Low Temperature Proton Magnetic Resonance Study of the Fluxional Molecule Tricarbonylcyclo-octatetraeneosmium

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Summary A detailed analysis of the limiting low temperature ^1H n.m.r. spectrum of tricarbonylcyclo-octatetraeneosmium as an eight-spin system is described, and the nature of the intramolecular process, which results in the observation of only a single line ^1H n.m.r. spectrum at room temperature, is discussed.

THERE have been a number of investigations directed towards obtaining an understanding of the fluxional behaviour of tricarbonylcyclo-octatetraeneiron.[1] However, although the molecular structure in the crystal state was established[2] as tricarbonyl-1,2,3,4-tetrahaptocyclo-octatetraeneiron, the instantaneous structure of the molecule in solution, and the details of the mechanism of the intramolecular rearrangement, which results in the observation of only a single line ^1H n.m.r. spectrum at room temperature, are not understood. Studies of the analogous ruthenium complex, $C_8H_8Ru(CO)_3$, which is isostructural with the iron complex in the crystalline state, have been more useful in that the ^1H n.m.r. spectrum measured at −147° shows four discrete peaks, each showing poorly resolved fine structure.[1] This suggests that the instantaneous structure of the ruthenium complex is also of the 1,2,3,4-tetrahapto-type. It has been suggested on the basis of a classical analysis of the line-shape changes of the spectrum of $C_8H_8Ru(CO)_3$ over a wide range of temperatures, and by the assignment of the chemical shifts at low temperature, that the intramolecular rearrangement proceeds *via* a succession of 1,2-shifts.[1]

We have examined the variable temperature ^1H n.m.r. spectrum of tricarbonylcyclo-octatetraeneosmium[3] in CS_2 at 100 MHz. This complex shows[3] a single sharp line at 30°; on cooling the system behaves in an analogous way to that observed for the ruthenium system. However, with the osmium complex the limiting four-line spectrum (Figure 1) is reached at −100°, whereas, with the ruthenium complex a temperature invarient spectrum is apparently reached at −147°, and then, as comparison of the spectra shows (Figure 1, reference 1), the osmium system shows a far superior spectral resolution. It is possible that the limiting spectrum of the ruthenium complex has not been obtained, because we find that the appearance of the detailed fine structure for the osmium complex is very dependent upon the last few degrees change in temperature. An additional difference in the spectra of two complexes is that resonance C moves to high field by 34 Hz in the ruthenium complex, otherwise the width of the spectrum (resonances A to D) and the relative positions of the resonances are very similar.

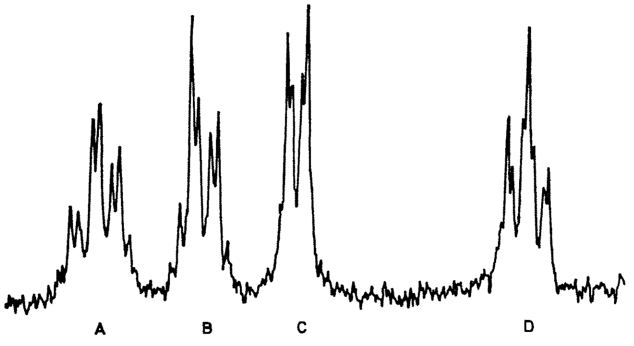

FIGURE 1

Double resonance experiments showed the coupling scheme B $\longleftrightarrow$ A $\longleftrightarrow$ D $\longleftrightarrow$ C. If we assume that the chemical shifts of the protons in the diene-fragment bonded to the metal will occur at higher field, then AA′BB′CC′DD′ may be assigned as in Figure 2. The B and C resonances resemble those of an AA′XX′ system in which coupling between one pair of chemically equivalent nuclei is approximately zero; we have set $J_{AA'}$ and $J_{DD'}$ to zero. Further, the A and D resonances can be regarded as the result of the splitting, $J_{AD'}$, upon an AA′XX′ system. The basic spectrum and the double resonance experiments show that the couplings $J_{AD'}$, J_{DB}, J_{AC}, $J_{DB'}$, $J_{AC'}$, J_{CB}, and $J_{CB'}$ are vanishingly small; they have been set to zero in our analysis.

