Pentakis(methoxycarbonyl)cyclopentadiene Chemistry: Unexpected Replacement of CO_2Me Groups by H: Formation and the *X*-Ray Crystal Structure of a Novel Rhodicinium Salt $[Rh\{\eta^5\text{-}C_5H_2(CO_2Me)_3\}_2][C_5(CO_2Me)_5]$

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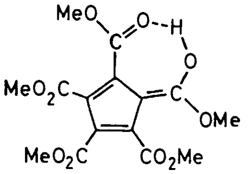
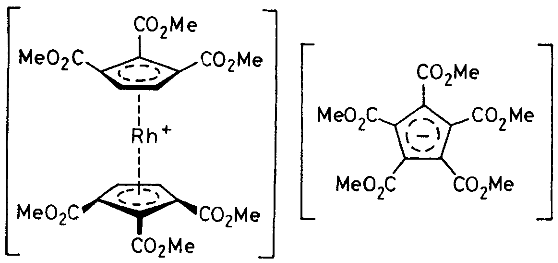
Summary Tetra-acetatodirhodium reacts with $HC_5(CO_2Me)_5$ to give $[Rh\{\eta^5\text{-}C_5H_2(CO_2Me)_3\}_2][C_5(CO_2Me)_5]$ by unusual replacement of two CO_2Me groups on each η^5-ligand by H, as revealed by an *X*-ray structural determination.

WE have recently described the preparation of a series of transition metal derivatives of the strong organic acid, pentakis(methoxycarbonyl)cyclopentadiene, $[HC_5(CO_2Me)_5]$ (**1**), including the mixed ligand complex $[Ru(\eta\text{-}C_5H_5)\{\eta\text{-}C_5(CO_2Me)_5\}]$, in which both C_5 rings are η^5-bonded to the metal.[1,2] Extension of these reactions to rhodium has resulted in the discovery of the unusual cationic rhodocene derivative described below.

The major product isolated from reactions between (**1**) and $Rh_2(OAc)_4$, carried out in refluxing methanol, forms red needles (**2**), m.p. 245 °C, which are soluble in the more polar solvents as a 1 : 1 electrolyte. Neither analytical nor spectroscopic data† enabled (**2**) to be identified conclusively, and a single-crystal *X*-ray diffraction study was undertaken.



(1)



(2)

Crystal data: $C_{22}H_{22}O_{12}Rh^+.C_{15}H_{15}O_{10}^-$, *M* 936·60, triclinic, space group $P\bar{1}$, $a = 10{\cdot}284(5)$, $b = 11{\cdot}615(2)$, $c = 17{\cdot}012(8)$ Å, $\alpha = 86{\cdot}84(2)$, $\beta = 85{\cdot}05(4)$, $\gamma = 87{\cdot}40(2)°$, $U = 2021{\cdot}8$ Å^3; $Z = 2$, $D_c = 1{\cdot}538$ g cm^{-3}; $F(000) = 960e$; $\mu(\text{Mo-}K_\alpha) = 4{\cdot}64$ cm^{-1}.

The rhodium atom was located by Patterson techniques using the SHELX system of programmes. Successive

