Synthesis of Novel Donor–Acceptor Manganese(I) Complexes of Ferrocenylacetylene: Crystal Structure of $[(C_5H_5)Fe(C_5H_4)C{\equiv}CMn(CO)_3\{Ph_2PCH(Me)CH_2PPh_2\}]$ which has Potential for Second-order Non-linear Optics

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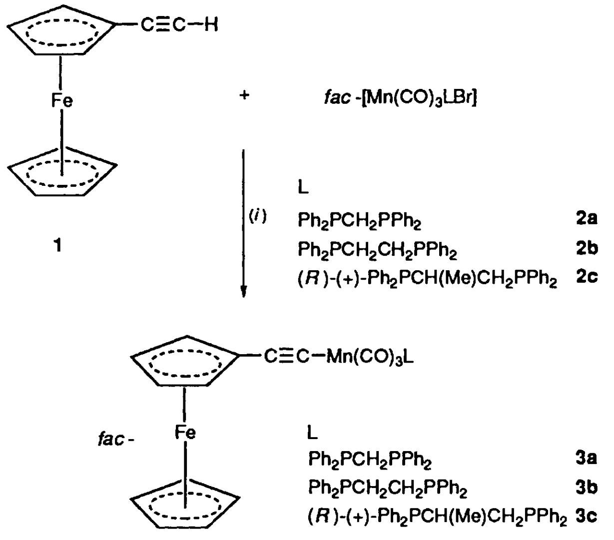
Three novel manganese(I) ferrocenylacetylide complexes have been synthesised and characterised and the crystal structure of $[(C_5H_5)Fe(C_5H_4)C{\equiv}CMn(CO)_3\{Ph_2PCH(Me)CH_2PPh_2\}]$ has been determined, in which the incorporation of a chiral chelating phosphine leads to crystallisation in the non-centrosymmetric space group $P2_12_12_1$.

There is currently great interest in ferrocene-containing complexes owing to the rapid growth of material science. Metallocenes, and in particular ferrocene, has been of use in molecular ferromagnets,[1,2] molecular sensors,[3–5] electrochemical agents,[6,7] liquid crystals[8] and non-linear optics.[9,10] Recent reports also indicate the importance of ferrocenyl derivatives in heterobimetallic mixed-valence species[11–13] and as donors in charge-transfer complexes.[14–16] Increasing demand for new materials has encouraged us to design a new system featuring '*donor–acceptor*' bimetallic characteristics,[17] which might exhibit properties essential for second-order non-linear optical (NLO) phenomena. Introduction of another metal in close proximity to the metallocenyl complex gives us a wider diversity of oxidation states and ligands which increase the possible architectural flexibility and fine-tuning of the properties required for device application.

Complexes **3a**–**3c** were formed by treating the bromocarbonyl derivative of manganese with the silver(I) acetylide, formed *in situ* from a mixture of $AgBF_4$ and the ferrocenylacetylene, in CH_2Cl_2–H_2O.[18] The syntheses are outlined in Scheme 1.[†] The starting materials **1**, **2a**–**2c** were prepared using standard literature procedures[19,20] adapted slightly for inclusion of the various phosphines. The reactions were monitored by infrared spectroscopy and the final manganese ferrocenylacetylide complexes were isolated as fine orange powders in *ca.* 40% yield. Orange crystals of **3c** were obtained from a CH_2Cl_2–EtOH two-layered system.

The crystal structure of **3c** was determined by single crystal X-ray diffraction.[‡] The molecular structure is shown in Fig. 1 which includes some selected bond parameters. The geometry around the Mn^I centre is octahedral with the three terminal carbonyl ligands defining the *fac* isomer. The chelating chiral phosphine displays the expected *R* configuration at C(4). The manganese is linked to the ferrocene moiety by the linear acetylide unit.



Scheme 1 Syntheses of **3a**–**3c**: (*i*) $AgBF_4$, CH_2Cl_2–H_2O (3:1), 24 h

The crystal packing is non-centrosymmetric (as is illustrated in Fig. 2) due to crystallisation in the space group $P2_12_12_1$ rendering the material potentially second-order non-linear optically active. Design of second-order NLO materials is now quite advanced as, over the years, criteria have been discovered that are essential for exhibition of large hyperpolarisabilities.[23] The basic requirements are: (*i*) polarisable material, (*ii*) asymmetric charge distribution, (*iii*) a pathway of π-conjugated electrons and (*iv*) acentric crystal packing. With all the points apparently covered by **3c**, we are hopeful of some interesting NLO activity and NLO measurements are currently in progress.