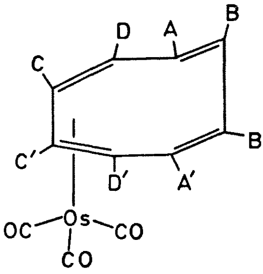

FIGURE 2

Approximate parameters calculated from the spectrum were adjusted by trial and error using a six-spin version of the simulation program FREQUINT[4] on the sets $[DAB]_2$ and $[ADC]_2$. The final results (Table) were checked by an eight-spin simulation (Figure 3). Thus the analysis of the ^1H n.m.r. spectrum of the osmium complex shows that the spectrum falls into the general class of "deceptively simple spectra." Since the separations of the A and B resonances and of the C and D resonances are slightly smaller (by 5 Hz and by 28 Hz respectively at 100 MHz) in the ruthenium complex, this will result in a still greater deviation from a first-order spectrum assuming that the coupling constants are similar for the two systems. The separation of resonances B and C is much greater in the ruthenium compound but this should have little effect since J_{BC} is vanishingly small.

^1H N.m.r. chemical shifts (τ) and coupling constants (Hz.) for $C_8H_8Os(CO)_3$ *in* CS_2 (−100°)

Assignment	AA′	BB′	CC′	DD′
Shift	3·89	4·39	4·84	5·92

Coupling constants $J_{AB} = J_{A'B'}$ 12·1; $J_{AB'} = J_{A'B}$ 0·7; $J_{BB'}$ 8·0; $J_{AD} = J_{A'D'}$ 9·7; $J_{CD} = J_{C'D'}$ 9·0; $J_{CC'}$5·0; and $J_{CD'} = J_{C'D}$ 0·5.

The second-order character of the spectra has serious implications for previous attempts to derive a mechanism for the intramolecular ring shift occurring with these complexes. An analysis in which the exchange is treated as an "eight-site" problem where a modified form of the Bloch equations is employed, can only be rigorously justified for an ensemble of independent spins.[5] This is particularly important if the researcher wishes to obtain quantitative information on rate constants *etc.*

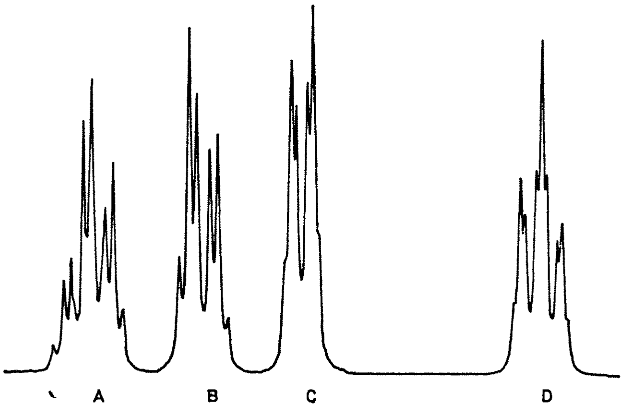

FIGURE 3

The non-first-order character of the ^1H n.m.r. spectrum of $C_8H_8Os(CO)_3$, and by implication that of the ruthenium complex, thus introduces a degree of uncertainty in our ability to "label" the spin-states, and the chemically non-equivalent sites to which exchange occurs. The degree of mixing of the spin-states increases with increase in the $J:\Delta\nu$ ratios for the spectrum. In simple situations a correction factor may be applied to the derived rate constant,[6] and the overall *shape* of the spectrum may not be unduly distorted. However, in a system with the complexity of the osmium and ruthenium compounds a rigorous quantum mechanical analysis may be necessary in order to establish a definite mechanism for the fluxional behaviour.

The complexity of the spectra places this beyond our present computing facilities.

The line shapes observed in the collapse of the spectrum of the osmium complex with increasing temperature are similar to those reported[1] for the ruthenium complex, in particular the spectrum shows a broadened double hump at intermediate temperatures.[7] The naive theory for the rate exchange also indicates a 1,2-shift about the ring in one direction (the possibility of omnidirectional shifts was not considered by previous workers). We would, however, discount this analysis and suggest that statements[1] to the effect that the intramolecular shift proceeds *via* a 1,2-shift mechanism with an upper limit of 30% on the occurrence of 1,3 or other shift processes are premature. Moreover, the quotation[1] of activation parameters and exchange rates are meaningless.[5,6,8]

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