Pentakis(methoxycarbonyl)cyclopentadiene Chemistry. Part 7.[1] Preparation and Characterisation of Some Ruthenium Complexes: Crystal and Molecular Structure of η-Cyclopentadienyl[η-1,2,3,4,5-pentakis(methoxycarbonyl)cyclopentadienyl]ruthenium, $[Ru(\eta\text{-}C_5H_5)\{\eta\text{-}C_5(CO_2Me)_5\}]$ †

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The salt $Tl[C_5(CO_2Me)_5]$ reacts with $[RuCl(PPh_3)_2(\eta\text{-}C_5H_5)]$ in acetonitrile to give the complex $[Ru(NCMe)(PPh_3)_2(\eta\text{-}C_5H_5)][C_5(CO_2Me)_5]$; in air the reaction affords $[Ru(\eta\text{-}C_5H_5)\{\eta\text{-}C_5(CO_2Me)_5\}]$. The crystal structure of the latter has been determined by single-crystal *X*-ray diffraction methods at 295 K, being refined to a residual of 0.026 for 6 438 'observed' reflections. Crystals are triclinic, space group $P\bar{1}$, with a = 15.790(5), b = 8.968(4), c = 7.947(3) Å, α = 67.52(3), β = 89.52(3), γ = 80.90(3)°, and Z = 2. Both ligands have an η^5 relationship to the ruthenium in what is essentially an eclipsed sandwich compound. For the C_5H_5 ring, Ru–C is 2.178(2)—2.186(3) Å, while for the $C_5(CO_2Me)_5$ ligand, Ru–C is 2.157(2)—2.178(2) Å; although these distances are uncorrected for libration, their relativity seems valid. The $C_5(CO_2Me)_5$ ligand is displaced in reactions with tertiary phosphines in nitrile solvents, and this reaction forms the basis of a process for the oxidation of PPh_3 catalysed by the metallocene. The protonation of $[RuH(PPh_3)_2(\eta\text{-}C_5H_5)]$ by $HC_5(CO_2Me)_5$ is also described.

In several recent papers we have described some of the novel chemistry centred about the strong organic acid, pentakis(methoxycarbonyl)cyclopentadiene, $HC_5(CO_2Me)_5$ (1) (Hpmcp). We have shown by extensive *X*-ray structural studies that the proton is *O*-co-ordinated in (1),[2] as is the metal ion in its alkali-metal,[2] alkaline-earth-metal,[3] cadmium and zinc,[3] thallium(I),[2] and first-row transition-metal compounds,[1,4] in obvious contrast to analogous derivatives of the well known cyclopentadiene. Metal–ring carbon interactions have been found in several Group 1B complexes, including $[\{Ag(OH_2)(pmcp)\}_2]$ and $[\{Ag(PPh_3)(pmcp)\}_2]$, in which asymmetric η^2 bonding of the pmcp ligand is found, together with the usual carboxylate co-ordination.[5] In $[Ag(PPh_3)_2(pmcp)]$, the ring carbons are displaced by the second tertiary phosphine molecule.[5] The formally analogous gold(I) complex, $[Au(PPh_3)(pmcp)]$, has a strong Au–C bond with one ring carbon,[6] although two other carbons are close enough to constitute a weak η^3 interaction, analogous to that found for $[Au(PPh_3)(C_5Ph_4H)]$.[7] With all the complexes mentioned above, a characteristic feature of their chemistry is the ready formation of the stable $[C_5(CO_2Me)_5]^-$ anion, particularly in solution.

Even before the structural investigations, model studies suggested that the formation of complexes $M[\eta^5\text{-}C_5(CO_2Me)_5]_2$ would be inhibited by the steric interactions between the CO_2Me groups of the two rings. It is not possible for all five CO_2Me groups to become coplanar with the ring carbons; at best, coplanarity is achieved by the 1, 2, and 4 substituents, and formation of the fulvenoid form of the anion is commonly found in metal derivatives and the parent diene. The remaining CO_2Me groups adopt a conformation with their planes approximately perpendicular to the C_5 ring, and thus would interact strongly with the substituents of the second ring in a classical sandwich complex. Indeed, the size of the first-row transition metals suggests that similar interactions with an $\eta^5\text{-}C_5H_5$ ring would also be significant.

We have previously reported one example of a poly-CO_2Me-substituted metallocene, obtained from $[Rh_2(O_2CMe)_4]$ and (1), and structurally characterised as $[Rh\{\eta^5\text{-}C_5H_2(CO_2Me)_3\}_2][C_5(CO_2Me)_5]$ (2).[8] In the cation of this complex, the two C_5 rings are staggered to minimise the interaction of the CO_2Me groups, which again are found to have their planes nearly perpendicular to the C_5 ring planes. As far as we are aware, the extensive chemistry of ferrocene has afforded only three compounds containing one or more CO_2Me groups as the only substituents, namely the mono-, 1,1′-di-, and 1,1′,2-tri-(methoxycarbonyl) derivatives.[9] In an extension of the chemistry of compound (1), we sought to prepare complexes of the type $[M(\eta\text{-}C_5H_5)\{\eta\text{-}C_5(CO_2Me)_5\}]$ (M = Ru or Os); this paper reports the chemistry of the ruthenium systems, where the dimensions of the central atom suggest a minimum of steric interaction between the ring substituents.