Preliminary electrochemical studies of **3a**–**3c** indicate some

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[†] Synthesis and physical data. **3a**. A mixture of **1** (0.050 g, 0.24 mmol) and $AgBF_4$ (0.047 g, 0.24 mmol) in dichloromethane (45 cm^3) and water (15 cm^3) was stirred for 15 min with the exclusion of light. Compound **2a** (0.145 g, 0.24 mmol) was then added and the stirring continued until infrared spectroscopy indicated the completion of the reaction. After the usual work-up, including purification by silica TLC using dichloromethane–hexane (1:1) as eluent, **3a** (0.069 g, 39%) was isolated as an orange microcrystalline powder (Found: C, 65.9; H, 4.7. $C_{40}H_{31}FeMnO_3P_2$ requires C, 65.6; H, 4.2%); FAB mass spectrum *m/z* 732.5 (M^+) (calc. 732). Compounds **3b** and **3c** were prepared similarly: **3b** (Found: C, 65.7; H, 4.4. $C_{41}H_{33}FeMnO_3P_2$ requires C, 66.0; H, 4.4%); *m/z* 746.6 (M^+) (calc. 746). **3c** (Found: C, 66.4; H, 4.5. $C_{42}H_{35}FeMnO_3P_2$ requires C, 66.3; H, 4.6%); *m/z* 760.7 (M^+) (calc. 760).

[‡] Crystal data for **3c**: $C_{42}H_{35}FeMnO_3P_2$, $M = 760.43$, orthorhombic, space group $P2_12_12_1$, $a = 10.795(2)$, $b = 17.991(4)$, $c = 18.634(4)$ Å, $U = 3619.0(13)$ Å^3, $Z = 4$, $D_c = 1.396$ Mg m^{-3}, λ(Mo-Kα) = 0.710 73 Å, μ(Mo-Kα) = 0.877 mm^{-1}, $F(000) = 1568$, crystal dimensions 0.30 × 0.25 × 0.21 mm. Data collected at room temperature on a Rigaku AFC7 diffractometer. Structure solved by the Patterson method and from subsequent Fourier-difference syntheses. Refinement by full-matrix least squares on F_o^2 using SHELXTL PLUS[21] and SHELXL 93[22] to give $R = 0.0579$ [$F > 4\sigma(F)$] and $R' = 0.1661$ (all data), where $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R' = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}}$. Weighting scheme of the form $w = 1/[\sigma^2(F_o^2) + (0.0813P)^2 + 1.92P]$ where $P = \{F_o^2 + 2F_c^2\}/3$. 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.

