Synthetic and Structural Characterisation of Metal Complexes of Ferrocenylacetylene: Novel Donor–Acceptor Heterobimetallic Materials

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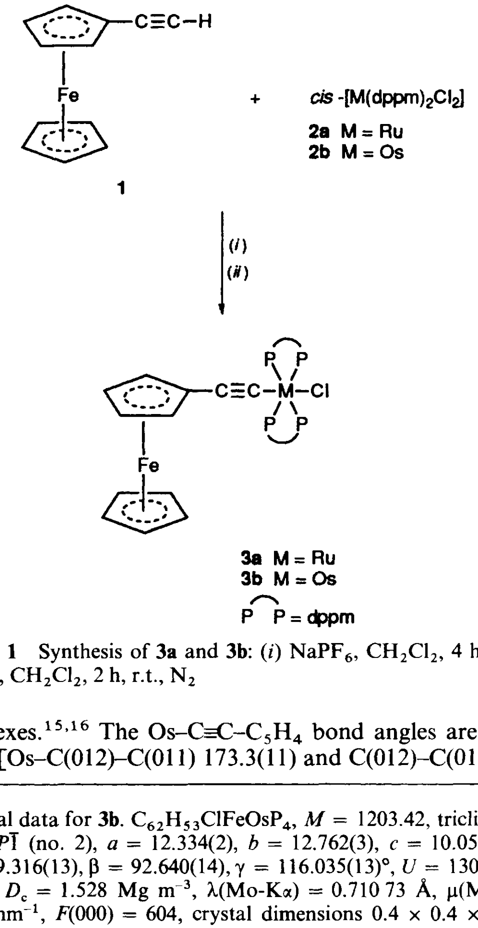
Two novel metal (ruthenium or osmium) complexes of ferrocenylacetylene have been synthesised and the crystal structure of $[Fe(C_5H_5)\{C_5H_4C{\equiv}C[Os(dppm)_2Cl]\}]$ [dppm = 1,2-bis(diphenylphosphino)-methane] has been determined; their solution redox chemistry indicated metal–metal interaction *via* the conjugated ligand group.

There is currently great interest in ferrocene-containing complexes owing to the rapid growth of material science. Metallocenes, and in particular ferrocene, have been of use as molecular ferromagnets,[1,2] molecular sensors,[3,4] electrochemical agents[5] and non-linear optics.[6,7] Increasing demand for new materials for the development of opto-electronic technology has encouraged us to design a new system featuring 'donor–acceptor' characteristics, which might exhibit properties essential for second-order non-linear optical (NLO) phenomena.[6,8,9] This system is similar to one reported by Green *et al.*,[10] which showed excellent second harmonic generation efficiency, underlining its potential in the field of second-order non-linear optics. Introduction of another metal in close proximity to the metallocenyl complex gives a wider diversity of oxidation states and ligands which increase the possible architectural flexibility and fine-tuning of the properties essential for device application.



Scheme 1 Synthesis of **3a** and **3b**: (*i*) $NaPF_6$, CH_2Cl_2, 4 h, r.t., N_2; (*ii*) dbu, CH_2Cl_2, 2 h, r.t., N_2

Complexes **3a** and **3b** were synthesised according to Scheme 1 [dppm = 1,2-bis(diphenylphosphino)methane],† which is a modification of a synthetic route developed by Dixneuf and co-workers,[11] with compounds **1**, **2a** and **2b** being prepared using standard literature procedures.[12,13] The ferrocenylacetylide–metal complexes were isolated as fine orange powders in *ca.* 30% yield. Complex **3b** was recrystallised from a CH_2Cl_2–$(C_2H_5)_2O$ two-layered system which gave dark orange rhombic crystals, and its structure (Fig. 1) was determined by single crystal X-ray diffraction.‡ The structure shows an octahedral osmium centre bound by an acetylide linkage to a ferrocene moiety. The Os atom sits on a centre of symmetry with the Cl and $C{\equiv}C(C_5H_4)Fe(C_5H_5)$ units disordered about it, each with 50% occupancy. The eclipsed nature of the cyclopentadienyl rings is confirmed. The acetylide bond length is in the range of those reported for analogous ferrocenylacetylide and metal–acetylide complexes.[15,16] The Os–C≡C–C_5H_4 bond angles are close to linear [Os–C(012)–C(011) 173.3(11) and C(012)–C(011)–C(06)