Experimental

General experimental techniques have been described previously. Diene (1) and its thallium(I) derivative were prepared as described earlier.[2]

Preparation of $[Ru(NCMe)(PPh_3)_2(\eta\text{-}C_5H_5)][C_5(CO_2Me)_5]$.—The salt $Tl[C_5(CO_2Me)_5]$ (230 mg, 0.41 mmol) was added to a suspension of $[RuCl(PPh_3)_2(\eta\text{-}C_5H_5)]$ (290 mg, 0.40 mmol) in acetonitrile (50 cm³). The mixture was stirred under nitrogen at room temperature (2 h); the initial orange-red suspension gradually changed to a bright yellow solution over a white precipitate (TlCl). Filtration, evaporation, and recrystallisation (MeOH) afforded large well formed bright yellow crystals of $[Ru(NCMe)(PPh_3)_2(\eta\text{-}C_5H_5)][C_5(CO_2Me)_5]$ (3) (390 mg, 90%), m.p. 164—168 °C (decomp.) (Found: C, 63.85; H, 4.80; N, 1.30. $C_{58}H_{53}NO_{10}P_2Ru$ requires C, 64.10; H, 4.90; N, 1.30%). N.m.r.: ^1H ($CDCl_3$), δ 1.89 (m, 3 H, MeCN), 3.78

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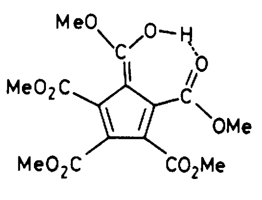
† *Supplementary data available* (No. SUP 23654, 23 pp.): thermal parameters, H-atom co-ordinates, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.



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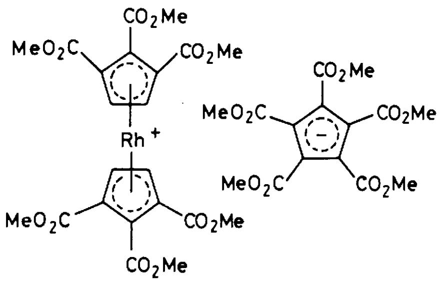


(2)

(s, 15 H, OMe), 4.43 (s, 5 H, C_5H_5), and 7.18 (m, 30 H, Ph); ^{13}C ($CDCl_3$), δ 3.52 (s, *Me*CN), 51.14 (s, OMe), 83.32 (s, C_5H_5), 117.45 [s, *C*(CO_2Me)], 128.39—137.01 (m, PPh_3), 143.57 (s, Me*C*N) and 168.10 (s, *C*O_2Me). Conductivity (acetone): 73.0 ohm^{-1} cm^2 mol^{-1}.

Preparation of [Ru(η-C_5H_5){η-$C_5(CO_2Me)_5$}].—(*a*) *From* [RuCl$(PPh_3)_2$(η-C_5H_5)]. A mixture of Tl[$C_5(CO_2Me)_5$] (780 mg, 1.40 mmol) and [RuCl$(PPh_3)_2$(η-C_5H_5)] (1 000 mg, 1.38 mmol) in methanol (40 cm^3) was stirred for 2 h at 60 °C in air. The white precipitate (TlCl) was filtered off and washed with MeOH (5 cm^3); the combined pale yellow-green filtrates were cooled overnight (−30 °C) to give well formed yellow-green crystals of pure [Ru(η-C_5H_5){η-$C_5(CO_2Me)_5$}] (4) (610 mg, 85%), m.p. 145—146 °C [Found: C, 45.75; H, 3.80%; *M* (mass spectrometry) 522. $C_{20}H_{20}O_{10}Ru$ requires C, 46.05; H, 3.85%; *M* 522]. N.m.r.: ^1H ($CDCl_3$), δ 3.80 (s, 15 H, OMe) and 4.93 (s, 5 H, C_5H_5); ^{13}C ($CDCl_3$), δ 52.96 (s, OMe), 78.83 (s, C_5H_5), 82.23 [s, $C_5(CO_2Me)_5$], and 165.98 (s, *C*O_2Me). Conductivity (acetone): 1.0 ohm^{-1} cm^2 mol^{-1}.

The filtrate was evaporated, and the resulting solid extracted with boiling light petroleum (b.p. 40—60 °C, 3 × 20 cm^3). Filtration and cooling (0 °C) gave white crystals of PPh_3O (422 mg, 55%), m.p. 151—154 °C. Infrared (Nujol): ν(PO) at 1 187s cm^{-1}.

(*b*) *From* [RuCl$(CO)_2$(η-C_5H_5)]. The salt Tl[$C_5(CO_2Me)_5$] (109 mg, 0.195 mmol) was added to [RuCl$(CO)_2$(η-C_5H_5)] (50 mg, 0.194 mmol) dissolved in MeOH (40 cm^3). After stirring at reflux for 16 h, a yellow-green solution containing a white precipitate (TlCl) was obtained. The filtered solution was reduced in volume to *ca.* 10 cm^3, from which well formed yellow-green crystals of [Ru(η-C_5H_5){η-$C_5(CO_2Me)_5$}] (60 mg, 60%) were deposited on cooling.

Preparation of [$RuH_2(PPh_3)_2$(η-C_5H_5)][$C_5(CO_2Me)_5$].—Twice-recrystallised $HC_5(CO_2Me)_5$ (330 mg, 0.9 mmol) was added to a suspension of [RuH$(PPh_3)_2$(η-C_5H_5)] (600 mg, 0.84 mmol) in dry methanol (45 cm^3), whereupon the colour rapidly faded. After 30 min the white precipitate was filtered off, washed with methanol (4 × 20 cm^3) and diethyl ether (2 × 10 cm^3), and dried to give [$RuH_2(PPh_3)_2$(η-C_5H_5)]-[$C_5(CO_2Me)_5$] (5) (830 mg, 94%), m.p. 136—137 °C (turns orange at 134 °C) (Found: C, 63.95; H, 5.20. $C_{56}H_{52}O_{10}P_2Ru$ requires C, 64.2; H, 5.00%). The complex is insoluble in most solvents (alkanes, benzene, Et_2O, CS_2, 1,2-dimethoxyethane, MeCN, Me_2CO, alcohols, and water); it dissolves with rapid reaction in chlorinated solvents to give [RuCl$(PPh_3)_2$(η-C_5H_5)].

