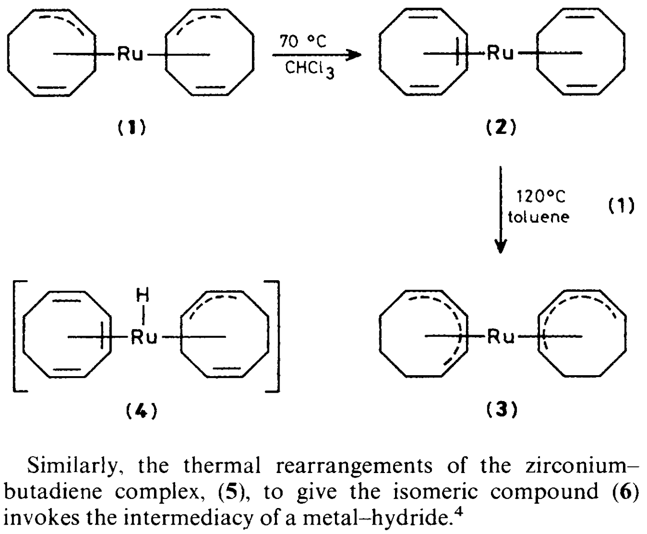
A Comparison of the Rates of Intramolecular Hydrogen Migration in the Molecules $[Mo(\eta\text{-}C_7H_8)_2]^{n+}$ to give $[Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_7H_9)]^{n+}$, n = 0 or 1: Crystal Structures of $[Mo(\eta\text{-}C_7H_8)_2]$, $[Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_7H_9)]$, and $[Mo(\eta\text{-}C_7H_8)_2][BF_4]$ *

Malcolm L. H. Green and Paul A. Newman
Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR
Judith A. Bandy
Chemical Crystallography Laboratory, 9 Parks Road, Oxford OX1 3PD

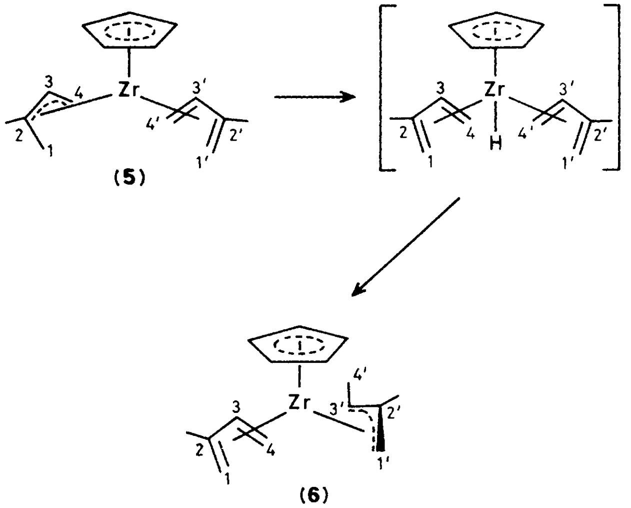
Co-condensation of molybdenum atoms with cycloheptatriene gives $[Mo(\eta\text{-}C_7H_8)_2]$ (**7**), which rearranges thermally to $[Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_7H_9)]$, (**8**). Oxidation of (**7**) gives the cation $[Mo(\eta\text{-}C_7H_8)_2]^+$, (**9**), which rearranges thermally to give $[Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_7H_9)]^+$, (**10**). The crystal structures of (**7**), (**8**), and (**9**) have been determined. The isomerizations of (**7**) to (**8**), and of (**9**) to (**10**) are clean, first-order, intramolecular processes, and, surprisingly, the rate of conversion of (**9**) to (**10**) ($E_{act.}$ = 115 kJ mol^{-1}) is slower than for the conversion of (**7**) to (**8**) ($E_{act.}$ = 101 kJ mol^{-1}).

Intramolecular rearrangements of hydrocarbon ligands are very common for organotransition metal compounds and normally involve the migration of hydrogens of the hydrocarbon ligands.[1] However, there have been few quantitative studies of such hydrogen migrations. The direct observation of hydrogen migration, or the detection of intermediate species is rare: presumably the activation barriers for these processes must in general be rather low.[2] It is also likely that degenerate or reversible shifts are common, but normally these are undetected.

