In memory of S. M. Nelson and T. A. Stephenson

The Mechanism of Fluxionality of $[Ru(\eta^6\text{-}C_8H_8)(\eta^4\text{-}C_7H_8)]$, $[Ru(\eta^4\text{-}C_8H_8)(\eta^4\text{-}C_7H_8)L]$ [L = PEt_3 or $P(OMe)_3$], and $[Os(\eta^6\text{-}C_8H_8)(\eta^4\text{-}C_8H_{12})]$ (C_8H_8 = Cyclo-octatetraene, C_7H_8 = Norborna-2,5-diene, and C_8H_{12} = Cyclo-octa-1,5-diene)†

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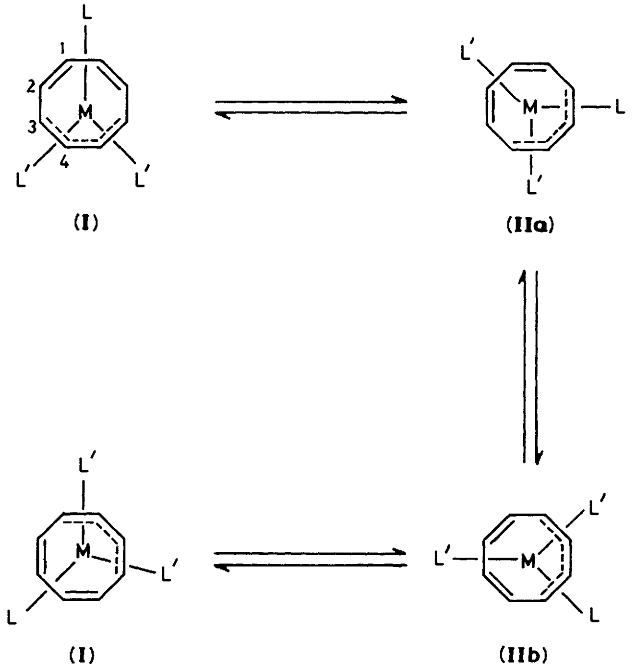
Magnetization transfer measurements have been applied to determining the mechanism of fluxionality of $[Ru(\eta^6\text{-}C_8H_8)(\eta^4\text{-}C_7H_8)]$ (C_8H_8 = cyclo-octatetraene, C_7H_8 = norborna-2,5-diene) and $[Os(\eta^6\text{-}C_8H_8)(\eta^4\text{-}C_8H_{12})]$ (C_8H_{12} = cyclo-octa-1,5-diene) in $[^2H_8]$toluene. Contrary to a previous report on the ruthenium complex, which was based on lineshape analysis, the dominant mechanism of cyclo-octatetraene fluxionality for both complexes is not a random shift, or a [1,3]-shift, but is a [1,5]-shift, with [1,3]-shifts occurring at a slower rate. In addition, the osmium complex shows two lower-energy processes consistent with a staggered relative arrangement of the two polyene ligands. The lowest energy process is an oscillation of the two ligands producing an apparent plane of symmetry, and the higher-energy process is the complete rotation of the two ligands. It appears that the ruthenium complex behaves similarly, but the activation energy for rotation is lower, and only signal broadening is observed at low temperature. It is also shown that the metal shifts in $[Ru(\eta^4\text{-}C_8H_8)(\eta^4\text{-}C_7H_8)L]$ [L = PEt_3 or $P(OMe)_3$] are [1,2]-shifts.