Reactions of [Ru(η-C_5H_5){η-$C_5(CO_2Me)_5$}] (4).—(*a*) *With* PPh_3 *in acetonitrile*. A mixture of complex (4) (100 mg, 0.19 mmol) and PPh_3 (200 mg, 0.76 mmol) was heated in refluxing MeCN (50 cm^3) for 5 d. During this time the colour of the initially yellow-green solution intensified to bright yellow. Work-up (preparative t.l.c.) gave unreacted PPh_3, recovered (4) (17 mg, 17%), and yellow crystals (from MeOH) of [Ru(NCMe)$(PPh_3)_2$(η-C_5H_5)][$C_5(CO_2Me)_5$] (3) (120 mg, 55%), m.p. 164—168 °C (decomp.), identical with the product made as described above.

(*b*) *With* PPh_3 *in benzonitrile*. Similarly, a mixture of complex (4) (100 mg, 0.19 mmol) and PPh_3 (100 mg, 0.38 mmol) was heated at 120 °C in benzonitrile (15 cm^3) for 72 h. Evaporation of the resulting bright yellow solution, extraction of the residue with boiling light petroleum (3 × 25 cm^3) and Et_2O (3 × 25 cm^3), and recrystallisation (MeOH–Et_2O) of the remaining solid gave yellow crystals of [Ru(NCPh)$(PPh_3)_2$-(η-C_5H_5)][$C_5(CO_2Me)_5$] (6) (70 mg, 32%), m.p. 145—148 °C (Found: C, 65.75; H, 5.00; N, 1.20. $C_{63}H_{55}NO_{10}P_2Ru$ requires C, 65.85; H, 4.80; N, 1.20%). ^1H N.m.r. ($CDCl_3$): δ 3.70 (s, 15 H, OMe), 4.50 (s, 5 H, C_5H_5), and 7.23 (m, 35 H, Ph).

(*c*) *With dppe in acetonitrile*. A solution of complex (4) (250 mg, 0.48 mmol) and $Ph_2PCH_2CH_2PPh_2$ (dppe) (200 mg, 0.5 mmol) in acetonitrile (50 cm^3) was heated in an autoclave under nitrogen [140 °C, 45 atm (4.56 × 10^5 Pa), 15 h]. Evaporation of the resulting yellow solution, extraction of the residue with boiling light petroleum (b.p. 40—60 °C, 3 × 50 cm^3), benzene (3 × 50 cm^3), and Et_2O (3 × 50 cm^3), and recrystallisation (MeOH–Et_2O) afforded large bright yellow crystals of [Ru(NCMe)(dppe)(η-C_5H_5)][$C_5(CO_2Me)_5$]·0.25MeCN (7) (256 mg, 56%), m.p. 148—152 °C (Found: C, 59.05; H, 5.05; N, 1.40. $C_{48}H_{47}NO_{10}P_2Ru$·0.25MeCN requires C, 60.0; H, 4.95; N, 1.80%). ^1H N.m.r. ($CDCl_3$): δ 1.35 [s, 3 H, MeCN (co-ordinated)], 1.97 [s, 0.75 H, MeCN (free)], 2.37, 2.57 (s, 2 H each, CH_2), 3.66 (s, 15 H, OMe), 4.60 (s, 5 H, C_5H_5), and 7.50 (m, 20 H, Ph).

Catalytic Oxidation of Triphenylphosphine.—Oxygen was bubbled through a mixture of [Ru(η-C_5H_5){η^5-$C_5(CO_2Me)_5$}] (20 mg, 0.038 mmol) and triphenylphosphine (1 000 mg, 3.81 mmol) in refluxing EtOH (50 cm^3) for 6 h. The solution was then taken to dryness and the off-white solid was extracted with hot light petroleum (b.p. 40—60 °C, 5 × 20 cm^3), filtered, and the combined extracts cooled to give white crystals of triphenylphosphine oxide (850 mg, 80%), m.p. 148—153 °C, ν(PO) 1 187s cm^{-1}, identified by comparison with an authentic sample.

Crystallography.—The general procedure has been outlined in ref. 2.

Crystal data. $C_{20}H_{20}O_{10}Ru$ (4), $M = 521.5$, Triclinic, space group $P\bar{1}$ (C_i^1, no. 2), $a = 15.790(5)$, $b = 8.968(4)$, $c = 7.947(3)$ Å, $\alpha = 67.52(3)$, $\beta = 89.52(3)$, $\gamma = 80.90(3)°$, $U = 1\,025.0(6)$ Å^3, $D_m = 1.69(1)$, $Z = 2$, $D_c = 1.69$ g cm^{-3}, $F(000) = 528$. Specimen size: 0.25 × 0.35 × 0.41 mm. $\mu_{Mo} = 7.7$ cm^{-1}; $2\theta_{max.} = 65°$; $N = 7\,459$, $N_o = 6\,438$, $R = 0.026$, $R' = 0.037$, $S = 1.14$.

