloride ligands. Both Zn^{2+} cations are distorted tetrahedrally coordinated by two 2-pyridyl substituents and two chloride ligands similar to the structure of **2**. It seems noteworthy that the resulting seven-membered ZnN_2C_4 chelate rings have different conformations. The chelate ring associated with Zn1 clearly adopts a boat conformation, whereas the chelate ring associated with Zn2 displays a chair conformation. As a consequence, Zn1 is located 1.67 Å below the cyclobutadiene C_4 plane (formed by C7, C8, C7′, C8′), while Zn2 is located 0.15 Å above the same plane. Different from the structures of **2** and **3**, there is no coordinative interaction between the known [K([18]-crown-6)-(thf)]$^+$ cation and the anion in this structure.[14]

The ^1H and $^{13}C\{^1H\}$ NMR data of **2** and **4** support the solid-state molecular structures. Two distinct sets of 2-pyridyl resonances are observed for **2** in agreement with the coordination of only *one* $ZnCl_2$ unit. In contrast, one set of 2-pyridyl resonances is detected in the spectrum of **4** due to the presence of

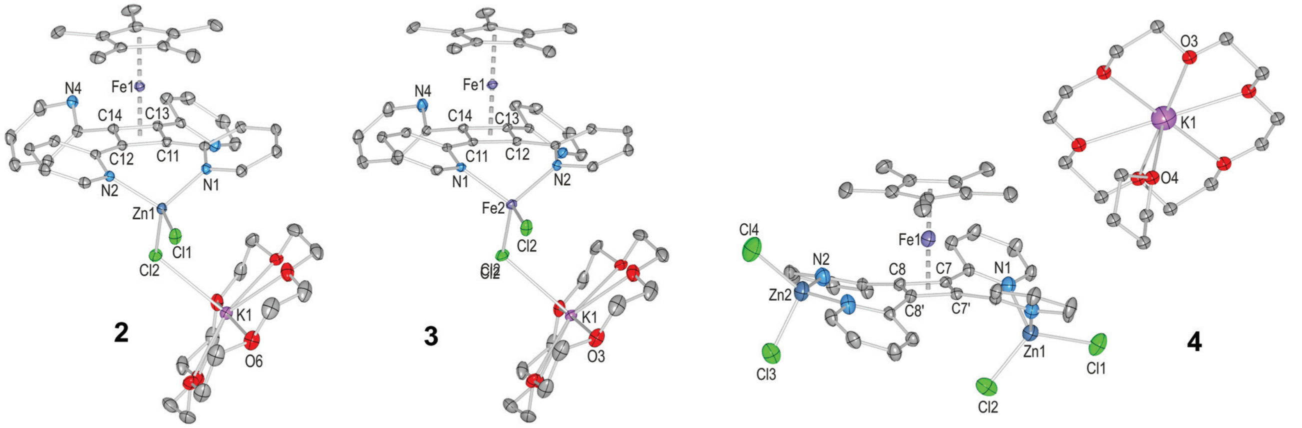


Fig. 3 Molecular structures of **2–4**, displacement ellipsoids are drawn at the 35% probability level, H atoms and THF molecules are omitted for clarity, important bond lengths (Å) and angles (°) of **2**: av. Fe1–C(Cp*) 2.065, av. Fe1–C(C_4py_4) 2.011, N1–Zn1 2.0158(17), N2–Zn1 2.0198(16), Zn1–Cl1 2.2447(6), Zn1–Cl2 2.2465(6), K1–Cl2 3.0306(7), N1–Zn1–N2 106.87(7), N1–Zn1–Cl1 109.00(5), N1–Zn1–Cl2 109.52(5), N2–Zn1–Cl1 109.19(5), N2–Zn1–Cl2 108.86(5), Cl1–Zn1–Cl2 113.20(2), dihedral C11–C14/N1,C111–C115 17.8, C11–C14/N2,C121–C125 18.3, C11–C14/N3,C131–C135 67.3, C11–C14/N4,C141–C145 33.2; important bond lengths (Å) and angles (°) of **3**: av. Fe1-(Cp*) 2.063, av. Fe1–C(C_4py_4) 2.006, N1–Fe2 2.062(2), N2–Fe2 2.054(2), Fe2–Cl1 2.2814(7), Fe2–Cl2 2.2690(7), K1–Cl2 3.0243(9), N1–Fe2–Cl1 108.76(6), N1–Fe2–Cl2 111.01(6), N2–Fe2–N1 103.06(8), N2–Fe2–Cl1 108.32(6), N2–Fe2–Cl2 111.52(6), Cl2–Fe2–Cl1 113.60(3), dihedral C11–C14/N1,C111–C115 17.8, C11–C14/N2,C121–C125 33.6, C11–C14/N3, C131–C135 18.0, C11–C14/N4,C141–C145 33.4; important bond lengths (Å) and angles (°) of **4**: av. Fe1–C(Cp*) 2.067, av. Fe1–C(C_4py_4) 2.008, av. K1–O1,O2,O3 2.793, K1–O4 2.892(9), N1–Zn1 2.013(4), N2–Zn2 2.023(4), Zn1–Cl1 2.234(2), Zn1–Cl2 2.2371(19), Zn2–Cl3 2.276(2), Zn2–Cl4 2.219(2), N1′–Zn1–N1 102.5(2), N1′–Zn1–Cl1 107.80(12), N1–Zn1–Cl1 107.80(12), N11–Zn1–Cl2 111.39(12), N1–Zn1–Cl2 111.39(12), Cl1–Zn1–Cl2 115.16(9), N2–Zn2–N21 115.2(2), N2–Zn2–Cl3 101.97(13), N2′–Zn2–Cl3 101.97(13), dihedral N1,C71–C75/C7,C8,C7′,C8′ 27.8, dihedral N2,C81–C85/C7,C8,C7′, C8′ 23.1, symmetry operation to generate equivalent atoms: ′ +*x*, 1/2 − *z*, +*z*.