A previous investigation of $[Ru(\eta^6\text{-}C_8H_8)(\eta^4\text{-}C_7H_8)]$ has shown that the cyclo-octatetraene ligand (C_8H_8) is fluxional.[1] All the signals broaden by the same amount at the onset of fluxionality, and coalesce to give a singlet at high temperatures. It was therefore deduced that the mechanism is either a [1,3]- or a random-shift. The case for a random shift was strongly argued. Subsequently, it was suggested that the [1,3]-shift mechanism is more likely,[2] and this was shown to be the dominant mechanism for $[M(\eta^6\text{-}C_8H_8)(CO)_3]$ (M = Cr or W) by the use of magnetization transfer measurements.[3,4] Recently, we have examined $[Os(\eta^6\text{-}C_8H_8)(\eta^4\text{-}C_8H_{12})]$ (C_8H_{12} = cyclo-octa-1,5-diene) and shown that the dominant mechanism for cyclo-octatetraene fluxionality is a [1,5]-shift. A preliminary report of this work has appeared.[5] We have therefore used magnetization transfer measurements to reinvestigate the mechanism of fluxionality of $[Ru(\eta^6\text{-}C_8H_8)(\eta^4\text{-}C_7H_8)]$ [C_7H_8 = norborna-2,5-diene (bicyclo[2.2.1]hepta-2,5-diene)]. We also present here a full report of the work on $[Os(\eta^6\text{-}C_8H_8)(\eta^4\text{-}C_8H_{12})]$.

The quantitative analysis of the data for $[Ru(\eta^6\text{-}C_8H_8)(\eta^4\text{-}C_7H_8)]$ proved to be beyond the available analyses of magnetization transfer data. As a result we have had to develop a method to analyse the data.[6]

Previous work has shown that $[Ru(\eta^6\text{-}C_8H_8)(\eta^4\text{-}C_7H_8)]$ readily reacts with phosphorus(III) ligands (L) to yield $[Ru(\eta^4\text{-}C_8H_8)(\eta^4\text{-}C_7H_8)L]$.[7] An analysis of the fluxionality of $[M(\eta^4\text{-}C_8H_8)L'_2L]$ has suggested that in favourable cases, novel shifts could be observed when only one of the two possible isomers is present, see Scheme 1.[8] Thus, when (I) is more stable, three sequential [1,2]-shifts are required to return to the stable isomer, producing an overall [1,4]-shift. When (II) is more stable, then there should be a low-energy [1,2]-shift, resulting in a 'twitch,' before the onset of more extensive exchange. As yet no such case has been observed; all the systems so far studied undergo interisomer exchange with both isomers being present,[8] or high-energy [1,2]-shifts. $[Ru(\eta^4\text{-}C_8H_8)(\eta^4\text{-}C_7H_8)L]$ offers a previously unexamined group of compounds which could give rise to this fluxional mechanism, and are examined here.



Scheme 1. The fluxional mechanism for a $[M(\eta^4\text{-}C_8H_8)L'_2L]$ system. Note that (IIa) and (IIb) represent an enantiomeric pair

Experimental

The n.m.r. spectra were recorded on a Bruker WH-400 n.m.r. spectrometer operating at 400.13 MHz for ^1H and 100.62 MHz for ^{13}C observation. The selective 180° ^{13}C pulses were applied using the DANTE pulse sequence.[9] The temperatures of the

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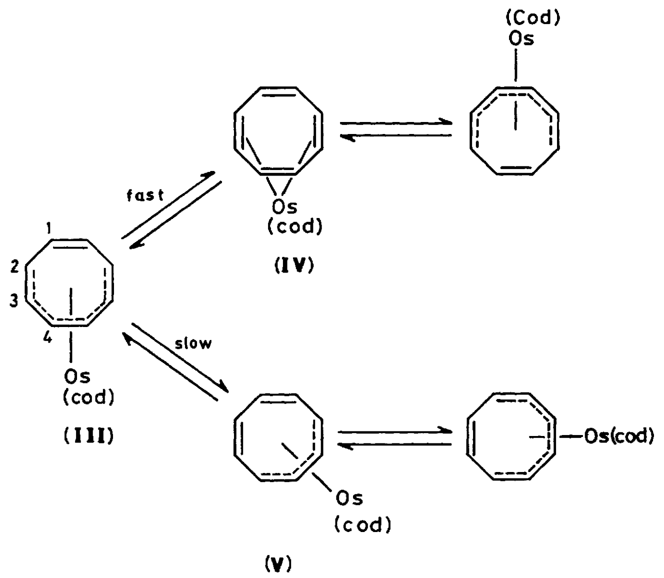
† *Non-S.I. unit employed:* cal = 4.184 J.



