A Comparison of the Rates of Intramolecular Hydrogen Migration in the Molecules [Mo(η-C₇H₈)₂]ⁿ⁺ to give [Mo(η-C₇H₇)(η-C₇H₉)]ⁿ⁺, n = 0,1

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The new compound, Mo(η-C₇H₈)₂, rearranges thermally, in solution, to give Mo(η-C₇H₇)(η-C₇H₉) at a rate faster than that at which its 17-electron analogue, [Mo(η-C₇H₈)₂]BF₄ rearranges to give [Mo(η-C₇H₇)(η-C₇H₉)]BF₄.

Co-condensation of molybdenum atoms and cycloheptatriene (cht) gives air-sensitive green crystals of Mo(η-C₇H₈)₂, (**1**). This compound is thermally unstable and isomerizes quantitatively, as judged by visible and n.m.r. spectroscopy, to give the red compound Mo(η-C₇H₇)(η-C₇H₉), (**2**). Previously, (**2**) was reported to be the only product isolable from the reaction of molybdenum atoms and cht.[1]

Both (**1**) and (**2**) have been characterized fully by microanalysis, n.m.r. spectroscopy, and by crystal structure determination. Variable-temperature n.m.r. spectroscopy demonstrates that (**1**) is a fluxional molecule: the changes in its spectra are consistent with the occurrence of hindered rotation of the cht rings about the metal–ligand axis, with the molecule adopting, in the low-temperature limit, a conformation of C₂ symmetry.† Compounds (**1**) and (**2**) are oxidised by silver tetrafluoroborate to give the crystalline compounds [Mo(η-C₇H₈)₂]BF₄, (**3**), and [Mo(η-C₇H₇)(η-C₇H₉)]BF₄, (**4**), respectively; these have been characterized by microanalysis, e.s.r.,‡ and field-desorption mass spectrometry, and, for (**3**), by crystal structure determination. Cyclic voltammetry has been used to show that these oxidations are, electrochemically, quasi-reversible in tetrahydrofuran: E₁/₂ = +0.19 V for (**1**), +0.43 V for (**2**) vs. Pt quasi-reference/0.19 mol dm⁻³ Bu₄NPF₆.

Furthermore, (**3**) rearranges smoothly to give (**4**) in solution, in a process analogous to that for (**1**) (see Scheme 1). It was possible to monitor the rearrangements of (**1**) and (**3**) by visible absorption spectroscopy because, for both reactions, the spectra of starting material and product are well differentiated. Isosbestic points were maintained during the course of both transformations, over the temperature range 40—85 °C, from which it can be inferred that the concentration of any intermediates must be too low to be spectrally significant. Monitoring the conversion of (**1**) into (**2**) by n.m.r. spectroscopy allowed a similar conclusion to be reached. Kinetics were followed through to 80—90% conversion in all but the very slowest reactions (t₁/₂ > ca. 1 day), for which at least 50% was covered. Clean first-order kinetics were obeyed without exception, and representative rate data are given in Tables 1 and 2. The rates of the conversions were essentially insensitive to changes of solvent, to irradiation (by a medium-pressure Hg lamp) and, for (**3**), to a change of the counter-ion from BF₄⁻ to PF₆⁻. It is clear that (**3**) isomerizes considerably more *slowly* than (**1**), as is consistent with the activation-energy difference of 12 ± 3 kJ mol⁻¹.§

The perdeuterio-derivatives of (**1**)—(**4**) have been prepared starting from molybdenum atoms and C₇D₈.¶ They have been characterized, in particular, by comparison of their mass spectra with those of the protio-analogues. Thermal rearrangement of mixtures of (**1**) and [²H₁₆]-(**1**) produced only (**2**) and [²H₁₆]-(**2**); no H/D crossover could be detected by mass spectrometry. This was similarly established for the conversion of mixtures of (**3**) and [²H₁₆]-(**3**). These results show unequivocally that the migrations are indeed intramolecular. Moreover, similar values of kinetic isotope effect are observed (see Tables), which support the assertion that a common mechanism is operating.