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† Syntheses and physical data. **3a**. To a stirred solution of **1** (0.050 g, 0.24 mmol) in dichloromethane (50 cm^3) was added **2a** (0.226 g, 0.24 mmol) and $NaPF_6$ (0.108 g, 0.59 mmol). After 4 h, one drop of 1,8-diazabicyclo[5.4.0]undec-7-ene (dbu) was added to the yellow solution, which immediately turned orange. After further stirring at room temperature (r.t.) for 2 h, the solution was evaporated to dryness and washed with diethyl ether (2 × 20 cm^3). Recrystallisation from CH_2Cl_2–$(C_2H_5)_2O$ gave orange, crystalline **3a** (0.081 g, 30%) (Found: C, 66.3; H, 4.8. $C_{62}H_{53}ClFeP_4Ru$ requires C, 66.9; H, 4.8%); FAB mass spectrum: m/z 1113.5 (M^+) (calc. 1112.2).

3b. This complex was prepared as for **3a** (Found: C, 61.7; H, 4.4. $C_{62}H_{53}ClFeOsP_4$ requires C, 61.9; H, 4.4%); m/z 1203.4 (M^+) (calc. 1203.4).

‡ Crystal data for **3b**. $C_{62}H_{53}ClFeOsP_4$, $M = 1203.42$, triclinic, space group $P\bar{1}$ (no. 2), $a = 12.334(2)$, $b = 12.762(3)$, $c = 10.0549(13)$ Å, $\alpha = 109.316(13)$, $\beta = 92.640(14)$, $\gamma = 116.035(13)°$, $U = 1307.5(4)$ Å^3, $Z = 1$, $D_c = 1.528$ Mg m^{-3}, λ(Mo-Kα) = 0.710 73 Å, μ(Mo-Kα) = 2.918 mm^{-1}, $F(000) = 604$, crystal dimensions 0.4 × 0.4 × 0.3 mm. Data collected at room temperature on a Rigaku AFC7 diffractometer; structure solved by Patterson method and subsequent Fourier-difference syntheses; disorder about Os (atom sits on a crystallographic centre of symmetry); Cl and $C{\equiv}C(C_5H_4)Fe(C_5H_5)$ atoms refined with 50% occupancy. Refinement by full-matrix least squares on F_o^2, R (= $\Sigma\|F_o| - |F_c\|/\Sigma|F_o|$) = 0.0225 [$F > 4\sigma(F)$] and R' {= $[\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$} = 0.0574 (all data) (non-hydrogen atoms anisotropic, H-atoms allowed to ride on relevant C atoms; cyclopentadienyl rings treated as rigid groups).[14] Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

