

Some Transition Metal Complexes of Pentakis(methoxycarbonyl)cyclopentadiene: Water-soluble Metallocenes, and the X-Ray Crystal Structure of $\text{Ru}(\eta\text{-C}_5\text{H}_5)[\eta\text{-C}_5(\text{CO}_2\text{Me})_5]$

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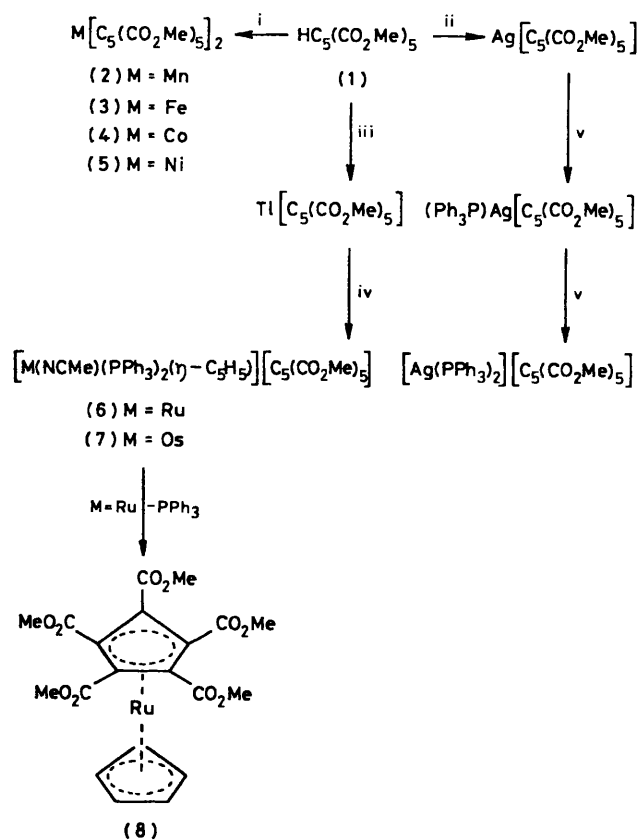
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Summary Some metal derivatives of the $[\text{C}_5(\text{CO}_2\text{Me})_5]^-$ anion (cpp⁻) are described, of which transition metal complexes $\text{M}(\text{cpp})_2$ are fully ionised in aqueous solution and the mixed complex $\text{Ru}(\eta\text{-C}_5\text{H}_5)[\eta\text{-C}_5(\text{CO}_2\text{Me})_5]$ contains a symmetrically bonded cpp ring; covalent Group IB metal complexes $\text{M}^{\text{I}}(\text{cpp})(\text{PPh}_3)$ react further with PPh_3 to give ionic $[\text{M}(\text{PPh}_3)_2](\text{cpp})$.

THE chemistry of fully-substituted cyclopentadienyl complexes is largely confined to the pentamethyl derivatives, for which many interesting differences from their $\eta\text{-C}_5\text{H}_5$ (cp) analogues have been described.¹ Compounds with electron-withdrawing substituents are much rarer, and we report a range of new complexes of this type, containing the $\text{C}_5(\text{CO}_2\text{Me})_5$ (cpp) ligand. Pentakis(methoxycarbonyl)cyclopentadiene, $\text{HC}_5(\text{CO}_2\text{Me})_5$ (**1**) is a strong organic acid,

which was first described in 1942,² but to our knowledge, only the iron(II)³ and silver(I) derivatives^{4,5} have been described previously.

Useful synthetic approaches are (i) reactions between the potassium or thallium salts of $\text{HC}_5(\text{CO}_2\text{Me})_5$ and transition metal halides, and (ii) reactions between (1) and metal salts of weaker acids, e.g. carbonate or acetate. The Scheme summarises some of the derivatives obtained so far.



SCHEME. i, $\text{M}(\text{OAc})_2$, ii, AgOAc , iii, Tl_2CO_3 , iv, $\text{MCl}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)$ in MeCN, v, PPh_3 .

First-row transition metals readily form water-soluble compounds $\text{M}(\text{cpp})_2$ [Mn (2), pale green; Fe (3), yellow; Co (4), pink; Ni (5), green] (Scheme), some of which can be obtained free of solvent; the nickel(II) derivative crystallises as $\text{Ni}(\text{cpp})_2 \cdot 6\text{MeOH}$, however. In water, solutions containing $[\text{M}(\text{OH})_2]_6^{2+}$ and $[\text{C}_5(\text{CO}_2\text{Me})_5]^-$ ions are obtained; in D_2O , the singlet resonance for the CO_2Me protons is somewhat broadened by paramagnetic metal ions. In addition to their solution properties, complexes (2)–(5) differ from their C_5H_5 analogues in being involatile and air-stable although thermally stable to $>300^\circ\text{C}$.