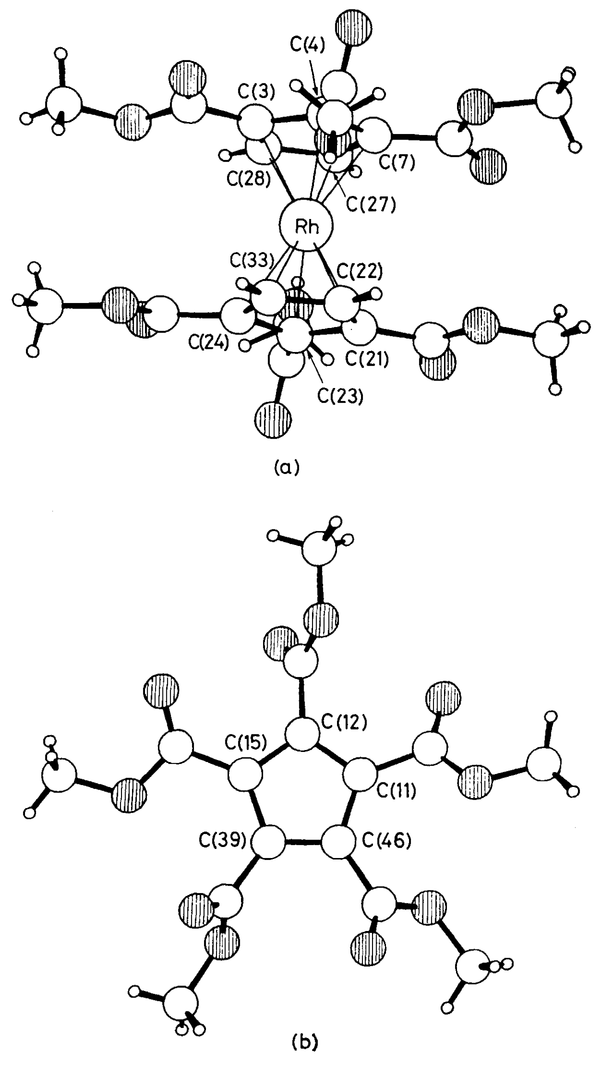


FIGURE. Molecular structure of $[Rh\{\eta^5\text{-}C_5H_2(CO_2Me)_3\}_2][C_5(CO_2Me)_5]$. (a) Cation. Selected bond distances: Rh–C(3) 2·153(16), Rh–C(4) 2·161(16), Rh–C(7) 2·170(17), Rh–C(21) 2·156(8), Rh–C(22) 2·182(7), Rh–C(23) 2·171(7), Rh-C(24) 2·175(7), Rh–C(27) 2·179(15), Rh–C(28) 2·185(15), Rh–C(33) 2·169(6); C(3)–C(4) 1·43(2), C(4)–C(7) 1·43(2), C(7)–C(27) 1·43(2), C(27)–C(28) 1·41(3), C(28)–C(3) 1·42(2), C(21)–C(22) 1·46(1), C(21)–C(23) 1·42(1), C(23)–C(24) 1·43(1), C(24)–C(33) 1·43(1), C(33)–C(22) 1·39(1) Å. (b) Anion. Selected bond distances: C(11)–C(12) 1·40(1), C(12)–C(15) 1·40(1), C(15)–C(39) 1·43(1), C(39)–C(46) 1·39(1), C(46)–C(11) 1·42(1) Å.

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† I.r. (Nujol): ν(CO) at 1745s, 1710s, and 1670s cm^{-1}; u.v. (Nujol): λ_{max} 410 nm; ^{1}H n.m.r.: δ($CDCl_3$) 3·89 [s, $C_5(CO_2\mathit{Me})_5$] and 3·73 [s, $C_5(CO_2\mathit{Me})_2$], 6·30 [d, C*H*, *J*(HRh) 1 Hz]; ^{13}C n.m.r.: δ ($CDCl_3$) 51·38 (s, $CO_2\mathit{Me}$), 117·45 (s, ring C), 167·80 {s, $\mathit{C}O_2Me$ [for $C_5(CO_2Me)_5$ anion]}, 54·05 [s, 1,3-$(CO_2\mathit{Me})_2$], 54·60 (s, 2-$CO_2\mathit{Me}$), 91·52 (d) and 94·44 [d, *C*H and 1,3-*C*(CO_2Me), not distinguished, *J*(CRh) 7 Hz (both)], 104·8 [d, 2-*C*(CO_2Me), *J*(CRh) 7 Hz], 159·78 [d, 1,3-$(CO_2Me)_2$, *J*(CRh) 5 Hz], and 176·55 (s, 2-$\mathit{C}O_2Me$) p.p.m.

difference Fourier syntheses revealed the remaining non-hydrogen atoms. All hydrogen atom co-ordinates were calculated geometrically with C–H distances fixed at 0·965 Å. The structure was refined by block-matrix least-squares to $R = 4{\cdot}99\%$ for 5301 independent reflexions [$I \geqslant 2{\cdot}5\sigma(I)$; $1{\cdot}5° \leqslant \theta \leqslant 26{\cdot}0°$, Enraf-Nonius CAD 4F diffractometer].‡

The molecular structure of (**2**) is shown in the Figure, which also includes some relevant bond parameters. The complex is the $[C_5(CO_2Me)_5]^-$ salt of the $[Rh\{\eta^5\text{-}C_5H_2(CO_2Me)_3\}_2]^+$ cation. In the latter, both C_5 rings are η^5-bonded, and are fully staggered to allow the bulky CO_2Me groups to intermesh satisfactorily. The Rh–C (ring) distances range from 2·153(16)—2·185(15) Å, there being no significant difference between Rh–CH and Rh–C(CO_2Me) distances. The two rings are almost parallel (dihedral 2·1°), and separated by 3·60 Å.

The counter-ion is the pentagonal $[C_5(CO_2Me)_5]^-$ anion [mean C–C (ring) 1·405 Å]; in contrast with the anion found in the lithium salt of (**1**), which has a fulvenoid structure,[2] the symmetry of the anion found in (**2**) suggests that the negative charge is delocalised over all ring carbons. In the crystal, the anions and cations alternate in stacks, with the anion ring planes being inclined at *ca.* 22° to the C_5 ring planes of the cation. The separation of the centres of these two rings is 3·45 Å.

This is the first example of a rhodicinium salt to have been crystallographically characterised. Model studies show that η^5-attachment of two C_5 rings to a metal atom or ion is severely hindered if the ring contains four or five CO_2Me substituents, and this may provide a driving force for the elimination of two of these groups from each ring. The precise mechanism of the elimination is presently unknown, but may proceed *via* nucleophilic attack at the ester group. The cation is readily isolated as a salt with the large $[C_5(CO_2Me)_5]^-$ anion; this anion is a useful new aid for the isolation of cationic complexes, recent examples being $[H_2Ru(PPh_3)_2(\eta\text{-}C_5H_5)]^+$[3] and $[Os(NCMe)(PPh_3)_2(\eta\text{-}C_5H_5)]^+$.[1]

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

[1] M. I. Bruce, B. W. Skelton, R. C. Wallis, J. K. Walton, A. H. White, and M. L. Williams, *J. Chem. Soc., Chem. Commun.*, 1981, 428.

[2] M. I. Bruce, J. K. Walton, M. L. Williams, B. W. Skelton, and A. H. White, *J. Organomet. Chem.*, 1981, **212**, C35.

[3] M. I. Bruce and M. L. Williams, unpublished work.