Table 1. Infrared spectra (cm^{-1}) obtained from Nujol mulls

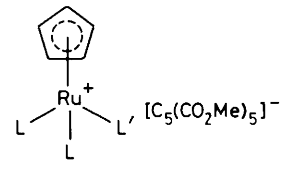
Compound	Significant bands	Other bands
(3) [Ru(NCMe)(PPh$_3$)$_2$(η-C$_5$H$_5$)][C$_5$(CO$_2$Me)$_5$]	ν(C≡N) 2 265w ν(C=O) 1 721 (sh), 1 710s, 1 690s ν(C–O) 1 270m, 1 199s, 1 170s, 1 160 (sh)	1 585w, 1 467w, 1 455s, 1 436w, 1 420 (sh), 1 310w, 1 090m, 1 070 (sh), 1 064m, 1 005 (sh), 1 000m, 972w, 938w, 841m, 832m, 820w, 788w, 765m, 750m, 723w, 697s, 684w
(4) [Ru(η-C$_5$H$_5$){η-C$_5$(CO$_2$Me)$_5$}]	ν(C=O) 1 758s, 1 745w, 1 734vs, 1 723vs ν(C–O) 1 263s, 1 225vs, 1 210 (sh), 1 181s, 1 173 (sh)	1 495 (sh), 1 409s, 1 399s, 1 393 (sh), 1 378w, 1 370 (sh), 1 357w, 1 105w, 1 063m, 995s, 985m, 952w, 871m, 851w, 844w, 825m, 807m, 785m, 773m, 757w, 678m
(5) [RuH$_2$(PPh$_3$)$_2$(η-C$_5$H$_5$)][C$_5$(CO$_2$Me)$_5$]	ν(Ru–H) 2 013w ν(C=O) 1 730w, 1 708vs, 1 691vs ν(C–O) 1 277m, 1 200vs, 1 163vs	1 588w, 1 483w, 1 439 (sh), 1 435m, 1 425w, 1 419w, 1 120 (sh), 1 093s, 1 075m, 1 065m, 1 028w, 1 009m, 1 001m, 972w, 950w, 864w, 851w, 839s, 834s, 800w, 784w, 751s, 720m, 706w, 698s, 690 (sh), 660m
(6) [Ru(NCPh)(PPh$_3$)$_2$(η-C$_5$H$_5$)][C$_5$(CO$_2$Me)$_5$]	ν(C≡N) 2 228w ν(C=O) 1 739w, 1 734w, 1 720 (sh), 1 710s, 1 700w, 1 687vs ν(C–O) 1 275m, 1 200vs, 1 175s	1 587w, 1 574w, 1 480w, 1 440 (sh), 1 436m, 1 420 (sh), 1 370 (sh), 1 312w, 1 117 (sh), 1 090m, 1 087m, 1 070m, 1 012m, 1 000m, 975w, 940m, 865 (sh), 849m, 835m, 799w, 788w, 751s, 721w, 698s, 685m
(7) [Ru(NCMe)(dppe)(η-C$_5$H$_5$)][C$_5$(CO$_2$Me)$_5$]	ν(C≡N) 2 278w ν(C=O) 1 736 (sh), 1 725w, 1 721w, 1 714vs, 1 695vs, 1 677s ν(C–O) 1 277m, 1 207vs, 1 169s	1 587w, 1 572w, 1 436m, 1 420(sh), 1 310w, 1 100m, 1 069m, 1 015m, 999m, 980 (sh), 939w, 870w, 841m, 835w, 812m, 790w, 754m, 741w, 706 (sh), 701s, 679w

Specific comments. Data were corrected for absorption (analytical correction). In Table 2 a dummy atom C(0) is given at the centre of each C$_5$ ring. Hydrogen atom co-ordinates (x,y,z,U_{iso}) were refined. As in ref. 2, a Syntex $P2_1$ four-circle diffractometer was employed; refinement was made using the *X*-RAY 76 program system.

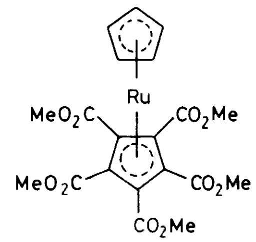
Results and Discussion

Our initial approach to the synthesis of [Ru(η-C$_5$H$_5$){η-C$_5$(CO$_2$Me)$_5$}] was an investigation of the reaction between [RuCl(PPh$_3$)$_2$(η-C$_5$H$_5$)] and Tl[C$_5$(CO$_2$Me)$_5$]. Previously it had been established that the reaction between [RuCl(PPh$_3$)$_2$-(η-C$_5$H$_5$)] and Tl(C$_5$H$_5$) gave a mixture of ruthenocene, triphenylphosphine, and TlCl, no intermediate σ-C$_5$H$_5$ complex being detected.[10] The analogous reaction with Tl[C$_5$(CO$_2$Me)$_5$], carried out in acetonitrile, afforded a beautifully crystalline, bright yellow complex which contained triphenylphosphine and acetonitrile (n.m.r.). This compound (3) was readily characterised as the [C$_5$(CO$_2$Me)$_5$]$^-$ salt of the well known cation [Ru(NCMe)(PPh$_3$)$_2$(η-C$_5$H$_5$)]$^+$, and again demonstrates the usefulness of this anion for the isolation of large cationic complexes (see also below). Although well formed crystals of (3) were obtained, attempted structural determinations were thwarted by disorder problems.

The stability of these salts contrasts with the result obtained with C$_5$H$_5^-$. However, small and variable yields of a pale yellow-green compound were obtained after heating a mixture of [RuCl(PPh$_3$)$_2$(η-C$_5$H$_5$)] and Tl[C$_5$(CO$_2$Me)$_5$] in other solvents such as tetrahydrofuran, acetone, alcohols, *etc.*, and this compound was identified as the desired metallocene. The observation, in one of the more successful reactions, that triphenylphosphine oxide was also found, suggested that the conversion of complex (3) be attempted in air. This proved to be successful, and high, reproducible yields of [Ru(η-C$_5$H$_5$)-{η-C$_5$(CO$_2$Me)$_5$}] (4) were finally obtained by running the reaction which originally afforded (3) in air.



(3) L = PPh$_3$, L' = NCMe
(6) L = PPh$_3$, L' = NCPh
(7) L$_2$ = dppe, L' = NCMe



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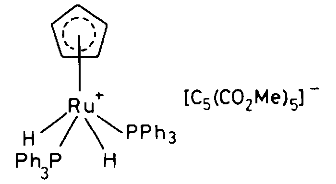

(5)

The new metallocene forms pale yellowish green crystals which melt without decomposition. The i.r. spectrum (Table 1) is relatively simple, having bands assigned to ν(CO) between 1 723—1 758 and 1 181—1 263 cm^{-1} and the characteristic bands of a metallocene at 995 cm^{-1}; there is only a weak absorption at *ca.* 1 100 cm^{-1}. The n.m.r. spectra are also simple, all five substituents being equivalent, and indicate that the CO$_2$Me groups are freely rotating (about the ring C–CO$_2$Me bond) in solution. Thus the protons of the C$_5$H$_5$

