

## Four Separate Fluxional Processes in $(\eta^6\text{-Cyclo-octatetraene})(\eta^4\text{-cyclo-octa-1,5-diene})\text{osmium}$ . A Novel Example of a Metal [1,5] Shift on a $\pi$ -Co-ordinated Polyene Ligand

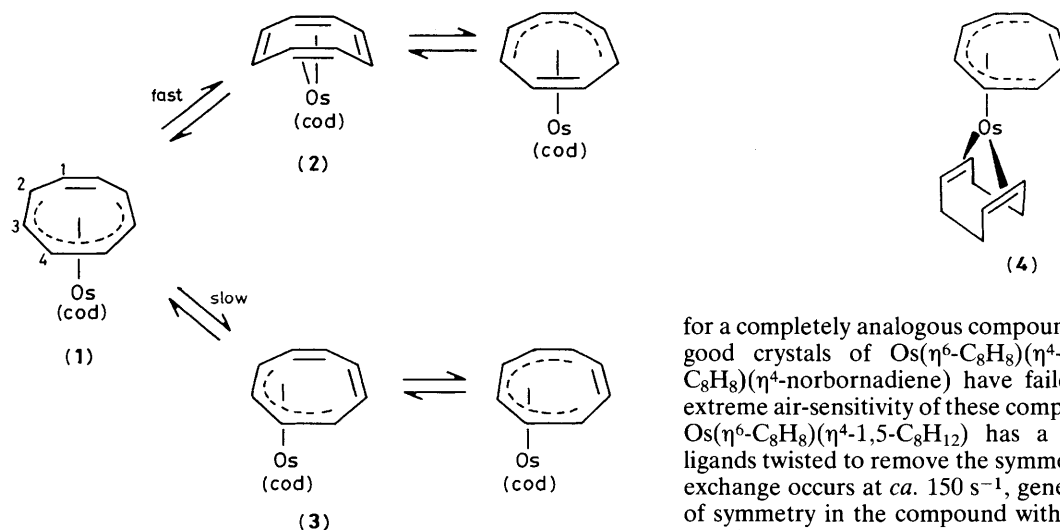
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The  $^{13}\text{C}$  n.m.r. spectrum of  $\text{Os}(\eta^6\text{-C}_8\text{H}_8)(\eta^4\text{-C}_8\text{H}_{12})$  in  $[\text{}^2\text{H}_8]\text{toluene}$  at  $-93\text{ }^\circ\text{C}$  shows that the molecule possesses no symmetry, and a low energy twitch occurs with  $\Delta G^\ddagger$  8.9 kcal mol $^{-1}$  producing an apparent plane of symmetry; at higher temperature, the cyclo-octatetraene and cyclo-octadiene ligands mutually rotate, with  $\Delta G^\ddagger$  ca. 11.5 kcal mol $^{-1}$ , exchange commencing at room temperature on the cyclo-octatetraene ring by a novel [1,5] shift mechanism with  $\Delta G^\ddagger = 16.5$  kcal mol $^{-1}$  and at slightly higher temperature a general shift of the metal around the cyclo-octatetraene ring occurring with  $\Delta G^\ddagger$  ca. 19.5 kcal mol $^{-1}$  (1 cal = 4.184 J).

The vast majority of cyclic  $\pi$ -polyene and  $\pi$ -polyenyl metal complexes have been shown to undergo [1,2] shifts of the metal around the ring, and the mechanism has been rationalised using the Woodward–Hoffmann rules.<sup>1–3</sup> In cases where the fluxionality is forbidden by these rules, then other mechanisms operate. For  $\eta^6$ -cyclo-octatetraene complexes,

the usual mechanism is a [1,3] shift, as demonstrated for  $(\eta^6\text{-C}_8\text{H}_8)\text{Cr}(\text{CO})_3$  and  $(\eta^6\text{-C}_8\text{H}_8)\text{W}(\text{CO})_3$ , involving an intermediate  $(1\text{---}4\text{-}\eta^4\text{-C}_8\text{H}_8)$  16-electron complex.<sup>4</sup> As part of a study of factors influencing the fluxionality of such systems, we have examined the known compound  $\text{Os}(\eta^6\text{-cyclo-octatetraene})(\eta^4\text{-1,5-cyclo-octadiene})$ , (**1**).<sup>5</sup> The  $^1\text{H}$  and  $^{13}\text{C}$



Scheme 1. cod = cyclo-octa-1,5-diene.