The complex balance between kinetic and thermodynamic preferences in a sequence of rearrangements is exemplified by the ruthenium system in equation (1).[3] The bis(1—3:5—6-η-dienyl) compound, (**1**), undergoes isomerization to (**2**), then to the most stable complex, (**3**). It is probable that these conversions proceed *via* a common hydride species, (**4**).



Similarly, the thermal rearrangements of the zirconium–butadiene complex, (**5**), to give the isomeric compound (**6**) invokes the intermediacy of a metal–hydride.[4]



Related, but degenerate, (η-crotyl)–(η-butadiene) equilibria have been detected by dynamic n.m.r. spectroscopy in Nb,[5] Mo,[6] and Mn[7] systems. These few rearrangements illustrate the general class of metal-to-ligand hydrogen migration reactions. Other examples are: the interconversion of an (η-allyl)hydride complex and the corresponding η-propene species[2,8–12] and interconversion between η-cyclopentadienyl–hydrido compounds and isomeric η-cyclopentadienes.[13–15] In other cases, the metal-to-ring hydrogen shift forms a metal–hydrogen bond irreversibly.[16–19] The reverse reaction of transfer of M–H to a η-C_5H_5 ligand giving a η-cyclopentadiene ligand has also been observed[20] or has been proposed as an intermediate step.[21] Here we describe studies of hydrogen migrations of bis(η-C_7-ring) compounds of molybdenum. A preliminary communication of this work has appeared.[22]

Results and Discussion

Previous studies of the reactions of transition-metal vapours with cycloheptatriene have found, in all cases, that the products reflect the occurrence of hydrogen migration,[23,24] the stable η-C_7H_7 ligand being commonly observed in the products. In contrast, co-condensation of molybdenum atoms and cycloheptatriene gives the green, crystalline bis(triene) complex, $[Mo(\eta^6\text{-}C_7H_8)_2]$, (**7**).

Compound (**7**) is thermally unstable and undergoes quantitative isomerization, in the solid state or in solution, to give the previously described red compound, $[Mo(\eta\text{-}C_7H_7)(\eta^5\text{-}C_7H_9)]$,

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* Bis(η-cycloheptatriene)molybdenum, (η-cycloheptadienyl)(η-cycloheptatrienyl)molybdenum, and bis(η-cycloheptatriene)molybdenum tetrafluoroborate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: 1 eV = 1.6 × 10^{-19} J.