two equivalent $ZnCl_2$ moieties. The ^1H NMR spectra of the iron(II) complex **3** were not informative due to its paramagnetism. The effective magnetic moment of 4.1(1)μ_B per molecule (Evans method, [D_8]THF) agrees with the expected high-spin configuration for a tetrahedrally coordinated Fe^{2+} cation.

Complexes **2–4** show similar UV/vis spectra in THF or 1,2-difluorobenzene (Fig. S1†). Each spectrum displays two strong bands in the UV region at 327 and 397 nm for **2**, 320 and 402 nm for **3**, and 309 and 405 nm for **4**. A weaker, broad absorption was detected in the visible at 538 nm (**2**), 532 nm (**3**) and 527 nm (**4**). The observed spectra are similar to that of **K1** (333, 371, and 518 nm, see above). The similar electronic absorption spectra are thus dominated by transitions which arise from the [Cp*Fe(η^4-C_4py_4)]$^-$ anion. The electronic structure of this anion appears to be only weakly perturbed by metal coordination.

In line with this result, the zinc complex **2** in CH_3CN–TBAH shows similar redox properties as parent **K1** according to its cyclic voltammogram (Fig. S3†). A reversible redox event at −1.19 V *vs.* Fc/Fc$^+$ presumably corresponds to the oxidation of **2** to neutral [Cp*Fe(η^4-C_4py_4)($ZnCl_2$)] ($E_{1/2}$ = −1.57 V for the analogous process for **K1**). In addition, an irreversible process is observed for **2** at a peak potential of +0.20 V (−0.07 V for **K1**). Obviously, the redox potentials of **2** are shifted to more positive potentials due to the coordination of the $ZnCl_2$ unit. The CVs of **3** and **4** (Fig. S4 and S5†) are more complex,¶ and a detailed analysis is beyond the scope of this work. Further investigations, including spectroelectrochemistry experiments, are warranted to analyse the nature of the associated redox processes.

Conclusions

The first 2-pyridyl-substituted cyclobutadiene iron complex [K([18]crown-6){Cp*Fe(η^4-C_4py_4)}] (**K1**) was prepared by a straightforward synthetic procedure from an anionic iron naphthalene complex with bis(2-pyridyl)acetylene.[10] The electron-rich nature of **K1** is evident from its facile oxidation to 17e [Cp*Fe(η^4-C_4py_4)] (**1**) (−1.57 V *vs.* Fc/Fc$^+$ in acetonitrile), which could be performed on a preparative scale by using [CuBr(tht)] as an oxidant. First coordination studies with iron (II) and zinc(II) chloride resulted in 1 : 1 or 2 : 1 adducts **2–4**, in which the [Cp*Fe(η^4-C_4py_4)]$^-$ anion of **K1** behaves as a bidentate chelate ligand. The structure of the dizinc complex **4** shows that all four 2-pyridyl donors can be used for metal coordination. In future investigations, we will explore whether other coordination modes are also feasible with different metals. An extension of this chemistry to 3-pyridyl and 4-pyridyl-substituted derivatives is in hand.

Acknowledgements

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Notes and references

‡ See the ESI† for details regarding the synthesis and characterization of **K1** and **1–4**.

§ Crystals were mounted in paratone oil and transferred to the cold N_2 gas stream of an Agilent Technologies SuperNova diffractometer with Cu/Kα radiation (λ = 1.54178 Å). Semi-empirical multi-scan absorption corrections were applied to the data. The structures were solved by SHELXS or SIR and least-square refinements were performed on F^2.[15,16] CCDC 962751 (**K1**), 962752 (**1**), 962753 (**2**), 962754 (**3**) and 962755 (**4**) contain the supplementary crystallographic data for this paper. Further crystal data and refinement details are given in the ESI.†

¶ The CV of **K1** in 1,2-difluorobenzene shows a reversible wave at $E_{1/2}$ = −1.69 V and irreversible waves at peak potentials of −0.06 V and +0.47 V (see Fig. S3†). Additional redox processes are apparent at −1.1 to −1.4 V *vs.* Fc/Fc, which presumably arise from the irreversible anodic decomposition of **K1**. The cyclic voltammogram of **3** (CH_3CN/TBAH, Fig. S4†) shows broad reversible waves at −1.07 V and −0.37 V *vs.* Fc/Fc$^+$. The CV of **4** (Fig. S5†) features a dominant redox wave at −1.18 V *vs.* Fc/Fc$^+$, a reversible wave at −0.98 V and further irreversible processes at −1.58, −0.13 and +0.26 V.

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