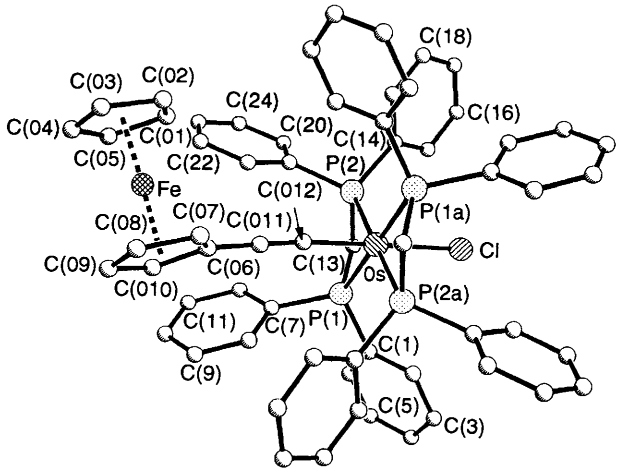

Fig. 1 Crystal structure of **3b**. Selected bond lengths (Å) and angles (°): Os–C(012) 2.031(11), Os–P(1) 2.3386(11), Os–P(2) 2.3481(11), Os–Cl 2.509(4), C(012)–C(011) 1.222(4), C(06)–C(011) 1.426(12), Fe–cp(1) 1.653, Fe–cp(2) 1.644 [cp(1) and cp(2) are centroids of C(01)–C(05) and C(06)–C(010) respectively]; P(1)–Os–P(2) 70.09(4), Os–C(012)–C(011) 173.3(11), C(012)–C(011)–C(06) 178.2(11), dihedral angle between C(01)–C(05) and C(06)–C(010) planes 1.0°

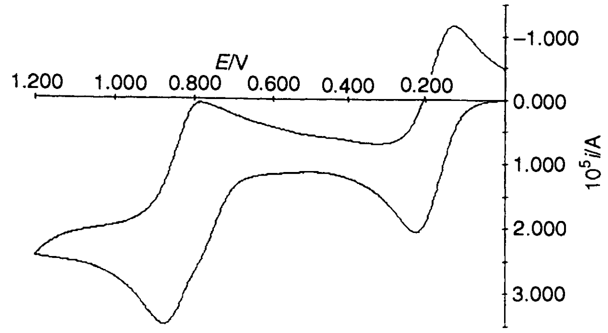

Fig. 2 Cyclic voltammogram of **3b**

178.2(11)°]. The crystal packing is centrosymmetric which precludes the possibility of second-order NLO behaviour in this system. However, studies are underway to introduce chirality by means of a functionalised ferrocene or chiral phosphine, which it is hoped will induce the non-centrosymmetric crystalline properties essential for second-order NLO behaviour.[17]

The electrochemical properties of **3a** and **3b** (Fig. 2) have been studied by cyclic voltammetry and the comparative half-wave potentials of the starting materials **1**, **2a** and **2b** are shown in Table 1. For complexes **3a** and **3b** two quasi-reversible processes are present. The half-wave potential of ruthenium in **3a** and osmium in **3b** is considerably less anodic than that of the metal centres in the precursors **2a** and **2b**. This is undoubtedly due to electron donation from the ferrocene through the acetylide bridge. Our results also indicate that the ruthenium centre acts as a better acceptor than the osmium species, presumably owing to better stabilisation of the +3 state by osmium. As expected, the half-wave potential of the ferrocene moiety is more anodic in complexes **3a** and **3b** than in **1** because of the loss of electron density to the ruthenium and the osmium respectively.

In conclusion ferrocene acts as an excellent electron donor here and the acetylide provides a convenient electron pathway for metal–metal interaction. Polarisation may also be possible within these systems, which could be enhanced by use of a different co-ordinated metal (*e.g.* manganese) or substitution of the remaining chloride on the metal by an electron-withdrawing group. Synthetic investigations along these lines, together with NLO measurements, are in progress.

Table 1 Half-wave redox potentials for complexes **1**–**3** (M = Ru or Os)*

	$E_{\frac{1}{2}}$/V	
Complex	Fe^{II}–Fe^{III}	M^{II}–M^{III}
1	0.12	
2a		0.09
2b		−0.22
3a	0.37	−0.39
3b	0.21	−0.44

* Electrolyte 0.1 mol dm^{-3} [NBu^n_4][BF_4] in CH_2Cl_2; Pt electrode, 20 °C, scan rate 100 mV s^{-1}. $E_{\frac{1}{2}}$ Values are referenced to ferrocene in the same system. All processes are quasi-reversible with respect to the ΔE_p values.

Acknowledgements

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