

η^6 -Cyclooctatetraene-metal complexes revisited: A study of two-dimensional NMR exchange spectroscopy of tricarbonyl(η^6 -cyclooctatetraene)-chromium and -tungsten

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Abstract

The rates and associated activation energies for metal migration in $[\text{M}(\text{CO})_3(\eta^6\text{-C}_8\text{H}_8)]$ ($\text{M} = \text{Cr}$ or W) have been precisely determined by variable temperature ^1H two dimensional NMR exchange spectroscopy. For $\text{M} = \text{W}$ the 1,2 and 1,3 shifts are almost equally favoured, whereas for $\text{M} = \text{Cr}$ the 1,3-migration pathway is slightly preferred. Planar monocyclooctatriene($\eta^4\text{-C}_8\text{H}_8$) and/or bicyclo[4.2.0]octatriene are considered to be probable intermediates for this fluxionality.

Introduction

Organometallic complexes of the type $[\text{M}(\text{CO})_3(\eta^6\text{-C}_8\text{H}_8)]$ ($\text{M} = \text{Cr}$, Mo or W) have been known for many years to be fluxional by virtue of the temperature dependence of their NMR spectra [1–3], but because of the complex spin coupling found in these proton spectra the mechanism of the fluxionality could not at first be deduced. However, with the availability of pulse Fourier transform ^{13}C NMR the problem was examined afresh [4,5]. The four signals in the $^{13}\text{C}\{-^1\text{H}\}$ spectrum were all seen to broaden at the same rate when the temperature was raised, indicating either 1,3-metal shifts or a random shift mechanism, the two processes not being separable by bandshape analysis. It was then argued that because six of the eight carbon atoms in the C_8H_8 ring are almost coplanar, as revealed by the X-ray crystal structure of $[\text{Mo}(\text{CO})_3(\eta^6\text{-C}_8\text{H}_8)]$ [6], a planar symmetrical intermediate is probably formed, leading to random shifts [4,5]. However, a ^{13}C NMR study of $[\text{Mn}(\text{CO})_3(\eta^5\text{-C}_7\text{H}_7)]$ [7] revealed a 1,2-metal shift mechanism, implying that a 20-electron ($\eta^7\text{-C}_7\text{H}_7$) intermediate leading to random shifts is not formed. Extrapolation of these results to the $[\text{M}(\text{CO})_3(\eta^6\text{-C}_8\text{H}_8)]$ complexes led to the postulation of 1,3-metal shifts via a 16-electron ($\eta^4\text{-C}_8\text{H}_8$) intermediate [7]. More recently, ^{13}C

magnetisation transfer experiments have shown that 1,3-metal shifts do indeed predominate, but 1,2-metal migrations also occur at measurable rates [8,9].

In this paper we demonstrate the application of two-dimensional NMR exchange spectroscopy (2D-EXSY) [10–13] to the accurate measurement of metal migration activation energies in $[M(\text{CO})_3(\eta^6\text{-C}_8\text{H}_8)]$ ($M = \text{Cr}$ or W). We show that equally reliable data can be extracted from ^1H spectra as from ^{13}C - $\{^1\text{H}\}$ spectra, thus reducing considerably the experimental time involved. This is particularly advantageous when complexes, such as those studied here, have limited thermal stability in solution.

Experimental

Materials. The compounds $[M(\text{CO})_3(\eta^6\text{-C}_8\text{H}_8)]$ ($M = \text{Cr}$ and W) were prepared by a two stage procedure. The compound $[M(\text{CO})_3(\text{CH}_3\text{CN})_3]$ was obtained by heating $M(\text{CO})_6$ in CH_3CN under reflux conditions [14], and subsequent heating under reflux with cyclooctatetraene gave the desired product, which was isolated and purified as previously described [15,16].

