Unexpected Fluxional Behaviour in Hexacarbonyl-(π-cycloheptadienyl)-(π-cycloheptatrienyl)triruthenium

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Summary ^1H and ^{13}C n.m.r. studies of the title compound demonstrate that only the cycloheptadienyl group becomes stereochemically rigid at temperatures > -100 °C, the cycloheptatrienyl group remaining fluxional at this temperature; from the reported *X*-ray structure, the molecule probably undergoes at least three independent modes of topological rearrangement.

A recent report of Bau, Stone, and their co-workers[1] described the crystal structure determination of $(C_7H_7)(C_7H_9)Ru_3(CO)_6$ (I). These authors pointed out that the C_7H_7 ring of this molecule is probably fluxional at room temperature, since the protons on this ring are magnetically equivalent. We had isolated the same compound independently, and in our attempts to characterize it, studied its n.m.r. properties at low temperature. We find that at the temperatures experimentally available to us ($\geqslant$

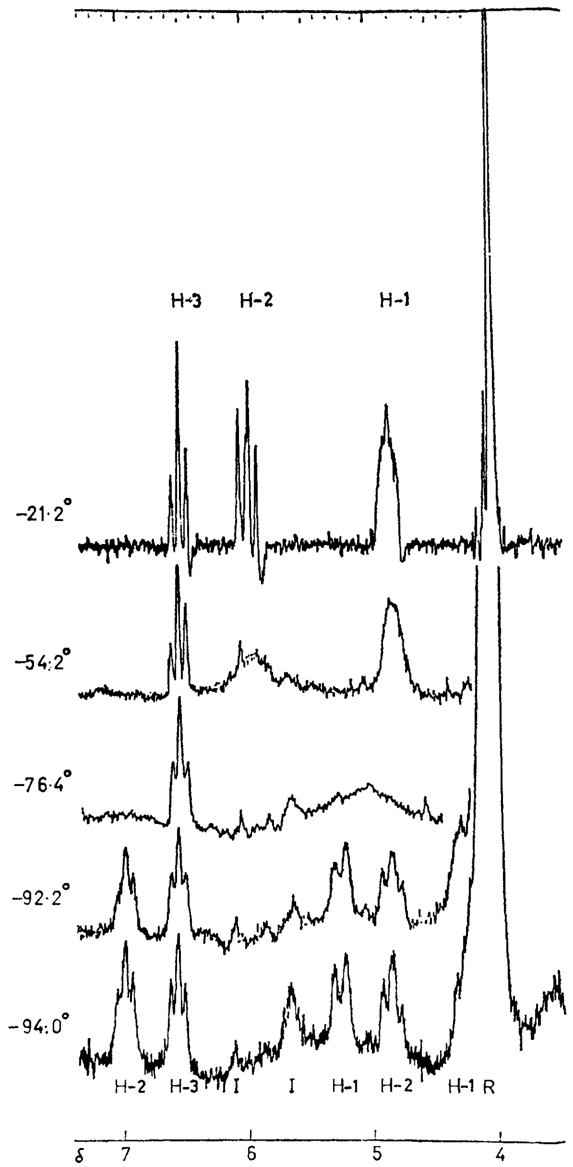
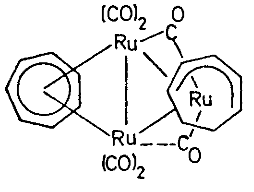
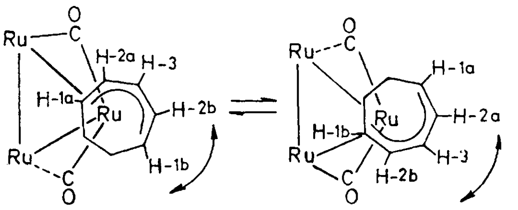


FIGURE. Temperature dependence of the n.m.r. spectrum of (I). On the spectra, I = impurity, R = C_7H_7.



(I)

— 100 °C) the resonances of the C_7H_7 ring remain averaged on the n.m.r. time scale. In contrast, the resonances of the partially saturated C_7H_9 ring, which are characteristic of a symmetrical h^5-pentadienyl unit at room temperature broaden and then split up as the temperature is lowered. Typical partial experimental spectra, and their assignments are shown in the Figure. We interpret this behaviour as resulting from rotation of the C_7H_9 ring relative to the Ru_3 triangle. In particular the H-3 resonance remains sharp. The free energy of activation at −55° is 9·5 ± 0·5 kcal/mol. Coupled with this rotation is very probably an exchange of the bridging and partially bridging carbonyl groups. We attempted to confirm this prediction by ^{13}C n.m.r. experiments paralleling the ^1H n.m.r. studies; however, the intensity of the metal carbonyl resonances was too small to be observed even at ambient temperature. The C_7H_9 ring carbons however showed resonances which were temperature dependent as expected. Solubility problems precluded the attainment of the low temperature limit in the carbon spectrum, and only the reversible collapse of the signals due to C-1a and C-1b (81·47 p.p.m.)† and C-2a and C-2b (104·59 p.p.m.)† could be observed. The signals due to C-3 and the carbon atoms of the C_7H_7 ring remained sharp (105·31 and 66·27 p.p.m. respectively).† Thus, compound (I) undergoes at least three types of fluxional behaviour: very rapid rotation of the C_7H_7 ring, somewhat slower rotation of the C_7H_9 ring, and a corresponding exchange of carbonyl groups.



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† Downfield from Me_4Si.

[1] R. Bau, J. C. Burt, S. A. R. Knox, R. M. Laine, R. P. Phillips, and F. G. A. Stone, *J.C.S. Chem. Comm.*, 1973, 726.