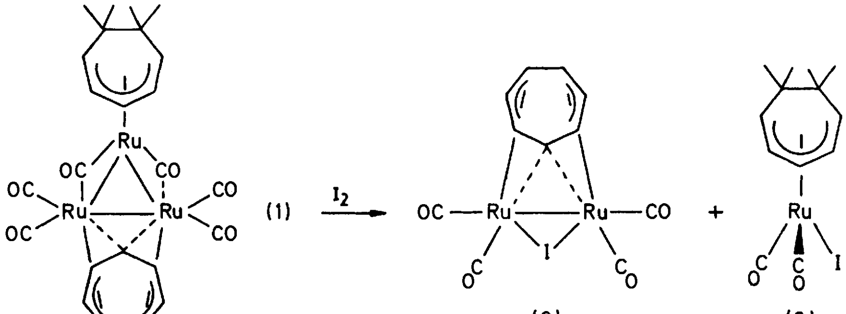
# Crystal and Molecular Structure of μ-Iodo-μ-3-phenylcycloheptatrienyl-bis(dicarbonylruthenium) (*Ru–Ru*): A Metal Complex with a Bridging Cycloheptatrienyl Ligand

By **Judith A. K. Howard** and **Peter Woodward**, Department of Inorganic Chemistry, The University, Bristol BS8 1TS

Crystals of the title compound are monoclinic, space group $P2_1/c$, with $Z = 4$ in a unit cell of dimensions: $a$ = 8.482(2), $b$ = 13.525(4), $c$ = 15.851(3) Å, β = 94.86(4)°. The structure was determined by heavy-atom methods from diffractometer data and refined to $R$ 0.031 for 2 200 independent reflections. The two ruthenium atoms are bridged by the iodine atom [Ru–Ru = 2.866(1) Å, Ru–I = 2.685(1) and 2.711(1) Å]; each Ru atom carries two terminal carbonyl groups orthogonal to one another and to the corresponding Ru–I bond, and eclipsed with respect to the Ru–Ru vector. The $C_7$ ring is symmetrically related to the plane which bisects the Ru–Ru bond perpendicularly. One carbon atom thus bridges the Ru–Ru bond, while the remaining six comprise two $\eta^3$-allyl moieties each bonded to the nearer Ru atom. The phenyl substituent is attached to the C atom adjoining the central bridging C atom. The $C_7$ ring presents a concave face to the Ru–Ru bond. Its mode of attachment is therefore in every respect different from that found in $[Ru_2(CO)_5(SiMe_3)(C_7H_8SiMe_3)]$.

Cycloheptatriene reacts with dodecacarbonyltriruthenium to give *inter alia* a fluxional complex $[Ru_3(CO)_6(C_7H_7)(C_7H_9)]$ (1) which has been characterised crystallographically.[1] Complex (1), when warmed with iodine in hexane, is cleaved smoothly to form complexes (2) and (3).[2] In order to compare the mode of bonding of the bridging cycloheptatrienyl ligand with that found in (1)[1] and with that found by us in an earlier structural study of $[Ru_2(CO)_5(SiMe_3)(C_7H_6SiMe_3)]$,[3,4] a crystallographic study of a derivative of complex (2) has been undertaken.



(2) (3)

## EXPERIMENTAL

Crystals of $[Ru_2I(CO)_4(C_7H_6Ph)]$ are prepared according to the above reaction with $C_7H_7Ph$ as starting material; they grow as small orange–red prisms. Diffracted intensities were collected from a crystal of dimensions 0.30 × 0.10 × 0.12 mm on a Syntex $P2_1$ four-circle diffractometer according to methods described earlier.[5] Of the total 3 084 reflections (complete for $2.9 < 2\theta < 50.0°$), 2 200 were deemed ' observed ' according to the criterion $I > 2.5\sigma(I)$.

## RESULTS

*Crystal Data.*—$C_{17}H_{11}IO_4Ru_2$, $M = 608.4$, monoclinic, $a = 8.482(2)$, $b = 13.525(4)$, $c = 15.851(3)$Å, $\beta = 94.86(4)°$, $D_m = 2.22$ g cm$^{-3}$, $Z = 4$, $D_c = 2.24$ g cm$^{-3}$, $F(000) = 1\,144$. Space group $P2_1/c$. Mo-$K_\alpha$ $X$-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å; $\mu(\text{Mo-}K_\alpha) = 33.2$ cm$^{-1}$.