n.m.r. spectra were fully assigned in  $[^2\text{H}_8]$ toluene using selective  $^1\text{H}$  decoupling in both spectra, and are consistent with the assignment in other complexes.<sup>4</sup> During these decoupling experiments at room temperature, it was observed that magnetization transfer occurred pairwise between  $\text{H}^1$ ,  $\delta$  5.13, and  $\text{H}^4$ ,  $\delta$  5.30, and between  $\text{H}^2$ ,  $\delta$  3.94, and  $\text{H}^3$ ,  $\delta$  5.05. These measurements were repeated quantitatively using selective  $\pi$ -pulses to invert  $\text{H}^2$  or  $\text{H}^4$ , and following the magnetization transfer into the other sites as a function of time. At 22 °C, these measurements only detected  $\text{H}^1$ - $\text{H}^4$ , and  $\text{H}^2$ - $\text{H}^3$  pairwise exchange, with a rate constant of 4  $\text{s}^{-1}$ . However, when the measurements were repeated at 36 °C, a slower general exchange of the cyclo-octatetraene protons was detected with a rate constant of *ca.* 0.1  $\text{s}^{-1}$ , while the pairwise exchange occurred at 12  $\text{s}^{-1}$ . The pairwise exchange is only explicable in terms of a [1,5] shift mechanism, with  $\Delta G^\ddagger$  16.6 kcal  $\text{mol}^{-1}$ .<sup>†</sup> Following the mechanism for the [1,3] shift observed in  $\text{Cr}(\eta^6\text{-C}_8\text{H}_8)(\text{CO})_3$ , involving a 1-4- $\eta^4$ -intermediate, it is proposed that the [1,5] shift occurs *via* a 1,2,5,6- $\eta^4$ -intermediate (2) (Scheme 1). The general shift occurring with the slow rate probably occurs *via* a 1-4- $\eta^4$ -intermediate (3), with  $\Delta G^\ddagger$  *ca.* 19.5 kcal  $\text{mol}^{-1}$ . The facility of the mechanism going *via* (2) is consistent with the tendency of osmium to bridge a cyclo-octatetraene ring in complexes such as  $\text{Os}(1-3,6-\eta^4\text{-C}_8\text{H}_8)(\text{CO})_3$ .<sup>6</sup>

At room temperature, the 100.62 MHz  $^{13}\text{C}$  n.m.r. spectrum posed a problem. Signals due to the cyclo-octatetraene ring were all present in  $[^2\text{H}_8]$ toluene:  $\text{C}^1$  at  $\delta$  139.2;  $\text{C}^2$ , 63.8;  $\text{C}^3$ , 103.3; and  $\text{C}^4$ , 97.2, but only the  $\text{CH}_2$  carbon atom of the cyclo-octa-1,5-diene ring was detected at  $\delta$  31.2. On cooling to -93 °C, all the carbon atoms in the molecule were observed, the majority being inequivalent, with the cyclo-octatetraene signals at:  $\text{C}^1$ ,  $\delta$  142.8 and 136.1;  $\text{C}^2$ , 63.0;  $\text{C}^3$ , 108.3 and 98.9 or 97.1 or 96.4;  $\text{C}^4$ , 98.9 and/or 97.1 and/or 96.4. The cyclo-octadiene signals are at  $\delta$  53.6, 48.8, 45.3, and 41.1 due to the olefinic carbon atoms, and the  $\text{CH}_2$  signals at  $\delta$  31.0 (intensity 2), 29.1, and 28.2. Clearly, the molecule must be of low symmetry. It is known from the crystal structures of molecules<sup>7,8</sup> such as  $\text{Fe}(\eta^4\text{-C}_8\text{H}_8)(\eta^6\text{-C}_8\text{H}_8)$  and  $\text{Ru}(\eta^5\text{-C}_7\text{H}_7)(\eta^5\text{-C}_7\text{H}_7)$  that the ligands do appear to prefer co-ordination with 60° between the symmetry planes of the ligands. No X-ray structure appears to have been determined

<sup>†</sup> 1 cal = 4.184 J.

for a completely analogous compound, and attempts to obtain good crystals of  $\text{Os}(\eta^6\text{-C}_8\text{H}_8)(\eta^4\text{-1,5-C}_8\text{H}_{12})$  and  $\text{Ru}(\eta^6\text{-C}_8\text{H}_8)(\eta^4\text{-norbornadiene})$  have failed, mainly owing to the extreme air-sensitivity of these compounds. It is proposed that  $\text{Os}(\eta^6\text{-C}_8\text{H}_8)(\eta^4\text{-1,5-C}_8\text{H}_{12})$  has a structure with the two ligands twisted to remove the symmetry, as in (4). At -83 °C, exchange occurs at *ca.* 150  $\text{s}^{-1}$ , generating an apparent plane of symmetry in the compound with  $\Delta G^\ddagger$  8.9 kcal  $\text{mol}^{-1}$ . By -40 °C, all the signals, with the exception of the cyclo-octadiene olefinic carbon atoms, have re-appeared as exchange averaged signals, albeit some still being broad. The cyclo-octadiene olefinic carbon atoms do not re-appear, even at room temperature. As the frequency-spread of these carbon atoms is only slightly greater than that of  $\text{C}^3$  of the cyclo-octatetraene ligand, this loss of signal due to exchange cannot arise from the same exchange process, and a second process is required. It is therefore proposed that the low-temperature process with  $\Delta G^\ddagger$  8.9 kcal  $\text{mol}^{-1}$  is a twitch, which only results in pairwise exchange of the cyclo-octadiene carbon atoms, resulting in two types of CH and  $\text{CH}_2$  signals. At higher temperature, the two ligands rotate completely with respect to each other, resulting in one CH and one  $\text{CH}_2$  signal. Owing to the greater frequency-spread of the CH signals, the signal is too broad to be detected at room temperature,<sup>‡</sup> while complete averaging of the  $\text{CH}_2$  signals has occurred. Applying the constraints of not seeing the signal at -40 °C and room temperature,  $\Delta G^\ddagger$  = *ca.* 11.5 kcal  $\text{mol}^{-1}$  for complete rotation.

It is rare for a molecule to show four separate fluxional processes which are accessible on the n.m.r. time-scale, and we believe this example to be the simplest molecule fitting into this category.

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<sup>‡</sup> Decomposition occurs on heating the sample.