Reactions between $\text{MCl}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)$ and $\text{Tl}(\text{cpp})$ in acetonitrile afford $[\text{M}(\text{MeCN})(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)][\text{C}_5(\text{CO}_2\text{Me})_5]$ [$\text{M} = \text{Ru}$ (6) or Os (7)] [e.g., for (6), ^1H n.m.r. $\delta(\text{CDCl}_3)$

1.89(s, MeCN), 3.74(s, CO_2Me), 4.40(s, C_5H_5), and 7.20(m br. PPh_3), ^{13}C n.m.r. $\delta(\text{CDCl}_3)$ 3.52 (MeCN), 51.14 (OMe), 83.32 (C_5H_5), 117.45 [$\text{C}_5(\text{CO}_2\text{Me})_5$], 128.6–137.0 (PPh_3), 143.57 (MeCN), and 168.10 (CO_2Me) p.p.m.] as large, well-formed pale yellow crystals. In contrast, a similar reaction in methanol carried out in the presence of dioxygen affords OPPh_3 and $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)[\eta^5\text{-C}_5(\text{CO}_2\text{Me})_5]$ (8) [^1H n.m.r. $\delta(\text{CDCl}_3)$ 3.80 (OMe) and 4.93 (C_5H_5), ^{13}C n.m.r. $\delta(\text{CDCl}_3)$ 52.96 [$\text{C}_5(\text{CO}_2\text{Me})_5$], 78.83 (C_5H_5), 82.23 [$\text{C}_5(\text{CO}_2\text{Me})_5$], and 165.98 (CO_2Me) p.p.m.]. The structure of this unusual ruthenocene derivative has been investigated to determine the effect, if any, of the five CO_2Me groups on the basic metallocene structure.

Crystal data: $\text{C}_{20}\text{H}_{20}\text{O}_{10}\text{Ru}$, $M = 521.5$, triclinic, space group $P\bar{1}$, $a = 15.790(5)$, $b = 8.968(4)$, $c = 7.947(7)$ Å, $\alpha = 67.52(7)$, $\beta = 89.52(7)$, $\gamma = 80.90(7)^\circ$, $U = 1025.0(6)$ Å³, $Z = 2$, $D_m = 1.69(1)$, $D_c = 1.69$ g cm⁻³. 7459 reflections were measured to $\theta = 32.5^\circ$. Current R value, 0.026.†

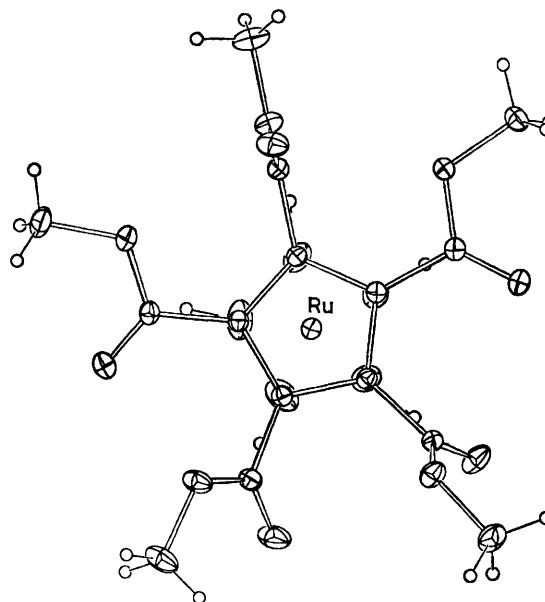


FIGURE. A single molecule of $\text{Ru}(\eta\text{-C}_5\text{H}_5)[\eta\text{-C}_5(\text{CO}_2\text{Me})_5]$ projected normal to the cpp ring plane. 20% thermal ellipsoids are shown for the non-hydrogen atoms; hydrogen atoms are shown as circles of arbitrary radius 0.1 Å.

The molecular structure of (8) (Figure) is that of a conventional ruthenocene derivative, with the C_5 rings almost completely eclipsed, and with the ruthenium atom almost equidistant from each ring [Ru–C(cp), 2.157–2.178(2); Ru–C(cpp), 2.17–2.186(3) Å; cf. Ru–C(cp) in ruthenocene, 2.174–2.187(6) Å].*† The formation of this and related complexes counters the prediction¹ that stable $\eta^5\text{-cpp}$ complexes would be found to be incapable of existence, as a result of the removal of electron density from the filled ring A and E_1 orbitals by the CO_2Me groups. However,

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

‡ Corrections for thermal motion have not been applied, so that apparent differences in these Ru–C distances may not be significant.

reaction between (8) and PPh_3 in acetonitrile gives (6), showing that the Ru-cpp bond is relatively weak, and providing the first example of displacement of a substituted η^5 -cyclopentadienyl group from a metallocene by simple 2e donor ligands under mild conditions.

The silver(I) derivative of (1), previously prepared and allowed to react *in situ*,^{4,5} can be isolated as a white crystalline solid which is photosensitive and thermally unstable. Addition of tertiary phosphines (L) affords, sequentially, Ag(L)(cpp) and $\text{Ag(L)}_2(\text{cpp})$. The latter compounds are ionic, and probably contain linear two-co-ordinate $[\text{Ag(L)}_2]^+$ cations and $[\text{C}_5(\text{CO}_2\text{Me})_5]^-$ anions. Similar compounds containing copper(I) and gold(I) have also been obtained.

The main difference between the complexes of C_5H_5^- , in which the ring-metal bond is predominantly covalent in

character, and those of $[\text{C}_5(\text{CO}_2\text{Me})_5]^-$, which has a strong tendency to form ionic complexes, results from the presence of the five strongly electron-withdrawing CO_2Me groups. In the limit, formation of the extremely stable anion occurs, and such derivatives behave as simple salts of a strong monobasic acid. In other cases, where a ring-metal bond is present, easy displacement of the cpp anion by other donor ligands may occur. The anion is protonated at the carbonyl oxygens, but alkylated (*via* the silver derivative) at the ring carbon.

We thank the Australian Research Grants Committee for support of this work.

(Received, 17th February 1981; Com. 180.)

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