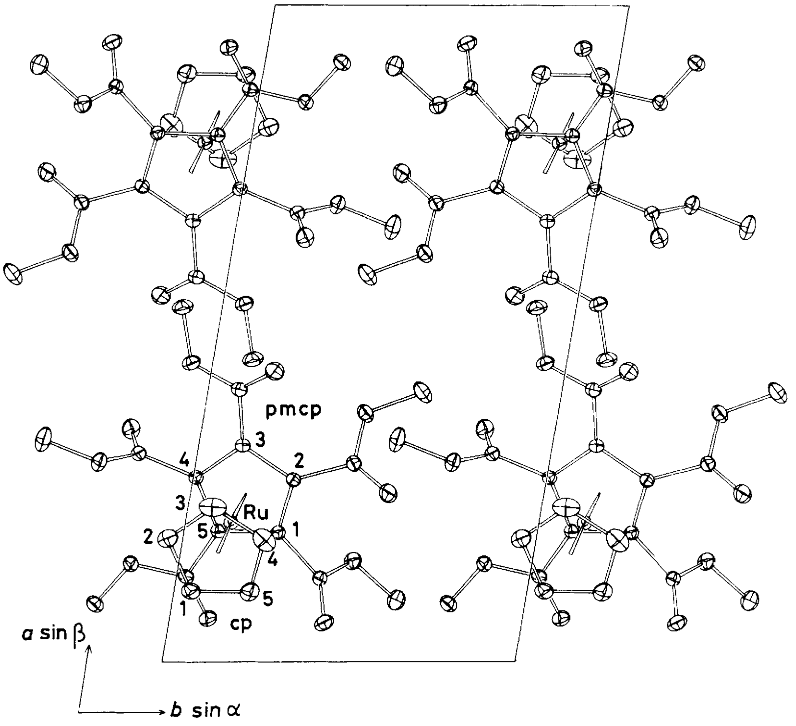

Figure 1. Unit-cell contents of [Ru(η-C_5H_5){η-$C_5(CO_2Me)_5$}], projected down *c*, showing 20% thermal ellipsoids for the non-hydrogen atoms and ring numbering

ring give rise to a sharp singlet at δ 4.93 (*cf.* ruthenocene, at δ 4.55), and the 15 CO_2Me protons also resonate as a singlet at δ 3.80. The ^{13}C n.m.r. spectrum contains four singlets corresponding to the two types of ring carbons [at δ 78.8 and 82.2 for C_5H_5 and $C_5(CO_2Me)_5$, respectively, *cf.* ruthenocene at δ 70.1], the methyl carbons (at δ 53.0), and the ester carbonyl groups (at δ 166.0). The mass spectrum contains a parent ion at *m/e* 522 (for ^{102}Ru) which fragments by loss of OMe and CO units.

Possible mechanisms for the reaction which affords complex (4) are of interest. We note first that in donor solvents the chloro-complex [RuCl$(PPh_3)_2$(η-C_5H_5)] readily forms cationic complexes; with methanol, for example, equilibrium (i) lies to the right. However, oxygen-donor ligands such as

$$[RuCl(PPh_3)_2(\eta\text{-}C_5H_5)] + MeOH \rightleftharpoons [Ru(MeOH)(PPh_3)_2(\eta\text{-}C_5H_5)]^+ + Cl^- \quad (i)$$

alcohols and ethers are weakly bonded, and are readily displaced by other ligands. Nitrogen-donor ligands, such as acetonitrile, are more strongly attached to the metal centre, and it is relevant to observe that complex (4) cannot be obtained from salt (3), even in oxygen.

We may suppose, however, that the methanol can be displaced by molecular oxygen to give an intermediate (which we have not yet detected), which may be formulated as a dioxygen complex or as an oxo-cation; this in turn undergoes an intramolecular oxygen transfer to phosphorus. The resulting $OPPh_3$ ligands are weakly bonded through oxygen, and can be displaced by the entering $[C_5(CO_2Me)_5]^-$ ligand to give complex (4). If an excess of triphenylphosphine is present, co-ordination of this ligand would be preferred over that of the bulky pmcp anion, leading to the catalytic cycle we demonstrate below. This process is similar to that proposed for the oxidation of PPh_3 by $[RuO(py)(bipy)_2]^{2+}$ (py = pyridine, bipy = 2,2′-bipyridyl), also in acetonitrile, which has been shown to involve an intermediate $OPPh_3$ complex.[11]

Crystal Structure of Complex (4).—It was of interest to determine the crystal structure of complex (4) and to compare it with that of ruthenocene. The first (and at the time, only) study of ruthenocene was reported some 23 years ago,[12] so we have also redetermined this solid-state structure. However, the detailed study of Seiler and Dunitz [13] has now appeared; our own results are in substantial agreement with theirs, and details will not be reiterated here.

The unit-cell contents of (4) (Figures 1 and 2, Tables 2—4) comprise discrete molecules of the complex [Ru(η-C_5H_5){η-$C_5(CO_2Me)_5$}] with one molecule comprising the asymmetric unit. As found for ruthenocene, the carbon atoms of the two C_5 rings in complex (4) are eclipsed; the planes of the various CO_2Me groups do not adopt any preferred positions, only two (1,3) being strictly coplanar with the C_5 ring. The dihedral angle between the two rings is 1.5°, which may be compared with the value of 0.0° found for ruthenocene. An appreciable difference in the thermal motion of the two C_5 rings is noted, that for the C_5H_5 substituent being greater than for the C_5 ring in $C_5(CO_2Me)_5$. Bearing this in mind, we note that the range of Ru–C(*n*) distances in C_5H_5 is 2.178(2)—2.186(3) Å [Ru–C(0) 1.817 Å] while that in $C_5(CO_2Me)_5$ is 2.176(2)—2.178(2) Å [for Ru–C(2)–C(5), Ru–C(1) being appreciably shorter at 2.157(2) Å; Ru–C(0) 1.796 Å]. This is reasonable, as librational corrections are likely to be greater for C_5H_5. The range of values reported for Ru–C in Ru(η-C_5H_5)$_2$ from a recent low-temperature study is 2.181—2.188 Å,[13] C–C ring distances lie in the range 1.428—1.438 Å, to be compared with 1.430(2)—1.442(2) Å in the present system. The latter C–C distance is appreciably longer than the mean C–C ring distances in $HC_5(CO_2Me)_5$ (1.41_4 Å),[2] Li[$C_5(CO_2Me)_5$] (1.41_2 Å),[2] K[$C_5(CO_2Me)_5$] (1.41_1

