Trimeric π-Cyclopentadienylcarbonylrhodium

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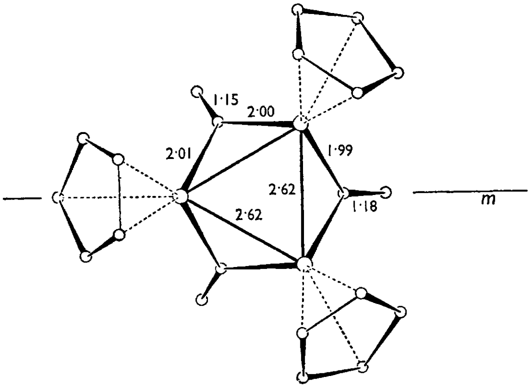
THE preparation of monomeric π-cyclopentadienyldicarbonylrhodium (I) and its dimerisation have been reported.[1,2] Exposure of solutions of (I) in light petroleum to ultraviolet light, however, results in the formation of a binuclear species of composition $(C_5H_5)_2Rh_2(CO)_3$ (II), which contains a single bridging CO group.[3] Prolonged irradiation of hexane solutions of (I) yields a trinuclear species (III) of composition $(C_5H_5RhCO)_3$.[4]

Crystals of (III) were kindly supplied by Professor E. O. Fischer. The black crystals belong to the monoclinic system with unit cell parameters $a = 7{\cdot}06$, $b = 12{\cdot}92$, $c = 9{\cdot}47$ Å, $\beta = 94{\cdot}75°$, $U = 861$ Å^3, $M = 588{\cdot}0$ and with $Z = 2$ molecules per cell $(C_{18}H_{15}Rh_3O_3)$. Systematic absences could arise from either of the space groups $P2_1$ or $P2_1/m$. In the latter case, the molecule would be required to have a mirror plane of symmetry. A study of the three-dimensional Patterson synthesis, together with three-dimensional electron density syntheses, showed no deviation from m symmetry and the final refinements were carried out with the space group $P2_1/m$. The atomic positions were first refined with a programme written by us for the Atlas computer based on the minimisation of R.[5] After two cycles the R-value was 11·0% (699 reflexions) which reduced to 7·97% after conventional full-matrix least-squares refinement.

The figure shows that the trimer consists, within experimental error, of an equilateral triangle of rhodium atoms in which each pair of atoms is symmetrically bridged by a carbonyl group. All the carbonyl groups are displaced to one side of this rhodium triangle; on the other side, attached one to each rhodium, are the cyclopentadienyl rings. The average Rh–C distances are 2·24 Å (Rh–ring) and 2·00 Å (Rh–carbonyl) both of which are in close agreement with the values, 2·26 and 2·01 Å, found in (II). The Rh–CO distance is midway between the values obtained for terminal CO groups, 1·87[3] and 1·86[6], and triple-bridging groups, 2·17 Å.[6] The Rh–Rh distance, 2·62 Å, is shorter than that found in (II), 2·68 Å, in the metal, 2·69 Å, or in $Rh_6(CO)_{16}$, 2·78 Å.[6] We can offer no explanation for this shortening at present; it cannot simply be a property of the tris(cyclopentadienylrhodium) ring system since in the one other compound which we have studied containing this system the corresponding distance is 0·1 Å greater.[7]



FIGURE

Average standard deviation of Rh–C 0·03 Å
Average standard deviation of C–C 0·04 Å

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[1] E. O. Fischer and K. Bittler, *Z. Naturforsch.*, 1961, **16**b, 225.
[2] E. O. Fischer and K. Bittler, *Z. Naturforsch.*, 1961, **16**b, 835.
[3] O. S. Mills and J. P. Nice, unpublished structure determination.
[4] E. O. Fischer and H. Schuster-Woldan, personal communication.
[5] A. K. Bhuiya and E. Stanley, *Acta Cryst.*, 1963, **16**, 981.
[6] E. R. Corey, L. F. Dahl, and W. Beck, *J. Amer. Chem. Soc.*, 1963, **85**, 1202.
[7] $Rh_3C_{20}H_{21}$; preparation and structure to be reported.