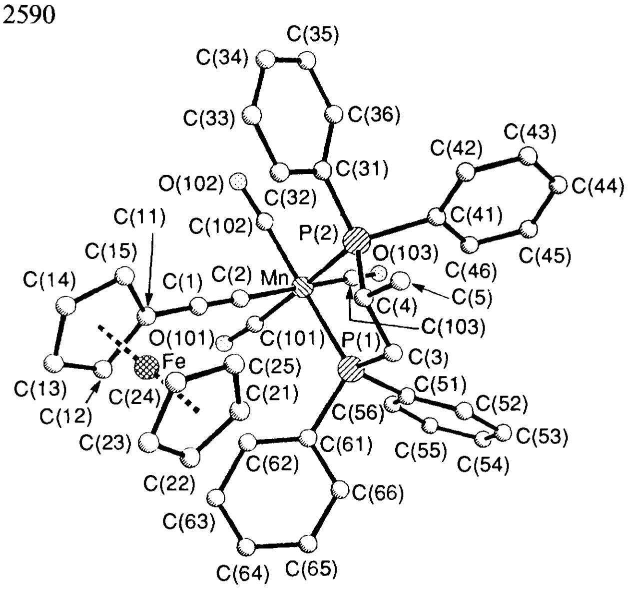

Fig. 1 Molecular structure of [$(C_5H_5)Fe(C_5H_4)C{\equiv}CMn(CO)_3\{Ph_2PCH(Me)CH_2PPh_2\}$] **3c**. Selected bond lengths (Å) and angles (°): Mn–C(101) 1.807(10), Mn–C(102) 1.803(11), Mn–C(103) 1.797(9), Mn–C(2) 1.999(8), Mn–P(1) 2.324(2), Mn–P(2) 2.317(2), C(1)–C(2) 1.194(11), C(1)–C(11) 1.439(11), Fe–C(11) 2.054(9), Fe–C(12) 2.043(10), Fe–C(13) 2.024(11), Fe–C(14) 2.044(11), Fe–C(15) 2.067(10), Fe–C(21) 2.054(10), Fe–C(22) 2.033(11), Fe–C(23) 2.015(11), Fe–C(24) 2.019(11), Fe–C(25) 2.036(11); C(101)–Mn–C(102) 89.7(4), C(101)–Mn–C(103) 90.2(4), C(102)–Mn–C(2) 85.5(4), C(103)–Mn–C(2) 177.0(2), C(101)–Mn–P(1) 95.9(3), C(102)–Mn–P(1) 171.2(3), C(103)–Mn–P(1) 93.5(3), C(2)–Mn–P(1) 88.1(2), C(101)–Mn–P(2) 170.4(3), C(102)–Mn–P(2) 91.0(3), C(103)–Mn–P(2) 99.4(3), C(2)–Mn–P(2) 83.4(2), P(2)–Mn–P(1) 171.2(3), C(2)–C(1)–C(11) 179.0(9), C(1)–C(2)–Mn 177.2(7)

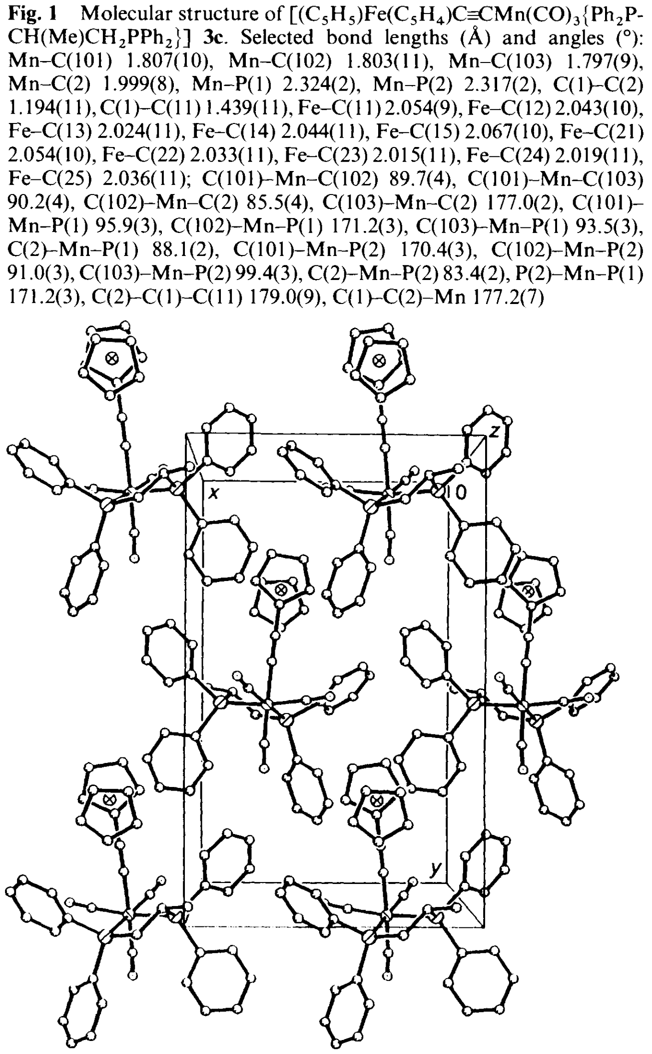

Fig. 2 The crystal packing diagram for **3c** viewed down the crystallographic *c* axis

very interesting redox behaviour with, once again, ferrocene imparting excellent electron donation through the acetylene bridge. The variation of the chelating phosphine does not have a great effect, however; isomerisation of the *fac* Mn^I centre to the *mer* isomer is apparent during the electrochemical experiment. This phenomena has been observed previously,[24–26] and is facilitated by oxidation to the metal(II) complex, where the *fac–mer* isomerisation rate is far greater than in the +1 oxidation state. Full electrochemical and non-linear optical discussion will be communicated forthwith.

Acknowledgements

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