Valence Tautomerism in Cyclo-octatetraeneruthenium Tricarbonyl

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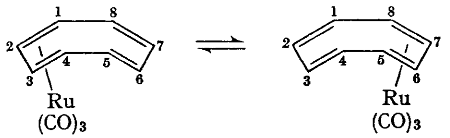
THE discovery of cyclo-octatetraeneiron tricarbonyl[1] and the observation of a single proton resonance in its n.m.r. spectrum has led to considerable interest in the geometry of this complex in solution, especially in view of the *X*-ray diffraction study,[2] which revealed that in the crystal the Fe(CO)$_3$ group is bonded to a butadiene-like moiety of the C_8H_8 ring. Recent low-temperature ^1H n.m.r. studies[3] have been interpreted as favouring three different rearrangement processes occurring in solution.

One of the products of the reaction between Ru$_3$(CO)$_{12}$[4] and cyclo-octetraene is the complex C_8H_8Ru(CO)$_3$, m.p. 75—76°, characterised fully by elemental analysis, and by its mass and infrared spectra. We now report a study of the low-temperature ^1H n.m.r. spectra of this compound.

At room temperature, the spectrum of C_8H_8Ru(CO)$_3$ consists of a sharp singlet (τ 4·79), and is thus similar to that of the iron complex (τ 4·76).[3c] On cooling, the signal broadens and collapses, disappearing completely at −95°. Further cooling results in the appearance of two broad signals at τ 4·19 and 5·31 (relative intensities ~1 : 1), which change below −109° to three signals centred at τ 4·03, 5·12, and 5·88 (relative intensities ~2 : 1 : 1). At −130°, these peaks show some evidence of fine structure and the signal at lowest field is partly resolved into two resonances centred at τ 3·88 and 4·17.

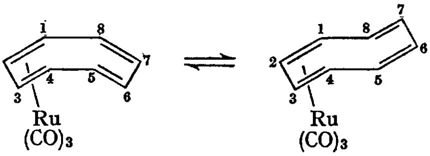
At room temperature, therefore, cyclo-octatetraeneruthenium tricarbonyl exhibits a valence tautomerism,[5] similar to that shown by the iron complex, resulting in the equivalence of all eight protons. We suggest that the appearance of two peaks between −95 and −109° corresponds to rapid (on the n.m.r. time-scale) isomerisation between (Ia) and (Ib).



(Ia) (Ib)

This is analogous to the process suggested by Pettit *et al.*[3c] for the iron complex, and as suggested by them, would result in a spectrum showing two peaks, assigned to the equivalent protons (2,3,6,7) and (1,4,5,8). We assign the bands at τ 4·19 and 5·31 respectively to these protons [*cf.* C_8H_8Fe(CO)$_3$ with corresponding absorptions at τ 4·06 and 5·44, at −120°[3c]].

Further cooling, resulting in three signals, then corresponds to the situation (IIa) ⇋ (IIb), where the diene group (5,6,7,8) is no longer involved in bonding to the metal, and is free to oscillate between the chair and tub forms of the ligand. With this equilibrium protons (5,6,7,8) may not be resolved, and could give rise to the broad signal at τ 4·03. Protons (2,3) will be at lower field than (1,4), and we observe two peaks at τ 5·12 and 5·88, which are so assigned.



(IIa) (IIb)

The further resolution seen at −130° may correspond to a final freezing of the complex into the form (IIb), corresponding to that found in the solid state for C_8H_8Fe(CO)$_3$.[2] At lower temperatures the complex crystallised from solution, so this interpretation seems reasonable. The further resolution enables the assignment of the band at τ 3·88 to protons (6,7) and at τ 4·17 to protons (5,8). These would average to give a signal at τ 4·03, as observed, and may be compared to the values of τ 3·6 and 3·9 *assumed* by Pettit *et al.*[3c] for the corresponding protons in C_8H_8Fe(CO)$_3$. These workers also assumed values of τ 4·6 and 7·0 for protons (2,3) and 1,4) respectively, which do not correspond to our values of τ 5·12 and 5·88. We suggest that cyclo-octatetraene constitutes an atypical cyclic diene and "typical" chemical shift values[3c] might not apply in this case.

We do not consider the hypothesis of a 1,5-diene–metal complex[3b] to be tenable in view of the observed asymmetry of the high-field band in the spectrum of C_8H_8Fe(CO)$_3$, and our resolution of the spectrum of C_8H_8Ru(CO)$_3$ into more than two bands. The asymmetry observed at −150° in the spectrum of C_8H_8Fe(CO)$_3$ could well represent the development of the third band, seen at higher temperatures at τ 5·88 in the case of C_8H_8Ru(CO)$_3$. However, this suggestion assumes that the structures in solution of the two complexes are directly comparable, which may not be so.

In the complexes $C_8H_8M(CO)_3$ (M=Cr, Mo, W), where the C_8H_8 is apparently bonded as a triene, the ease of valence tautomerism increases with atomic number.[3a] The reverse appears to occur with iron and ruthenium, where cyclo-octatetraene is bonded as a diene.

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