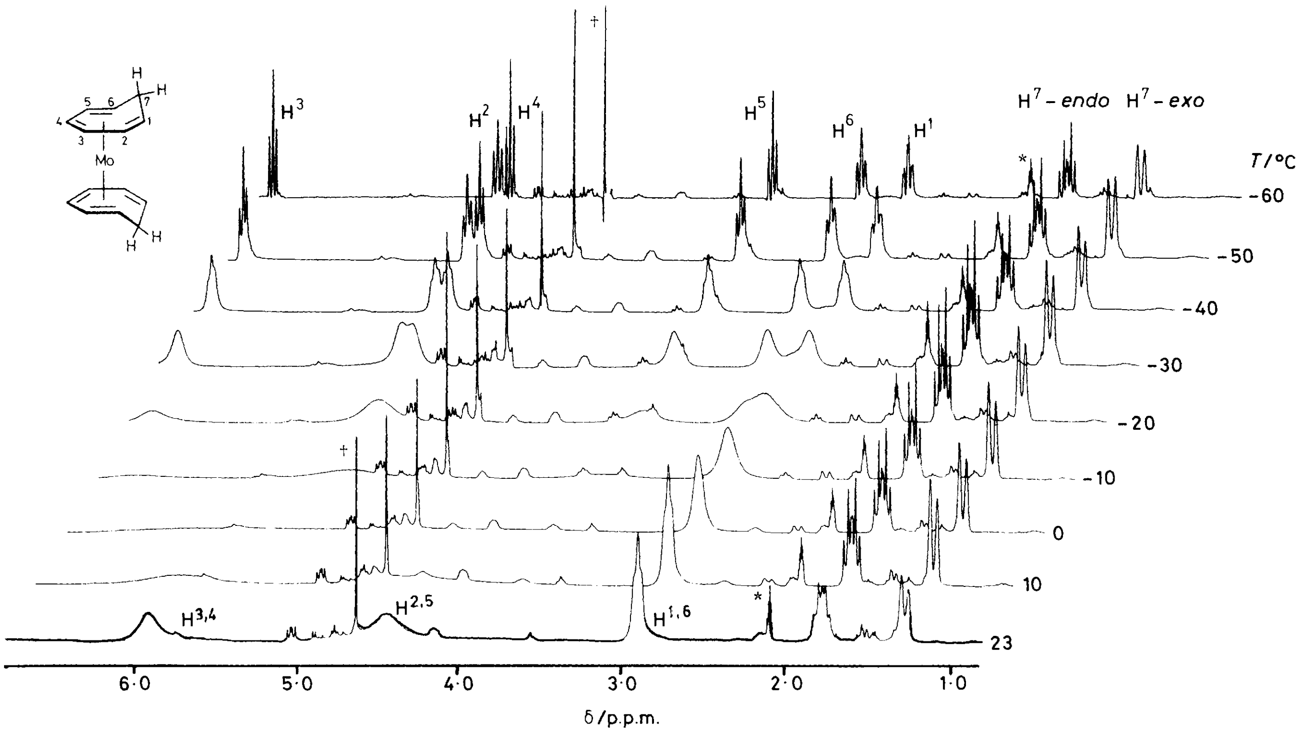


Figure 1. Variable-temperature ^{1}H n.m.r. spectra of (7) in [$^2H_8$] toluene: † indicates traces of (**8**), * indicates solvent

(**8**). This transformation is relatively slow at room temperature ($t_{\frac{1}{2}}$ *ca.* 200 h) and (**7**) can be isolated essentially pure at room temperature (r.t.). The ^{1}H n.m.r. spectrum of (**7**) (Figure 1) shows several broad bands indicating the molecule to be fluxional. Lowering the temperature further broadens these bands into the baseline and new bands reappear giving the low-temperature limit spectrum (at −60 °C) shown in Figure 1. There are also temperature-invariant bands at 1.3 and 1.8 p.p.m. which may be assigned to the methylene protons. The ^{1}H n.m.r. data are best accounted for by the occurrence of rotation about the metal–η-C_7-ring axis. The molecular conformation adopted at low temperature must be one that is skew with respect to the methylene groups, and can have, at most, C_2 symmetry, in order that the two rings should be equivalent but all protons within each ring inequivalent. At higher temperatures, the onset of ring rotation confers upon the molecule a quasi plane of symmetry that results in pairwise equivalencing of the ring protons. However, the fast-exchange limiting spectrum could not be attained even at 70 °C, above which temperature, the sample decomposed rapidly. Homonuclear decoupling experiments at −60 °C established the connectivity pattern between the eight protons of each ring. The assignments are given in the experimental section; the doublet at δ 1.8 is assigned to H^7-*endo* on the basis of chemical shift,[25] and the magnitude (2 Hz) of the vicinal coupling constant.[26]

Spin-saturation transfer studies show that irradiation of H^5 is accompanied by an *ca.* 70% decrease in the height of H^2, showing that site exchange must be occurring at a rate comparable to that of longitudinal relaxation at −60 °C. A reasonable estimate of the barrier to ring rotation can be made from the coalescence temperature for the H^2/H^5 pair (T_c = 0 °C). Their frequency separation in the slow-exchange limit (−60 °C) is 503.4 Hz. If the approximation is made that this value is essentially invariant then, from equation (2), a value of $k_{coal.}$ = 1 120 ± 20 s^{-1} can be calculated for the exchange process. According to the Eyring equation, (3), this corresponds to a free-energy barrier, $\Delta G^{\ddagger}$, of 50.7 ± 0.7 kJ mol^{-1}, a value closely similar to those observed in other η^6-cycloheptatriene complexes, such as [M(η-C_7H_8)$(CO)_3$], M = Cr, Mo, or W,[27] *e.g.* $\Delta G^{\ddagger}_{rot.}$ (kJ mol^{-1}) = 47.3 ± 0.8, M = Cr; 53.1 ± 0.8, M = Mo; and 48.1 ± 1.3, M = W.

$$k_{coal.} = \pi\Delta\nu/\sqrt{2} \qquad (2)$$

$$\Delta G = \frac{-RT\ln(Nhk)}{RT} \qquad (3)$$

The ^{13}C n.m.r. spectra of (**7**) support the above conclusions. We note that the methylene carbon is coupled equally to the *exo-* and *endo*-hydrogens and the value of *J*(C–H) is 133 Hz, which indicates that an agostic[28] ground-state structure for (**7**) is most unlikely.