NMR experiments. All spectra were recorded on a Bruker AM250 spectrometer with an ASPECT 3000 computer. The ^1H and ^{13}C spectra were recorded at frequencies of 250.1 and 62.9 MHz respectively. Two dimensional EXSY * spectra were obtained with the Bruker automation program NOESY(X), which performs the pulse sequence $\text{D1-90}^\circ\text{-D0-90}^\circ\text{-D9-90}^\circ\text{-FID}$. For ^{13}C experiments the ^1H decoupler was effectively off during D1 and gated on for the remainder of the sequence. The relocation delay time D1 was typically 2–4 s, D0 was initially 3×10^{-6} s, and D9 (the mixing time, τ_m) chosen to minimise errors in the determined exchange rates [13]. The data table used for proton 2D-EXSY spectra was 1024 words in the F_2 domain and 128 words, zero-filled to 512 words, in the F_1 domain. For ^{13}C 2D-EXSY experiments these sizes were all doubled to accommodate the larger chemical shift dispersion. For ^{13}C spectra 64 scans per experiment were used giving a total experimental time of ca. 16 h; for ^1H spectra 8 or 16 scans were used, giving an experimental time of 45–90 min. The calculation of exchange rate constants from 2D-EXSY signal intensities was carried out with the D2DNMR computer program [13].

The complexes were examined in CDCl_3 solution, and the spectra were recorded in the temperature range -10 to 0°C ($M = \text{Cr}$) and 0 to 20°C ($M = \text{W}$) by use of the standard variable temperature accessory.

Results

Exchange rate constants were determined from 2D-EXSY experiments as described previously [13] and values are listed in Table 1. The rates of site exchange on the C_8H_8 ring are shown as first-order rate constants k_{ij} . The rate constants are composite pairs of the four possible metal migrations 1,2-, 1,3-, 1,4- and 1,5-metal shifts, denoted by α , β , γ and δ shifts, respectively [9] (Fig. 1). Inspection of these relationships (Table 1) shows that it is not possible to determine all four metal

* EXSY = exchange spectroscopy.

Table 1

Proton 2D-EXSY rate constants ^a due to metal migration in $[M(CO)_3(\eta^6-C_8H_8)]$ compounds

Temperature (°C)	Mixing time(s)	$\frac{k_{12}}{\alpha + \beta}$	$\frac{k_{13}}{\beta + \gamma}$	$\frac{k_{14}}{\gamma + \delta}$	$\frac{k_{23}}{\alpha + \delta}$	$\frac{k_{24}}{\beta + \gamma}$	$\frac{k_{34}}{\alpha + \beta}$	Rate constant errors
<i>M = W</i>								
0	3.0	0.038	0.011	0.0045	0.013	0.027	0.022	±0.01
10	0.8	0.27	0.14	0.028	0.12	0.14	0.28	±0.03
10 ^b	0.8	0.26	0.15	-0.0005	0.12	0.15	0.27	±0.02
15	0.8	0.50	0.53 ^c	0.014	0.20	0.27	0.51	±0.04
20	0.5	1.11	0.96 ^c	0.04	0.47	0.63	1.08	±0.09
<i>M = Cr</i>								
-10	0.6	0.35	0.43 ^c	-0.0014	0.12	0.31	0.34	±0.04
0	0.5	2.13	1.43 ^c	0.33	0.46	1.22	1.49	±0.35
0	0.2	2.00	1.83 ^c	0.053	0.45	1.36	1.57	±0.16

^a Units rate/s⁻¹. ^b Data from ¹³C 2D-EXSY experiment. ^c Peak overlap leads to larger errors in these values than those given in the Table.

migration rates from the experimental site-exchange rate constants. However, it will be observed that in all cases k_{14} ($= \gamma + \delta$) is zero within experimental error, thus enabling the α and β shift rates to be determined explicitly. These rates are shown in Table 2, together with the ΔG^\ddagger data calculated from the temperature dependencies of these shift rates.

Initially, the tungsten compound was studied at a temperature of 10°C and rate data were obtained from separate ¹H and ¹³C 2D-EXSY experiments. In view of the excellent agreement between both data sets (Table 1), indicative of negligible contributions to cross-peak intensities from ¹H-¹H cross-relaxation in the ¹H spectra, it was considered justified to determine all subsequent rates from ¹H EXSY experiments only. The consequent reduction in experimental time allowed a full set of variable temperature rate data to be obtained from the same sample before