The structure was solved by conventional heavy-atom methods and in the final refinement anisotropic thermal parameters were used for all non-hydrogen atoms. Weights were applied according to the scheme $1/w = \sigma^2(F)$, where $\sigma(F)$ is the estimated standard deviation based on counting statistics. Hydrogen atoms were incorporated at positions estimated from electron-density maps, but neither their positional nor thermal ($10^2U = 6.33$) parameters were refined. The blocked-matrix least-squares refinement (block 1: 2Ru, I, 4CO; block 2: all other atoms) converged to $R$ 0.031 ($R'$ 0.031), and a final electron-density difference synthesis showed no peaks $>0.2$ or $<-0.3$ eÅ$^{-3}$. Positional and thermal parameters are in Table 1, interatomic distances and bond angles in Table 2, and some equations of least-squares planes with the interplanar angles, in Table 3. Atomic scattering factors were those of ref. 6 for Ru, I, C, and O, and of ref. 7 for hydrogen. Corrections for anomalous dispersion were applied for Ru($\Delta f'$ −1.2, $\Delta f''$ 1.0) and for I ($\Delta f'$ −0.6, $\Delta f''$ 2.3).[8] The intensities were corrected for the effects of $X$-ray absorption,[9] and all computational work was carried out at the University of London Computing Centre with the ' $X$-Ray System ' of programs.[9] Observed and calculated structure factors

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[8] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

[9] Technical Report TR 192, Computer Science Centre, University of Maryland, U.S.A., June 1972.

TABLE 1

Atomic positional (fractional co-ordinates) and thermal parameters † with standard deviations in parentheses