The room-temperature, magic-angle spinning, solid-state ^{13}C n.m.r. spectrum of (**7**) is very similar to the solution spectrum, which is consistent with a rapid ring rotation in the crystalline lattice. Intramolecular motion of this kind in the solid state is well known for other sandwich compounds.[29]

Cyclic voltammograms of (**7**) and (**8**), recorded in tetrahydrofuran (thf), with 0.19 mol dm^{-3} $[NBu_4]PF_6$ as supporting electrolyte, are shown in Figure 2. Both molecules undergo reversible one-electron oxidations: (**7**) at $E_{\frac{1}{2}}$ = 0.19 and (**8**) at $E_{\frac{1}{2}}$ = 0.43 V relative to a Pt quasi reference electrode {−0.43 and −0.19 V respectively relative to the [Fe(η-C_5H_5)$_2$]–[Fe(η-C_5H_5)$_2$]$^+$ ion couple}. The one-electron oxidations of (**7**) and (**8**) were achieved chemically by treating them with silver tetrafluoroborate in tetrahydrofuran, giving the crystalline salts, [Mo(η-C_7H_8)$_2$][BF_4], (**9**), and [Mo(η-C_7H_7)(η-C_7H_9)][BF_4], (**10**), respectively.

The e.s.r. spectra of (**9**) and (**10**) each show a single, rather broad resonance with ^{95}Mo/^{97}Mo satellites, consistent with the seventeen-electron formulation. Field-desorption (f.d.) mass spectra, in both cases, show the expected parent cation (base peak at m/z = 282), with the associated isotopomer envelope.

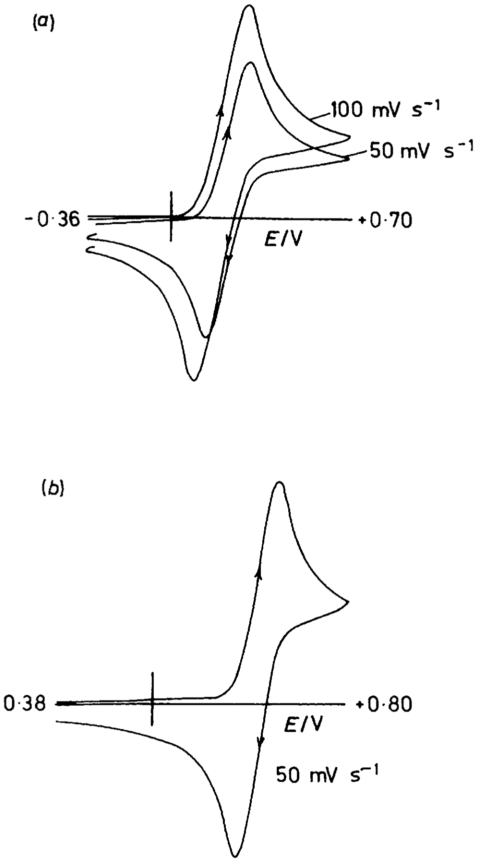


Figure 2. Cyclic voltammograms of (*a*) (**7**) and (*b*) (**8**)

Reduction of (**9**) and (**10**) back to the corresponding neutral molecules could be effected with 1% sodium amalgam. Conversion of (**9**) to (**7**) appeared to be quantitative (^{1}H n.m.r.). However, the reduction of (**10**) was accompanied by partial degradation of either the starting material or the product: the ^{1}H n.m.r. spectrum of the product indicated the presence of a substantial proportion of free cycloheptatriene.