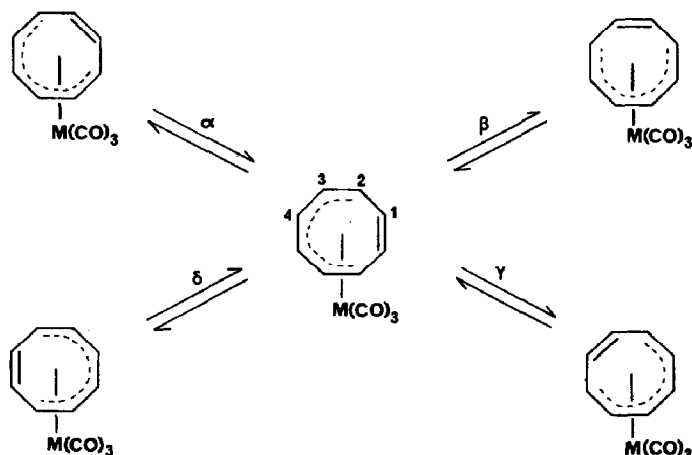


Fig. 1. The four possible metal migrations in $[M(CO)_3(\eta^6-C_8H_8)]$, namely 1,2-, 1,3-, 1,4-, and 1,5-metal shifts, denoted by α , β , γ , and δ shifts, respectively.

Table 2

Rates of 1,2- and 1,3-metal shifts ^a in $[\text{M}(\text{CO})_3(\eta^6\text{-C}_8\text{H}_8)]$

Temperature (°C)	1,2 shift (rate/s ⁻¹)	1,3 shift (rate/s ⁻¹)
<i>M</i> = <i>W</i>		
0	0.012	0.018
10	0.13	0.15
10 ^b	0.12	0.15
15	0.22	0.29
20	0.47	0.63
ΔG^\ddagger (298 K) (kJ mol ⁻¹)	72.4 ± 0.6	71.9 ± 0.4
<i>M</i> = <i>Cr</i>		
-10	0.078	0.27
0	0.53	1.29
0	0.44	1.35
ΔG^\ddagger (298 K) (kJ mol ⁻¹)	67.8	63.7

^a Rates marked *c* in Table 1 have not been used to calculate these rates. ^b Based on ¹³C 2D-EXSY data.

significant sample decomposition occurred. If ¹³C 2D-EXSY experiments had been employed, fresh solution samples would have been required for each temperature studied. The ¹H 2D-EXSY spectrum of $[\text{W}(\text{CO})_3(\eta^6\text{-C}_8\text{H}_8)]$ at 20 °C is shown in

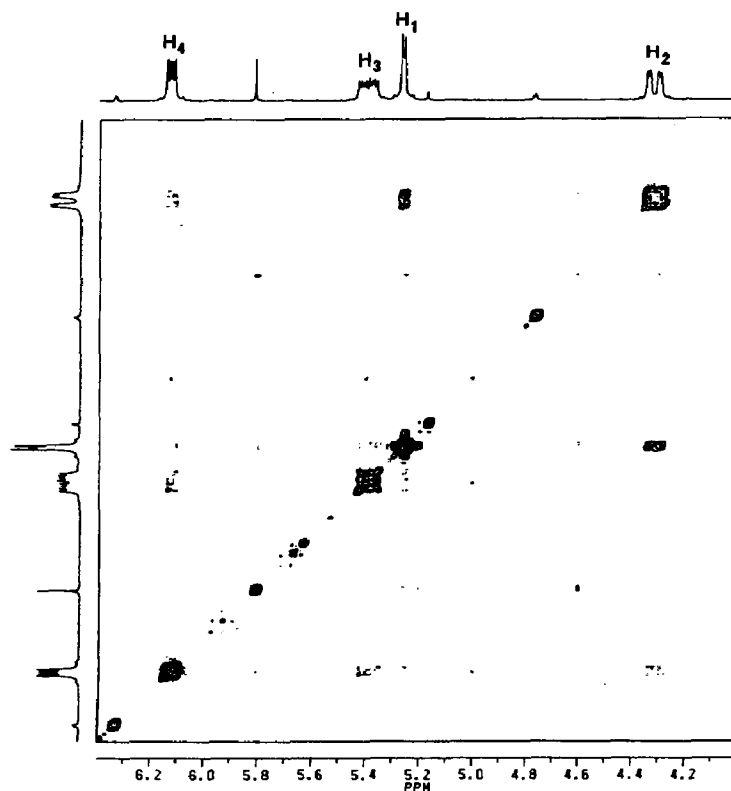


Fig. 2. The hydrogen-1 2D-EXSY spectrum of $[\text{W}(\text{CO})_3(\eta^6\text{-C}_8\text{H}_8)]$ at 20 °C showing the signal assignments.

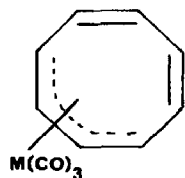
Fig. 2. The assignments are based on data from the previous study [8]. The relatively small internal chemical shift between the H(1) and H(3) protons in this compound, and more particularly in the chromium compound, increases somewhat the uncertainties associated with the k_{13} values. Also, in the case of the chromium complex, reliable rate data were restricted to a narrower temperature range.