Table 2. Non-hydrogen-atom co-ordinates of complex (4)

	pmcp ligand			cp ligand		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
C(0)	0.257 25(−)	0.155 8(−)	0.359 4(−)	0.164 95(−)	1.104 2(−)	0.025 3(−)
C(1)	0.197 40(10)	0.266 5(2)	0.340 7(2)	0.108 2(1)	0.047 9(3)	0.065 2(3)
C(11)	0.127 36(10)	0.406 4(2)	0.324 5(2)			
O(11)	0.059 57(9)	0.439 7(2)	0.241 4(2)			
O(12)	0.153 87(9)	0.490 8(2)	0.414 6(2)			
C(12)	0.094 1(2)	0.633 4(3)	0.408 7(4)			
C(2)	0.277 79(10)	0.284 1(2)	0.257 2(2)	0.188 1(1)	−0.042 5(3)	0.046 1(3)
C(21)	0.302 66(11)	0.447 4(2)	0.154 2(2)			
O(21)	0.256 96(11)	0.559 1(2)	0.041 6(2)			
O(22)	0.378 76(9)	0.455 0(2)	0.215 5(2)			
C(22)	0.410 9(2)	0.607 3(3)	0.126 3(4)			
C(3)	0.329 76(9)	0.124 5(2)	0.312 4(2)	0.235 8(2)	0.070 2(4)	−0.072 3(3)
C(31)	0.414 9(10)	0.087 8(2)	0.242 9(2)			
O(31)	0.442 75(10)	0.178 7(2)	0.108 4(2)			
O(32)	0.455 26(8)	−0.060 6(2)	0.349 2(2)			
C(32)	0.539 5(1)	−0.111 3(3)	0.297 0(4)			
C(4)	0.281 49(9)	0.007 7(2)	0.433 8(2)	0.185 9(2)	0.230 8(4)	−0.126 2(3)
C(41)	0.317 80(10)	−0.165 6(2)	0.552 2(2)			
O(41)	0.354 85(10)	−0.199 1(2)	0.695 9(2)			
O(42)	0.304 73(9)	−0.273 7(1)	0.481 4(2)			
C(42)	0.339 0(2)	−0.442 2(3)	0.595 3(4)			
C(5)	0.199 82(9)	0.096 2(2)	0.452 6(2)	0.106 8(1)	0.214 6(3)	−0.039 5(3)
C(51)	0.130 49(10)	0.027 7(2)	0.570 8(2)			
O(51)	0.066 64(8)	0.108 9(2)	0.592 8(2)			
O(52)	0.149 89(8)	−0.134 7(1)	0.650 3(2)			
C(52)	0.088 6(1)	−0.216 8(3)	0.774 5(3)			
Ru	0.212 08(1)	0.128 93(1)	0.168 25(2)			

Table 3. Molecular non-hydrogen geometry (entries in square brackets are for the corresponding cp ring); distances in Å, angles in degrees

C(1)–C(2)	1.430(2)	[1.427(3)]	C(5)–C(51)	1.487(2)	C(31)–O(32)	1.331(2)
C(2)–C(3)	1.438(2)	[1.406(4)]	C(11)–O(11)	1.196(2)	C(41)–O(42)	1.335(3)
C(3)–C(4)	1.441(2)	[1.433(4)]	C(21)–O(21)	1.192(2)	C(51)–O(52)	1.332(2)
C(4)–C(5)	1.442(2)	[1.422(4)]	C(31)–O(31)	1.200(2)	O(12)–C(12)	1.449(3)
C(5)–C(1)	1.438(2)	[1.402(3)]	C(41)–O(41)	1.195(2)	O(22)–C(22)	1.448(3)
C(1)–C(11)	1.502(2)		C(51)–O(51)	1.200(2)	O(32)–C(32)	1.447(3)
C(2)–C(21)	1.493(2)		C(11)–O(12)	1.334(3)	O(42)–C(42)	1.449(3)
C(3)–C(31)	1.485(2)		C(21)–O(22)	1.322(2)	O(52)–C(52)	1.452(2)
C(4)–C(41)	1.497(2)					
C(5)–C(1)–C(2)	108.1(1)	[109.0(2)]	C(5)–C(4)–C(41)	125.6(1)	C(5)–C(51)–O(52)	110.7(1)
C(1)–C(2)–C(3)	108.4(1)	[107.4(2)]	C(4)–C(5)–C(51)	127.0(1)	O(11)–C(11)–O(12)	125.3(2)
C(2)–C(3)–C(4)	107.8(1)	[108.2(2)]	C(1)–C(5)–C(51)	125.0(1)	O(21)–C(21)–O(22)	124.8(2)
C(3)–C(4)–C(5)	107.8(1)	[107.6(2)]	C(1)–C(11)–O(11)	125.9(2)	O(31)–C(31)–O(32)	124.8(2)
C(4)–C(5)–C(1)	107.9(1)	[107.8(2)]	C(2)–C(21)–O(21)	124.1(2)	O(41)–C(41)–O(42)	125.0(1)
C(5)–C(1)–C(11)	127.2(1)		C(3)–C(31)–O(31)	124.6(1)	O(51)–C(51)–O(52)	125.0(1)
C(2)–C(1)–C(11)	124.5(1)		C(4)–C(41)–O(41)	121.3(2)	C(11)–O(12)–C(12)	115.8(2)
C(1)–C(2)–C(21)	122.4(1)		C(5)–C(51)–O(51)	124.2(1)	C(21)–O(22)–C(22)	116.5(2)
C(3)–C(2)–C(21)	128.7(1)		C(1)–C(11)–O(12)	108.8(1)	C(31)–O(32)–C(32)	116.1(2)
C(2)–C(3)–C(31)	125.2(1)		C(2)–C(21)–O(22)	110.8(1)	C(41)–O(42)–C(42)	114.3(2)
C(4)–C(3)–C(31)	126.8(1)		C(3)–C(31)–O(32)	110.5(1)	C(51)–O(52)–C(52)	116.3(1)
C(3)–C(4)–C(41)	125.1(1)		C(4)–C(41)–O(42)	113.7(1)		