| Atom | $x$ | $y$ | $z$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Ru(1) | 0.273 74(7) | 0.341 93(4) | 0.361 32(3) | 5.74(6) | 3.35(6) | 4.30(6) | −0.05(3) | −0.23(3) | −0.21(3) |
| Ru(2) | 0.266 27(6) | 0.161 41(4) | 0.266 32(3) | 5.17(6) | 3.61(6) | 3.93(6) | −0.33(3) | 0.44(2) | −0.14(3) |
| I | 0.234 61(6) | 0.341 37(4) | 0.191 46(3) | 8.73(6) | 4.62(6) | 4.39(6) | −0.88(3) | −0.15(3) | 0.95(2) |
| *Carbonyl groups* | | | | | | | | | |
| C(11) | 0.055 9(11) | 0.355 8(6) | 0.376 4(5) | 7.9(6) | 4.8(5) | 9.2(6) | 1.7(5) | 2.8(5) | 0.6(4) |
| O(11) | $\bar{1}$.927 5(9) | 0.362 0(6) | 0.385 7(5) | 8.6(5) | 11.9(6) | 19.7(8) | 3.5(5) | 6.2(5) | 3.3(6) |
| C(12) | 0.304 8(10) | 0.475 1(6) | 0.385 3(4) | 9.0(6) | 3.9(5) | 5.8(5) | −0.1(5) | −1.3(4) | −0.2(4) |
| O(12) | 0.320 3(8) | 0.557 3(4) | 0.399 1(4) | 14.4(6) | 4.2(4) | 10.7(5) | 0.1(4) | −3.4(4) | −0.9(3) |
| C(21) | 0.045 4(10) | 0.128 8(5) | 0.261 3(4) | 6.0(5) | 4.1(4) | 5.4(5) | −0.6(4) | −1.1(4) | 0.6(3) |
| O(21) | $\bar{1}$.917 9(7) | 0.106 5(5) | 0.262 7(4) | 4.7(4) | 9.9(5) | 13.0(6) | −1.9(4) | −0.9(4) | 0.3(4) |
| C(22) | 0.291 8(10) | 0.082 6(5) | 0.169 6(5) | 9.3(6) | 4.6(5) | 5.0(5) | −0.6(5) | 0.6(4) | −0.1(4) |
| O(22) | 0.306 2(9) | 0.037 5(4) | 0.110 7(4) | 17.0(7) | 7.0(4) | 6.6(4) | −1.3(4) | 3.0(4) | −2.4(3) |
| *Cycloheptatrienyl ring and phenyl group* | | | | | | | | | |
| C(1) | 0.354 0(11) | 0.252 5(5) | 0.468 6(4) | 9.3(7) | 4.1(5) | 4.8(5) | 0.2(4) | 0.2(4) | 0.3(3) |
| C(2) | 0.271 7(8) | 0.173 1(5) | 0.421 4(4) | 5.0(4) | 4.1(4) | 4.2(4) | 0.7(3) | 0.7(3) | 0.1(3) |
| C(3) | 0.342 8(8) | 0.086 8(5) | 0.384 4(4) | 4.6(4) | 4.0(4) | 3.6(4) | −0.0(3) | −0.1(3) | 0.2(3) |
| C(4) | 0.475 3(8) | 0.098 7(5) | 0.337 3(4) | 4.8(5) | 4.3(5) | 7.0(5) | 0.8(4) | 0.2(4) | 0.1(4) |
| C(5) | 0.523 8(8) | 0.193 8(5) | 0.309 7(5) | 4.5(5) | 5.4(5) | 7.7(5) | 0.2(4) | 1.3(4) | 0.8(4) |
| C(6) | 0.528 4(9) | 0.287 2(6) | 0.360 5(6) | 4.8(5) | 5.9(6) | 10.3(7) | −0.9(4) | −1.9(5) | 0.7(5) |
| C(7) | 0.486 0(11) | 0.298 7(6) | 0.440 8(5) | 9.0(7) | 5.2(5) | 6.9(5) | 0.6(5) | −3.1(5) | −0.7(4) |
| H(1) | 0.312 | 0.263 | 0.501 | 6.3 * | | | | | |
| H(2) | 0.159 | 0.157 | 0.438 | 6.3 | | | | | |
| H(4) | 0.518 | 0.046 | 0.313 | 6.3 | | | | | |
| H(5) | 0.581 | 0.202 | 0.262 | 6.3 | | | | | |
| H(6) | 0.567 | 0.301 | 0.336 | 6.3 | | | | | |
| H(7) | 0.498 | 0.341 | 0.477 | 6.3 | | | | | |
| C(31) | 0.288 9(8) | $\bar{1}$.987 7(5) | 0.407 1(4) | 4.7(4) | 3.5(4) | 4.4(4) | 0.8(3) | −0.1(3) | −0.1(3) |
| C(32) | 0.240 1(9) | $\bar{1}$.968 2(6) | 0.485 9(4) | 8.4(6) | 4.4(5) | 4.7(5) | 0.1(4) | 0.4(4) | −0.2(4) |
| C(33) | 0.191 0(10) | $\bar{1}$.876 0(6) | 0.508 2(5) | 8.4(6) | 5.5(5) | 5.7(5) | 0.6(5) | 1.4(4) | 1.4(4) |
| C(34) | 0.189 4(9) | $\bar{1}$.799 9(6) | 0.454 0(5) | 5.7(5) | 4.6(5) | 7.7(6) | 0.1(4) | 0.6(4) | 2.0(4) |
| C(35) | 0.240 7(11) | $\bar{1}$.815 3(5) | 0.375 8(5) | 10.7(7) | 4.2(5) | 7.7(6) | −0.0(5) | 1.6(5) | −1.3(4) |
| C(36) | 0.287 3(10) | $\bar{1}$.907 5(5) | 0.353 2(5) | 9.6(7) | 3.6(5) | 6.6(5) | 0.2(4) | 2.8(5) | −0.4(4) |
| H(32) | 0.248 | 0.018 | 0.521 | 6.3 * | | | | | |
| H(33) | 0.147 | $\bar{1}$.871 | 0.556 | 6.3 | | | | | |
| H(34) | 0.140 | $\bar{1}$.743 | 0.469 | 6.3 | | | | | |
| H(35) | 0.244 | $\bar{1}$.763 | 0.334 | 6.3 | | | | | |
| H(36) | 0.321 | $\bar{1}$.914 | 0.309 | 6.3 | | | | | |

* $B = 8\pi^2U$. † Anisotropic thermal parameters ($\times 10^2$) in the form: $\exp\{-2\pi^2[U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl]\}$.

