A tetradeionate 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(η4-C4py4)]} (K1, py = 2-pyridyl, Cp* = C5Me5) 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 character of K1, which is reversibly oxidized to neutral [Cp*Fe(η4-C4py4)] (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 tetrahedral fullerene-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(η4-anthracene)2] with diphenylacetylene afforded the hexaphenylbenzene complex A (Fig. 1),7 while the analogous reaction with [K[[18]crown-6]Cp*Fe-η4-naphthalene] gave the tetraphenylcyclobutadiene compound B as a result of the cycodimerisation of the alkyne in the coordination sphere of iron.8

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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 voltamograms of K1 and 2–4 (Fig. S2–S5), and crystallographic data for K1 and 1–4. CCDC 962751–962755. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt52699b

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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(η4-C4py4)}] (K1). Cyclic voltammetry demonstrates the electron-rich character of this complex, while coordination studies show that the [Cp*Fe(η4-C4py4)]– 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(η4-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 confirms the formation of the desired sandwich complex (Fig. 1) with an η4-coordinated cyclo-butadiene moiety and an η4-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 C4 ring of the
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A reversible redox wave at addition to a broad absorption in the visible at 518 nm. The shows two intense absorptions in the UV at 333 and 371 nm in of C135 23.9, C11 N1,C111 corresponding to the one-electron oxidation of [Cp*Fe(η4-C4py4)]⁺ (Fig. 2) is similar to the [Cp*Fe(η4-C4py4)]⁻ (1) and [K[18]crown-6]Cp*Fe(η4-C4py4)]⁻ [FeCl2] (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(η4-C4py4)]⁻ 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 Zn2⁺ or Fe2⁺ 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. ZnCl2 (Scheme 1c) afforded the dizinc complex [K[18]crown-6][thf][Cp*Fe(η4-C4py4)](ZnCl2) (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(η4-C4py4)]⁻ ligand with two ZnCl2 fragments. The [Cp*Fe(η4-C4py4)]⁻ (ZnCl2)2⁻ molecule resides on a crystallographic mirror plane formed by iron, the two zinc cations and the chloride ligands. Both Zn2⁺ 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 ZnN4C4 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 C4 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 13C(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 ZnCl2 unit. In contrast, one set of 2-pyridyl resonances is detected in the spectrum of 4 due to the presence of
two equivalent ZnCl₂ moieties. The ¹H NMR spectra of the iron(3) complex 3 were not informative due to its paramagnetism. The effective magnetic moment of 4.11μB per molecule (Evans method, [D₈]THF) agrees with the expected high-spin configuration for a tetrahedrally coordinated Fe²⁺ 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, 309 and 405 nm for 4. A weaker, broad absorption was detected in the visible at 538 nm (3), 405 nm for 4 and 309 and 405 nm for 4. The observed spectra are similar to that of [K([18]crown-6){Cp*Fe(η⁴-C₄py₄)}](K1) which the [Cp*Fe(η⁴-C₄py₄)]⁻ anion behaves as a bidentate chelate ligand. The structure of the dizinc complex 4 shows that all four 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.

Conclusions

The first 2-pyridyl-substituted cyclobutadiene iron complex [K([18]crown-6){Cp*Fe(η⁴-C₄py₄)}] (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(η⁴-C₄py₄)] (1) (−1.57 V vs. Fe/Fe⁺ 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(η⁴-C₄py₄)]⁻ 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.

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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 N2 gas stream of an Agilent Technologies SuperNova diffractometer with Cu/Kα radiation (λ = 1.54178 Å). Semi-empirical multi-scan correlation corrections were applied to the data. The structures were solved by SHELXS or SIR and least-squares refinements were performed on F2.5.10; CCDC 962751 (K1), 962752 (I), 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 E1/2 = −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 (CH3CN/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.