Also: Ru–C(1,2,3,4,5)(pmcp) 2.157(2), 2.176(2), 2.178(2), 2.178(2), and 2.176(2); Ru–C(1,2,3,4,5)(cp) 2.178(3), 2.186(3), 2.183(3), 2.178(2), and 2.180(2) Å.

Å),[2] $Tl[C_5(CO_2Me)_5]$ (1.40_9 Å),[2] and $Ba[C_5(CO_2Me)_5]_2$ (1.40_8 and 1.40_9 Å).[3]

A number of features may be noted about the geometry of the $C_5(CO_2Me)_5$ ligand in $[Ru(\eta\text{-}C_5H_5)\{\eta\text{-}C_5(CO_2Me)_5\}]$. (*a*) The ranges of values observed for the internal ring distances [1.430(2)—1.442(2) Å (mean 1.43_8 Å)] and angles [107.8(1)—108.4(1)° (mean 108.0°)] are very narrow and indicative of a regular pentagonal geometry relatively unperturbed by substituent dispositions. (*b*) Substituent dispositions vary very widely; in the 'ionic' complexes of the $C_5(CO_2Me)_5$ ligand a tendency has been noted for two substituent planes (not adjacent in the substitution pattern) to lie quasi-normal to the C_5 ring plane with the other three quasi-parallel, perhaps a consequence of a tendency towards chelation of the metal ion. Here two substituents (1,4) are quasi-normal (dihedral angles 72.1 and 89.2°) and two quasi-parallel (3,5) (dihedral angles 17.9 and 5.2°), but the third (2) lies intermediate (47.2°). Examination of the geometries of the CO–OMe substituents shows no systematic variation with dihedral angle; all ranges are very narrow and, provided we can assume that η^5 attachment of the C_5 ring to the ruthenium and lack of librational corrections have little effect on the sub-

Table 4. Least-squares planes calculated through the five atoms of the C_5 rings of the two ligands and given in the form $pX + qY + rZ = s$, where the right-hand orthogonal Å frame is defined with X parallel to a and Z in the ac plane. Atom deviations, δ, and σ (defining atoms) are in Å. The dihedral angle between the two planes is 1.5°; that of the nth carboxylate plane to the pmcp C_5 ring is θ_n

	pmcp	cp		pmcp		pmcp
10^4p	4 200	4 362	δC(11)	0.068	δO(32)	0.222
10^4q	1 273	1 071	δC(21)	0.203	δO(42)	−0.831
10^4r	8 985	8 935	δC(31)	−0.109	δO(52)	0.006
s	5.015	1.429	δC(41)	0.272	δC(12)	1.519
σ	0.007	0.001	δC(51)	0.072	δC(22)	1.473
δC(1)	−0.009	−0.001	δO(11)	−0.820	δC(32)	0.168
δC(2)	0.008	0.001	δO(21)	−0.381	δC(42)	−0.581
δC(3)	−0.003	−0.001	δO(31)	−0.461	δC(52)	0.104
δC(4)	−0.003	0.000	δO(41)	1.389	θ_1	72.1
δC(5)	0.007	0.001	δO(51)	0.189	θ_2	47.2
			δO(12)	1.287	θ_3	17.9
			δO(22)	1.183	θ_4	89.2
					θ_5	5.2

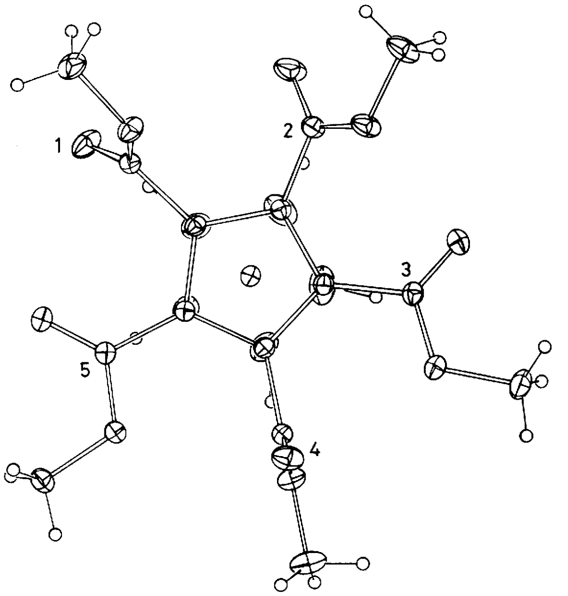

Figure 2. Molecular projection of [Ru(η-C_5H_5){η-$C_5(CO_2Me)_5$}] normal to the plane of the C_5 ring

stituent geometries (assumptions that may not be entirely valid), then we may take the mean geometries as being reasonably archetypal for this ligand, irrespective of dihedral angle, *viz.*:

	Range (Å)	Mean (Å)
C(n)–C(n1)	1.485(2)—1.502(2)	1.49_3
C(n1)–O(n1)	1.192(2)—1.200(2)	1.19_1
C(n1)–O(n2)	1.322(2)—1.335(3)	1.33_1
O(n2)–C(n2)	1.447(3)—1.452(2)	1.44_9