Scheme 2. The mechanism of cyclo-octatetraene fluxionality in [Os(η^6-C_8H_8)(η^4-C_8H_{12})] (C_8H_{12} = cod)

samples in the probe were determined using a copper–constantan thermocouple attached to a Comark 5235 electronic thermometer. The thermocouple was placed in an n.m.r. tube containing toluene which was then placed in the probe under identical conditions, apart from spinning, as the sample.

The compounds [Ru(η^6-C_8H_8)(η^4-C_7H_8)] and [Os(η^6-C_8H_8)(η^4-C_8H_{12})] were synthesized following the literature procedure.[7] Dried and deoxygenated solvents were used throughout. Solutions of the compounds in [$^2H_8$]toluene were studied using both ^{1}H and ^{13}C n.m.r. spectroscopy. Both the ^{1}H and ^{13}C n.m.r. spectra were completely assigned using selective ^{1}H decoupling. The compounds [Ru(η^4-C_8H_8)(η^4-C_7H_8)(PEt_3)] and [Ru(η^4-C_8H_8)(η^4-C_7H_8){P(OMe)$_3$}] were prepared *in situ* by titrating the appropriate phosphorus ligand in [$^2H_8$]toluene into a solution of [Ru(η^6-C_8H_8)(η^4-C_7H_8)] in [$^2H_8$]toluene and monitoring the reaction by ^{1}H n.m.r. spectroscopy.

The magnetization transfer data were analysed using a previously described computer program.[6]

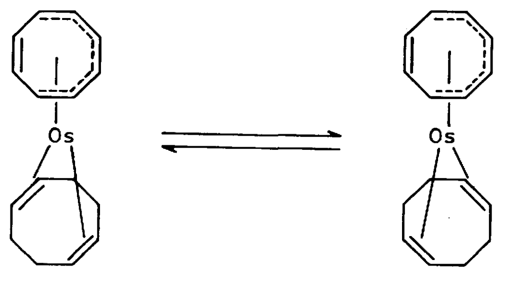
Results and Discussion

At the room temperature, the ^{1}H n.m.r. spectrum of [Os(η^6-C_8H_8)(η^4-C_8H_{12})] **(III)**, in [$^2H_8$]toluene shows the expected four resonances for the cyclo-octatetraene protons and three signals for the cyclo-octa-1,5-diene. Similarly, the ^{13}C n.m.r. spectrum shows four resonances for the cyclo-octatetraene. Only the CH_2 signal is detected for the cyclo-octa-1,5-diene ligand. The ^{1}H and ^{13}C n.m.r. spectra were fully assigned in [$^2H_8$]toluene using selective ^{1}H decoupling in both spectra, and are consistent with the assignment in other complexes.[10a] During these decoupling experiments at room temperature, it was observed that magnetization transfer occurred pairwise between H^1 (δ 5.13) and H^4 (δ 5.30), and between H^2 (δ 3.94) and H^3 (δ 5.05) [numbering as in **(III)**, Scheme 2]. These measurements were repeated quantitatively using selective 180° pulses to invert H^2 or H^4, and following the magnetization transfer into the other sites as a function of time. At 20 °C, these measurements only detected H^1–H^4 and H^2–H^3 pairwise exchange, with a rate constant of 1.5 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 0.1 s^{-1}, while the pairwise exchange occurred at 8 s^{-1}. The pairwise exchange is only explicable in terms of a [1,5]-shift mechanism, with $\Delta G^{\ddagger}$ = 16.8 kcal mol^{-1}. Following the mechanism for the [1,3]-shift observed in [Cr(η^6-C_8H_8)(CO)$_3$], involving a 1—4-η intermediate, it is proposed that the [1,5]-shift occurs *via* a 1—2,5—6-η intermediate, **(IV)**, see Scheme 2. The general shift occurring with the slow rate, and $\Delta G^{\ddagger}$ = 19.5 kcal mol^{-1}, probably occurs *via* a 1—4-η intermediate, **(V)**. The facility of the mechanism going *via* **(IV)** is consistent with the tendency of osmium to bridge a cyclo-octatetraene ring in complexes such as [Os(σ,η^3-C_8H_8)(CO)$_3$].[10b]