TABLE 2

Bond lengths (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) Distances

| | | | |
|---|---|---|---|
| Ru(1)–Ru(2) | 2.866(1) | Ru(1)–C(7) | 2.188(8) |
| Ru(1)–I | 2.685(1) | Ru(2)–C(3) | 2.177(6) |
| Ru(2)–I | 2.711(1) | Ru(2)–C(4) | 2.189(7) |
| Ru(1)–C(11) | 1.893(9) | Ru(2)–C(5) | 2.277(7) |
| C(11)–O(11) | 1.114(12) | C(1)–C(2) | 1.453(10) |
| Ru(1)–C(12) | 1.854(8) | C(2)–C(3) | 1.459(9) |
| C(12)–O(12) | 1.139(10) | C(3)–C(4) | 1.411(10) |
| Ru(2)–C(21) | 1.919(8) | C(4)–C(5) | 1.430(10) |
| C(21)–O(21) | 1.125(10) | C(5)–C(6) | 1.496(11) |
| Ru(2)–C(22) | 1.894(8) | C(6)–C(7) | 1.362(12) |
| C(22)–O(22) | 1.131(10) | C(7)–C(1) | 1.386(12) |
| Ru(1)–C(2) | 2.474(6) | C(3)–C(31) | 1.471(9) |
| Ru(2)–C(2) | 2.460(6) | | |
| Ru(1)–C(1) | 2.149(7) | Mean C–C(phenyl) | 1.37(2) |
| Ru(1)–C(6) | 2.284(8) | | |

(*b*) Angles

| | | | |
|---|---|---|---|
| Ru(1)–Ru(2)–I | 57.46(2) | C(2)–Ru(1)–C(12) | 145.3(3) |
| Ru(2)–Ru(1)–I | 58.36(2) | C(2)–Ru(1)–I | 112.3(1) |
| Ru(1)–I–Ru(2) | 64.18(2) | C(2)–Ru(2)–C(21) | 89.5(3) |
| Ru(2)–Ru(1)–C(11) | 99.9(2) | C(2)–Ru(2)–C(22) | 148.3(3) |
| I–Ru(1)–C(11) | 95.0(2) | C(2)–Ru(2)–I | 111.8(2) |
| C(11)–Ru(1)–C(12) | 90.1(3) | C(1)–C(2)–C(3) | 126.9(6) |
| Ru(2)–Ru(1)–C(12) | 158.6(2) | C(2)–C(3)–C(4) | 119.8(6) |
| I–Ru(1)–C(12) | 102.2(2) | C(3)–C(4)–C(5) | 121.8(6) |
| Ru(1)–Ru(2)–C(21) | 101.2(2) | C(4)–C(5)–C(6) | 126.1(7) |
| I–Ru(2)–C(21) | 97.3(2) | C(5)–C(6)–C(7) | 127.1(8) |
| C(21)–Ru(2)–C(22) | 90.9(3) | C(6)–C(7)–C(1) | 122.0(7) |
| Ru(1)–Ru(2)–C(22) | 154.9(2) | C(7)–C(1)–C(2) | 122.4(7) |
| I–Ru(2)–C(22) | 99.5(2) | | |
| Ru(1)–C(2)–Ru(2) | 71.0(2) | Mean C–C–C(phenyl) | 120.0(17) |
| C(2)–Ru(1)–C(11) | 90.2(3) | | |

TABLE 3

Least-squares planes and torsion angles

(*a*) Equations of some least-squares planes

Plane (1) Ru(1), Ru(2), I

$$8.4650x + 0.6772y - 1.9525z = 1.8433$$

Plane (2) C(1), C(2), C(3)

$$-1.2104x - 6.8402y + 13.6292z = 4.2307$$

Plane (3) C(4), C(5), C(6), C(7)

$$7.7391x - 2.7562y + 4.3785z = 4.8756$$

Plane (4) C(31), C(32), C(33), C(34), C(35), C(36) (phenyl group)

$$7.7341x - 3.0253y + 4.2127z = 3.9927$$

(*b*) Angles (°) between least-squares planes

(1)–(2) 78.4 (1)–(3) 27.5 (1)–(4) 27.7

(*c*) Torsion angles (°) around the $C_7$ ring

| | | | |
|---|---|---|---|
| C(1)–(2)–(3)–(4) | −46 | C(5)–(6)–(7)–(1) | −41 |
| C(2)–(3)–(4)–(5) | −13 | C(6)–(7)–(1)–(2) | +13 |
| C(3)–(4)–(5)–(6) | +41 | C(7)–(1)–(2)–(3) | −46 |
| C(4)–(5)–(6)–(7) | 0 | | |

are listed in Supplementary Publication No. SUP 21865 (9 pp., 1 microfiche).*

## DISCUSSION

The molecular structure of complex (2), and the atom numbering system, are given in the Figure. Apart from the phenyl substituent on the bridging cycloheptatrienyl ligand, the molecule possesses an approximate plane of