We propose, on the basis of both the present observations and available analogies, that ring-to-ring migration of hydrogen proceeds via intermediate formation of a metal–hydrogen bond. Such a step could be rate determining; or it could occur in a fast equilibrium prior to slow hydrogen transfer from metal to carbon, in the product-forming stage. The kinetic isotope effects do not distinguish between these possibilities. Their values seem rather low for primary effects,

Scheme 1

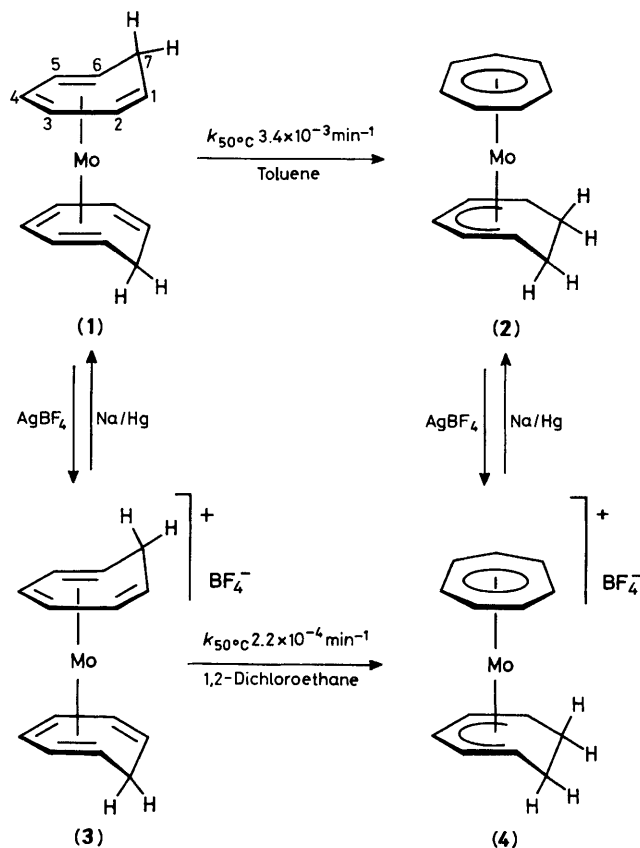
† 300 MHz ¹H N.m.r. ([²H₈]toluene) at 30 °C: 5.95 (br. s, 2H, 3-,4-H), 4.40 (br. s, 2H, 2-,5-H), 2.90 (br. s, 2H, 1-,6-H), 1.81 (m, 1H, 7-H-*endo*), 1.25 (br. d, 1H, 7-H-*exo*); at −60 °C: 6.71 (t, 1H, 3- or 4-H), 5.25 (t, 1H, 4- or 3-H), 5.32 (t, 1H, 2- or 5-H), 3.65 (t, 1H, 5- or 2-H), 3.11 (t, 1H, 6- or 1-H), 2.83 (d of t, 1H, 1- or 6-H), 1.87 (m, 1H, 7-H-*endo*), 1.42 (br. d, 1H, 7-H-*exo*). Bands due to 2-H and 5-H coalesce at 0 °C; this implies a barrier to rotation, ΔG 50 kJ mol⁻¹.

‡ <g> 1.98 for (**3**), 1.97 for (**4**).

§ The pre-exponential factors, A, in the Arrhenius expressions for the rates of the two processes differ slightly, but it is the exponential terms which are dominant in accounting for the difference in reactivity.

¶ [²H₈]cht was prepared from the CuCl-catalysed reaction of C₆D₆ and [²H₂]diazomethane.