Similar behaviour is observed for [Ru(η^6-C_8H_8)(η^4-C_7H_8)] at room temperature, with the exception that it was clear from the ^{1}H n.m.r. measurements that both [1,3]- and [1,5]-shifts could be occurring. The quantitative analysis of ^{1}H magnetization transfer measurements was not attempted due to the possibility of nuclear Overhauser enhancement (n.O.e.) effects between adjacent exchanging protons. This could confuse the separation of [1,3]- and [1,5]-shifts. This problem was avoided by using the magnetically dilute ^{13}C nuclei, with complete ^{1}H decoupling at 20 °C. Application of a DANTE 180° selective pulse to C^1 or C^2 of C_8H_8 produces exchange into other sites, but preferentially a [1,5]-shift occurs. Due to the symmetry of the system we could not derive separate values for all the exchange rates,[6] but the data show unambiguously that [1,5]-shifts are dominant. The data were analysed quantitatively on the basis of [1,3]- and [1,5]-shifts to yield rates k_{13} = 2.8 s^{-1} and k_{15} = 10.1 s^{-1}, corresponding to $\Delta G^{\ddagger}$ of 16.5 and 15.8 kcal mol^{-1}, respectively. This observation is consistent with the previous observation of equal broadening of all the sites.[1] An exclusive [1,5]-shift would exchange C^1 with C^4 and C^2 with C^3 resulting in two signals, but the [1,3]-shift is fast enough to exchange all sites to produce a singlet at high temperature as is observed. [1,3]-, [1,5]-, and random-shifts all produce the same broadening in all the sites and cannot be distinguished by lineshape analysis. [1,5]-Shifts only exchange signals pairwise, resulting in two signals at high temperatures, but if there is also a [1,3]-shift, complete scrambling will result.

The observation of relatively facile [1,3]- and [1,5]-shifts in [Ru(η^6-C_8H_8)(η^4-C_7H_8)] and [Os(η^6-C_8H_8)(η^4-C_8H_{12})] and [1,3]-shifts in [Cr(η^6-C_8H_8)(CO)$_3$] and [W(η^6-C_8H_8)(CO)$_3$] suggest these mechanisms are usual for the η^6-C_8H_8 ring. In these cases, there is an additional driving force for the formation of an η^4-C_8H_8 intermediate. It has been recognized that the C_8H_8 ring is strained in co-ordinating to a metal through six carbon atoms,[11] and this strain can be removed by returning to η^4-co-ordination. The absence of [1,5]-shifts in [Cr(η^6-C_8H_8)(CO)$_3$] and [W(η^6-C_8H_8)(CO)$_3$] is attributed to subtle electronic factors, as it is known that in [W(η^4-C_8H_8)(CO)$_4$], 1—2,5—6-η-C_8H_8 co-ordination occurs.[12]