	Range (°)	Mean (°)
C(n)–C(n1)–O(n1)	121.3(2)—125.9(2)	$124._0$
C(n)–C(n1)–O(n2)	108.8(1)—113.7(1)	$110._9$
O(n1)–C(n1)–O(n2)	124.8(2)—125.3(2)	$125._0$
C(n1)–O(n2)–C(n2)	114.3(2)—116.5(2)	$115._8$

The angles are less similar than the distances, and this is particularly true of C(n ± 1)–C(n)–C(n1) which vary between 122.4(1) and 128.7(1)°, suggesting that lattice forces can easily ' bend ' the ligand substituent about its point of attachment to the ring, irrespective of dihedral angle. The greatest distortions are observed for substituents 1 and 2 and the largest angle at the point of attachment is found alternatively ' *cis* ' and ' *trans* ' (to the carbonyl) in these two cases, suggesting that carbonyl disposition also does not greatly influence distortion at the point of attachment. Further, we find some remarkably large disturbances in regard to C(n1) deviations from the ring plane, ranging from 0.06_8 to 0.27_2 Å, and again there is no correlation with substituent dihedral angle.

Reactions of [Ru(η-C_5H_5){η-$C_5(CO_2Me)_5$}].—As expected for a metallocene bearing electron-withdrawing substituents, (4) is stable towards oxidation in air or oxygen, and also by molecular iodine; ruthenocene itself readily affords the ruthenium(IV) derivative [RuI(η-C_5H_5)$_2$]$^+$ with the latter reagent.[14] The most interesting reaction that we have found is the ready displacement of the pmcp ligand by other donor ligands to give pmcp salts of [RuL$_3$(η-C_5H_5)]$^+$ cations. Thus, complex (4) reacts with PPh_3 in acetonitrile to give (3); the similar compounds (6) and (7) were obtained with PPh_3 in benzonitrile and with dppe in acetonitrile, respectively. While fairly harsh reaction conditions are necessary, no added reagent (Lewis acid) is required, the displaced pmcp ligand being stable enough to act as the counter ion. Although the displacement of one C_5H_5 ring from ferrocene by CO [15] or arenes [16] in the presence of $AlCl_3$, or from ruthenocenes by arenes, also with $AlCl_3$ present,[17] has been documented, to our knowledge this is the first occasion on which simple displacement of a C_5 ring, albeit substituted, from a ruthenocene by two-electron donor ligands has been observed.

That the pmcp ring is displaced should occasion no surprise. Although the Ru–C distances to both rings are similar, we suggest that this is probably a steric phenomenon, and that the presence of the electron-withdrawing CO_2Me groups results in the Ru–pmcp bond being considerably weaker than the Ru–C_5H_5 bond. We recall that ruthenocene is probably the most stable metallocene.[18] The greater stability of the Ru–C_5H_5 bond is also shown by the presence of the intense ion [Ru(C_5H_5)]$^+$ (m/e 167) in the mass spectrum of complex (4); the ion [Ru{$C_5(CO_2Me)_5$}]$^+$ is not found.

The ready displacement of the pmcp ring by PPh_3 in acetonitrile to form [Ru(NCMe)(PPh_3)$_2$(η-C_5H_5)]$^+$, and the observation that, in the presence of air, metallocene (4) is readily formed from the chloro-complex and [$C_5(CO_2Me)_5$]$^-$, suggested that this system might act as a catalyst for the oxidation of PPh_3 to its oxide. Accordingly, we passed oxygen into an ethanol solution of PPh_3 containing 0.01 mol equivalent of the metallocene. After 6 h at 78 °C essentially quantitative conversion into $OPPh_3$ was found. A control experiment showed that, in the absence of the ruthenium complex, no oxidation of PPh_3 occurred under the same conditions. In considering possible mechanisms for this reaction we irradiated an acetonitrile solution of the metallocene; after 16 h, the solution was a deep yellow colour, but normal work-up procedures only recovered complex (4). In this regard we note the recent report of the isolation of yellow $[Ru(NCMe)_3(\eta\text{-}C_5H_5)]PF_6$ by irradiation of a solution of $[Ru(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)]^+$ in acetonitrile;[19] in our experiment, the related $[Ru(NCMe)_3(\eta\text{-}C_5H_5)][pmcp]$ salt is probably unstable with respect to formation of the metallocene (4) by loss of acetonitrile.

Addition of $HC_5(CO_2Me)_5$ *to* $[RuH(PPh_3)_2(\eta\text{-}C_5H_5)]$.—In an attempt to obtain complex (4) by displacement of the hydride ligand from $[RuH(PPh_3)_2(\eta\text{-}C_5H_5)]$ by the strongly acidic diene (1), we noticed that a suspension of the yellow hydride in methanol was rapidly converted into a white precipitate. Isolation and characterisation of this substance showed that it was an adduct, best formulated as the salt $[RuH_2(PPh_3)_2(\eta\text{-}C_5H_5)][C_5(CO_2Me)_5]$ (5). Unfortunately, the compound is insoluble in most solvents, except chlorinated hydrocarbons, with which it reacts rapidly to afford $[RuCl(PPh_3)_2(\eta\text{-}C_5H_5)]$. Identification of this compound is based largely on elemental microanalyses, the presence of ν(RuH) and ν(CO) bands in the i.r. spectrum, and comparison with the osmium complex, which will be described elsewhere. We have previously described the addition of HPF_6 to $[MX(PR_3)_2(\eta\text{-}C_5H_5)]$ (M = Ru, X = Cl; M = Os, X = Br; R = Me or Ph) to give the hydridometal(IV) salts $[MXH(PR_3)_2(\eta\text{-}C_5H_5)][PF_6]$.[20] The present reaction provides yet another example of the use of the strongly acidic nature of diene (1), and the bulk of the pmcp anion, to isolate stable salts of protonated organometallics.

Acknowledgements

We gratefully acknowledge receipt of a grant from the Australian Research Grants Committee in support of this work.

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Received 30*th December* 1982; *Paper* 2/2188