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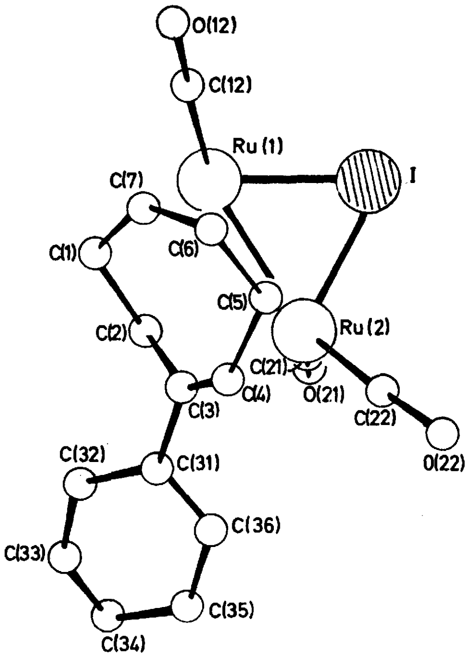
* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Dalton*, 1976, Index issue. (Items less than 10 pp. are supplied as full-size copies.)

mirror symmetry [the perpendicular bisector of the Ru(1)–Ru(2) bond]. Hence the two carbonyl groups on one ruthenium atom, which are in an approximately orthogonal orientation to one another, are eclipsed with respect to the two carbonyl groups on the other ruthenium atom, while the bridging iodine atom completes one facial set of co-ordination sites around the ruthenium atoms, if these are considered to be octahedral in their valence orientations. Because of the approximate mirror symmetry in the molecule, the two metal atoms make equal electronic demands on the $C_7$ ring. It is entirely in accord with this picture, therefore, that one carbon atom, C(2), is almost equidistant from the two metal atoms [Ru(1)–C(2) = 2.474(6); Ru(2)–C(2) = 2.460(6) Å], while the two sets of three carbon atoms adjacent to C(2), namely C(3), C(4), C(5) and C(1), C(7), C(6), each form an $\eta^3$-allyl attachment to the nearer ruthenium atom. The phenyl group is attached to the terminal atom of one of these allyl moieties, C(3).



The molecular structure of $[Ru_2I(CO)_4(C_7H_6Ph)]$. The carbonyl group C(11)–O(11) is obscured by the ruthenium atom Ru(1)

The bonding situation is thus notably different from that found in an earlier study of $[Ru_2(CO)_5(SiMe_3)(C_7H_6SiMe_3)]$,[4] where the asymmetry of the OC–Ru–Ru–$SiMe_3$ spine of the molecule imposes a corresponding asymmetry on the ring-to-metal bonding; the Ru atom carrying the axial carbonyl group requires three electrons, and so forms an $\eta^3$-allyl attachment to three carbon atoms of the ring, while the Ru atom carrying the axial trimethylsilyl group requires four electrons, and so forms an $\eta^4$-diene attachment to the remaining four carbon atoms. Whereas, therefore, such an arrangement implies approximate mirror symmetry through a plane containing the axis of the molecule, in the title compound the symmetry is of necessity through a plane which is the perpendicular bisector of the Ru–Ru bond. Moreover, and again in contrast, in $[Ru_2(CO)_5(SiMe_3)(C_7H_6SiMe_3)]$ the $C_7$ ring presents a convex face to the Ru–Ru bond, while in $[Ru_2I(CO)_4(C_7H_6Ph)]$ the ring is concave towards the Ru–Ru bond. In particular, the lines joining C(5) to C(6), C(4) to C(7), and C(1) to C(3), are all parallel to the line joining Ru(1) to Ru(2). The angles between the plane of the $Ru_2I$ moiety and the various planar sections of the $C_7$ ring are given in Table 3, together with the torsion angles around the ring. These again illustrate the mirror symmetry (disregarding the phenyl group). There is, however, a slight but significant departure from exact mirror symmetry in the $Ru_2I$ nucleus of the molecule, in that Ru(1)–I [2.685(1) Å] is shorter than Ru(2)–I [2.711(1) Å].

The n.m.r. spectrum of complex (2) is interesting and has been reported and discussed in detail.[2] In solution the molecule appears to possess mirror symmetry at 35 °C, interpreted as arising from a degenerate oscillatory fluxional process which does not become ' frozen out ' until the temperature is lowered to *ca.* −100 °C.

Among the carbonyl ligands, the mean Ru–CO distance is $1.89_0$ and the mean C–O is 1.12 Å, neither of which calls for special comment.

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