At room temperature, the 100.62-MHz ^{13}C n.m.r. spectrum of [Os(η^6-C_8H_8)(η^4-C_8H_{12})] posed a problem. Signals due to the cyclo-octatetraene ring were all present in [$^2H_8$]toluene [δ 139.2 (C^1), 63.8 (C^2), 103.3 (C^3), and 97.2 (C^4), numbering as in **(III)**] but only the CH_2 carbon atom of the cyclo-octa-1,5-diene ring was detected, at δ 31.2. On cooling to −93 °C, all the carbon atoms in the molecule are observed, the majority being inequivalent (cyclo-octatetraene signals: C^1, δ 142.8 and 136.1; C^2, δ 63.0; C^3, δ 108.3 and 98.9 or 97.1 or 96.4; C^4, δ 98.9 and/or 97.1 and/or 96.4). The cyclo-octa-1,5-diene signals are observed at δ 53.6, 48.8, 45.3, and 41.1 due to the olefinic carbon atoms, and the CH_2 signals at δ 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[13,14] such as [Fe(η^4-C_8H_8)(η^6-C_8H_8)] and [Fe(η^5-C_7H_7)(η^5-C_7H_9)] that the ligands do appear to prefer co-ordination with 60° between the symmetry planes of the ligands. No *X*-ray structure appears to



(VI)

Scheme 3. The proposed structure of [Os(η^6-C_8H_8)(η^4-C_8H_{12})] and the lowest-energy fluxional process

have been determined for a completely analogous compound, and attempts to obtain good crystals of [Os(η^6-C_8H_8)(η^4-C_8H_{12})] and [Ru(η^6-C_8H_8)(η^4-C_7H_8)] have failed, mainly due to the extreme air sensitivity of these compounds. It is proposed that [Os(η^6-C_8H_8)(η^4-C_8H_{12})] has a structure with the two ligands twisted to remove the symmetry, as in **(VI)**. At -83 °C, exchange occurs at *ca.* 150 s^{-1}, generating an apparent plane of symmetry in the compound with $\Delta G^{\ddagger} = 8.9$ kcal mol^{-1}. By -40 °C, all the signals, with the exception of the cyclo-octa-1,5-diene olefinic carbon atoms, have re-appeared as exchange-averaged signals, albeit some still being broad. The cyclo-octa-1,5-diene olefinic carbon atoms do not re-appear, even at room temperature. As the frequency spread of the these carbon atoms is only slightly greater than that of 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 mol^{-1} is a 'twitch', which only results in pairwise exchange of the cyclo-octa-1,5-diene carbon atoms, resulting in two types of CH and CH_2 signals, see Scheme 3. At higher temperature, the two ligands rotate completely with respect to each other, resulting in one CH and one CH_2 signal. Due to the greater frequency spread of the CH signals, the signal is too broad to detect at room temperature, while complete averaging of the 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 mol^{-1} for complete rotation.

It has been previously reported that [Ru(η^6-C_8H_8)(η^4-C_7H_8)] reacts quantitatively with a molar equivalent of a phosphorus ligand (L) to yield [Ru(η^4-C_8H_8)(η^4-C_7H_8)L].[7] This reaction was performed *in situ*, as an n.m.r.-monitored titration, to yield [Ru(η^4-C_8H_8)(η^4-C_7H_8)(PEt_3)] and [Ru(η^4-C_8H_8)(η^4-C_7H_8){P(OMe)$_3$}] using PEt_3 and P(OMe)$_3$ respectively as the titrants. At room temperature, the exchange rate is such that the cyclo-octatetraene protons are too broad to detect, but at -60 °C the signals are resolved. For [Ru(η^4-C_8H_8)(η^4-C_7H_8)(PEt_3)], in [$^2H_8$]toluene at -60 °C, the shifts are at δ 5.29 (H^1, *J* 8), 5.86 (H^2, *J* 8, 10), 2.38 (H^3, *J* 4, 10), and 4.90 (H^4, *J* 4 Hz), with the ^{13}C shifts at δ 134.0 (C^1), 115.9 (C^2), 48.8 (C^3), and 93.1 (C^4) [numbering as in **(I)**]. The remaining ^{13}C signals are observed for norborna-2,5-diene at δ 48.0 and 50.6[CH(sp^3)]; 39.4 and 43.5 [CH(sp^2)]; and 30.4 (CH_2) and for PEt_3 at δ 18.1 [CH_2, $^1J(^{31}P^{13}C)$ 22 Hz] and 7.8 (CH_3). The ^{31}P n.m.r. signal is at δ 40.6. For [Ru(η^4-C_8H_8)(η^4-C_7H_8){P(OMe)$_3$}], in [$^2H_8$]toluene at -60 °C, the shifts are at δ 5.40 (H^1, *J* 8), 5.82 (H^2, *J* 8, 10), 2.32 (H^3, *J* 4,10), and 4.94 H^4 (*J* 5 Hz), with the ^{13}C shifts at δ 131.7 (C^1), 116.7 (C^2), 49.0 (C^3), and 92.9 (C^4) [numbering as in **(I)**]. The remaining ^{13}C signals are observed for norborna-2,5-diene at δ 47.5(?) (obscured) and 50.9 [CH(sp^3)]; 39.5 and 47.5 [CH(sp^2)], and 30.4 (CH_2), and for P(OMe)$_3$ at δ 49.8. The ^{31}P chemical shift is δ 182.3.