We are, however, confident that the ΔG^\ddagger data (Table 2) accurately reflect the energies of the α (i.e. 1,2-) and β (i.e. 1,3-) metal migration pathways. The conclusions to be drawn are that for the tungsten complex both 1,2- and 1,3-metal shifts are equally favoured (within experimental errors), whereas for the chromium complex, both the activation energies are significantly lower, and the 1,3-metal shift is the energetically favoured mechanism. At a particular temperature, the rate of 1,3-metal shifts is approximately three times that of 1,2-metal shifts. Furthermore, these studies show that rates of 1,4- and 1,5-metal shifts are negligibly slow for both compounds. These conclusions are in general accord with the findings from the magnetisation transfer experiments [8,9]. They are, however, more definitive in that they are not based on assumptions regarding the spin-lattice relaxation rates of the exchanging nuclei, nor do they depend upon any iterative fitting procedure, which can have associated uncertainties arising from choice of the variables and restraints which are applied [9]. In addition, the temperature dependences of these rate constants have enabled activation energies for these 1,2- and 1,3-metal shift fluxions to be calculated for the first time.

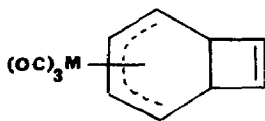
Discussion

According to the Woodward-Hoffmann rules [17] complexes containing a η^6 - C_8H_8 ligand should be "static" or have high fluxional activation energies. The sizeable ΔG^\ddagger values obtained here for $[M(CO)_3(\eta^6-C_8H_8)]$ ($M = Cr$ or W) are broadly in agreement with this prediction. However, their magnitudes are not excessively high, implying that the rules are not as rigidly applicable to organometallic systems as to organic systems, probably on account of the relative weakness of many M-C bonds compared with C-C or C-H bonds in organic species [18].

The intermediate previously proposed [7,8] to explain the fluxionality leading to both 1,2- and 1,3-metal shifts was the 16-electron η^4 - C_8H_8 species **1**. Such an intermediate, however, would be expected to be highly fluxional and, given finite existence of such a species, would rapidly rearrange by 1,4-shifts in addition to 1,2- and 1,3-shifts. The present work confirms the exclusive occurrence of 1,2- and 1,3-metal shifts in both the Cr and W complexes, and so weakens the argument in favour of a fluxion solely via an η^4 - C_8H_8 intermediate. An alternative to the η^4 - C_8H_8 species (**1**) is a bicyclo[4.2.0]octatriene intermediate (**2**) formed by inver-

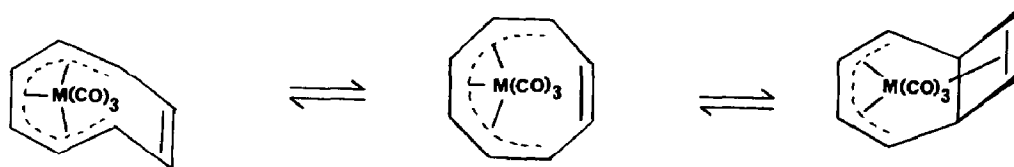


(1)



(2)

sion of the cyclooctatetraene ring (Scheme 1). This ring inversion process occurs via a planar (or near planar) intermediate, and seems unlikely to produce any bond shifts in the light of the energy data for ring inversion and bond shifting processes in uncoordinated cyclooctatetraene species [19]. The bicyclo intermediate can then ring-open in two ways to produce either 1,2- or 1,3-shifts. The arguments in favour of such an intermediate are that the metal can retain its favoured 18-electron structure and no 1,4- or 1,5-shifts are expected. Chemical evidence in support of such an intermediate comes from 1,2,3,4-tetramethylcyclo-octatetraene derivatives, for which the bicyclo[4.2.0]octatriene tautomer can be observed to be in equilibrium with the monocyclic cyclooctatetraene [19]. Furthermore, the iron tricarbonyl derivative of this ligand exists exclusively in the bicyclo form [20].



Scheme 1

The present results point to there being a very sensitive balance between 1,2- and 1,3-metal shift mechanisms such that the nature of the transition state intermediate(s) cannot be precisely defined. However, we defer further qualitative speculation on the matter, and simply present the new rate data for appraisal.

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