Table 1. Rate data for the isomerization of (1) in toluene.[a]

$T/°C$	k/min^{-1}
40.5	$1.10 \pm 0.02 \times 10^{-3}$
54.5	$5.5 \pm 0.1 \times 10^{-3}$
68.9	$2.81 \pm 0.05 \times 10^{-2}$
73.1	$4.02 \pm 0.09 \times 10^{-2}$
81.6	$1.08 \pm 0.03 \times 10^{-1}$
51.2[b]	$4.1 \pm 0.1 \times 10^{-3}$
$E_{act.}$	$103 \pm 2\,kJ\,mol^{-1}$
$\log_{10}(A/min^{-1})$[c]	14.1 ± 0.3
k_H/k_D	$2.5 \pm 0.4\,(50\,°C)$

[a] $k = 3.78 \pm 0.07 \times 10^{-3}$ min^{-1} in cyclohexane at 54.5 °C. [b] Irradiation of sample with Hg lamp. [c] Parameters in the Arrhenius equation, $k = A\exp(-E_{act.}/RT)$.

Table 2. Rate data for the isomerization of (3) in 1,2-dichloroethane.[a]

$T/°C$	k/min^{-1}
44.0	$9.8 \pm 0.3 \times 10^{-5}$
50.0	$2.20 \pm 0.05 \times 10^{-4}$
59.6	$8.1 \pm 0.2 \times 10^{-4}$
69.3	$2.41 \pm 0.08 \times 10^{-3}$
83.2	$1.18 \pm 0.03 \times 10^{-2}$
67.3[b]	$1.82 \pm 0.06 \times 10^{-3}$
$E_{act.}$	$115 \pm 2\,kJ\,mol^{-1}$
$\log_{10}(A/min^{-1})$[c]	14.8 ± 0.3
k_H/k_D	$2.7 \pm 0.3\,(50\,°C)$

[a] $k = 2.8 \pm 0.1 \times 10^{-3}$ min^{-1} in tetrahydrofuran–1,2-dichloroethane (2/1 v/v) at 69.3 °C and $k = 2.6 \pm 0.1 \times 10^{-3}$ min^{-1} for PF_6^- analogue of (3) in 1,2-dichloroethane at 69.3 °C. [b] Irradiation of sample with Hg lamp. [c] Parameters in the Arrhenius equation, $k = A\exp(-E_{act.}/RT)$.

though this is not entirely unexpected when the transition states involved are highly non-linear,[2] as is likely to be the case in the present systems.

That the rearrangement of (3) should be slower than that of (1) contrasts sharply with many other studies on the isomerizations of corresponding 17- and 18-electron complexes, as, for instance of $M(CO)_2(dppm)_2^{n+}$, dppm = $Ph_2PCH_2PPh_2$, M = Cr, Mo, W; $n = 0,1$,[3] in which the oxidised forms have greatly enhanced reactivity. It is also well established that the rates of ligand substitution reactions are increased by one-electron oxidation of the substrate.[4] There can be envisaged a number of possible explanations, each consistent with our data, for the unexpected order of reactivity for (1) and (3). We at present favour a simple rationalization which, at a general level, accommodates the wider body of experimental observations.

Oxidation of 18-electron compounds removes a weakly bonding electron. In general, this would be expected to lead to a weakening of metal–ligand bonds, which, in turn, could account for the observed increases in ligand lability in both rearrangements and substitution reactions. The diminished reactivity of (3) could equally result from a slight increase in the metal–ring distance associated with removal of a weakly bonding electron because hydrogen transfer would be then less favoured than in (1). The crystal structures of (1) and (3) unfortunately show the occurrence of disorder, so that the bond distances obtained were not sufficiently accurate for a comparison to be made. However, bond lengthening is observable in other, related systems: metal–carbon distances

in, for example, the ferricenium cation are ca. 0.04 Å greater than in ferrocene itself,[5] and the effect would seem likely to operate in the present system as well. Photoelectron spectroscopy shows that the first ionisation potential of (2) is 5.62 eV; cf. 6.88 eV for ferrocene.[6]

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