The cyclo-octatetraene exchange mechanism for both compounds [Ru(η^4-C_8H_8)(η^4-C_7H_8)L] [L = PEt_3 or P(OMe)$_3$] was determined by applying a selective DANTE 180° pulse to C^4 at -15 (L = PEt_3) or -25 °C [L = P(OMe)$_3$]. In both cases, the predominant exchange mechanism is unambiguously transferred to only C^2, showing a dominant [1,2]-shift mechanism. Quantitative analysis using our analysis program yielded the rates for the [1,2]-shifts of 58 s^{-1} for [Ru(η^4-C_8H_8)(η^4-C_7H_8)(PEt_3)] and 24 s^{-1} for [Ru(η^4-C_8H_8)(η^4-C_7H_8){P(OMe)$_3$}], corresponding to $\Delta G^{\ddagger}$ values of 12.9 and 13.1 kcal mol^{-1} respectively. These activation values can be compared with 7.7 kcal mol^{-1} found previously for [Ru(η^4-C_8H_8)(CO)$_3$],[15] and <6 kcal mol^{-1} found for [Ru(η^4-C_8H_8)(η^6-C_6Me_6)] and [Ru(η^4-C_8H_8)(η^6-$C_6H_5Bu^t$)].[16] Similar behaviour has been noted previously with similar iron derivatives.[17] At first sight, $\Delta G^{\ddagger}$ for cyclo-octatetraene fluxionality for [Ru(η^4-C_8H_8)(η^4-C_7H_8)L] should be intermediate in value between that for [Ru(η^4-C_8H_8)(CO)$_3$] and [Ru(η^4-C_8H_8)(η^6-arene)]. This anomaly has been resolved using the Woodward–Hoffmann rules to explain the fluxionality in terms of [1,5]-sigmatropic shifts.[8,18] The increase in activation energy arises from having to put in the energy for not only the shifts, but also for ligand scrambling on the metal. It is not possible to deduce whether the stereochemistry is **(I)** or **(II)** [M = Ru, L'_2 = C_7H_8, L = PEt_3 or P(OMe)$_3$]. The ^{13}C n.m.r. spectrum demonstrates an apparent plane of symmetry through the molecule, but this could arise from structure **(I)**, or structure **(II)** with rapid interconversion of **(IIa)** and **(IIb)**.

These results clearly demonstrate the inherent dangers in using lineshape analysis to determine the mechanism of multisite exchange problems. Lineshape analysis only gives the rate of leaving each site, from which it is necessary to deduce the mechanism. If mechanisms are not considered, or more than one mechanism is present, then errors can result. In magnetization transfer measurements, each site is labelled, in turn, with a non-equilibrium Boltzmann population and this label can then be followed as it migrates around the molecule. Such measurements are less subject to mechanistic errors.

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