Crystal Structure Determinations.—The molecular structure of (**7**) has been determined by *X*-ray diffraction methods and is shown in Figure 3[30] with bond lengths and angles given in Table 1(*a*). The molecule has crystallographic $\bar{1}$ symmetry but the cycloheptatriene ring is disordered and two partial occupancy orientations were found and refined subject to restraints. It appears that, in fact, we have seven-fold disorder of the rings but the model which was refined led to an acceptable agreement with observations, though the precision of the derived parameters is not sufficiently high to justify detailed examination. On average, the cycloheptatriene rings in an individual molecule are staggered and parallel. The molybdenum is found to be 1.69 and 1.71 Å out of the planes defined by the two alternative orientations of the cycloheptatriene rings, respectively. Atoms C(7) and C(107) deviate from these rings, away from molybdenum, by 0.26 and 0.23 Å, which is closer than observed in [Mo(η-C_7H_8)(CO)$_3$][31] (0.67 Å) and again indicative of disorder.

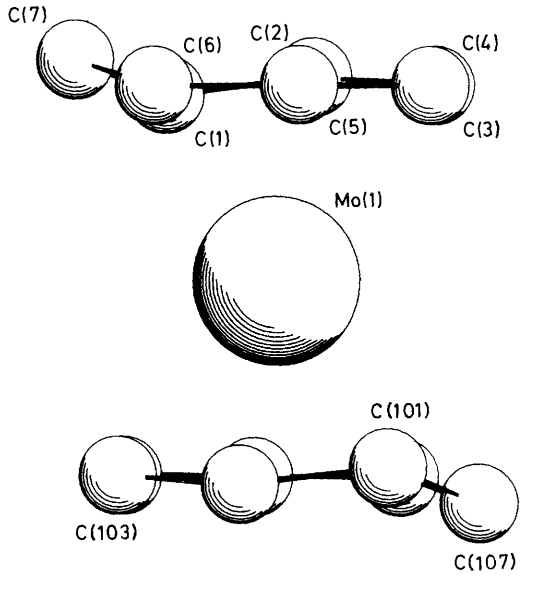


Figure 3. The molecular structure of (**7**). Only one orientation of the disordered ligand is shown and hydrogen atoms are omitted

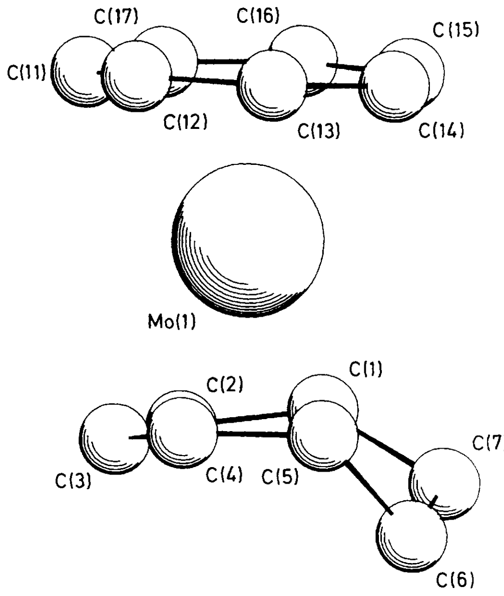


Figure 4. The molecular structure of (**8**)

The *X*-ray crystal structure of (**8**) has also been determined; the molecular structure being shown in Figure 4 and bond lengths and angles given in Table 1(*b*). The central molybdenum atom is sandwiched by the conventionally bound η^7-C_7H_7 and η^5-C_7H_9 rings. The former is a planar, regular seven-membered ring at a perpendicular distance of 1.591 Å from molybdenum. The perpendicular from Mo(1) intersects the ring at its centroid. The C_7H_9 ring is tilted with the distances from molybdenum to the terminal carbons of the C(1)—C(5) moiety being markedly longer than those to the internal carbons. The molybdenum is 1.783 Å from the plane defined by C(1)—C(5) with C(6) and C(7) being 1.093 and 0.701 Å respectively out of the plane, away from Mo(1).

The molecular structure of the cation (**9**) is shown in Figure 5 with bond lengths and angles in Table 1(*c*). The averaged structure has crystallographic mirror symmetry, but during refinement difference Fourier syntheses on a tightly restrained model indicated that the methylene groups of each molecule were disordered over all carbon sites. The C_7H_8 rings are found to be eclipsed [unlike (**7**)] and parallel (interplanar angle 0.6°)

Table 1. Bond lengths (Å) and angles (°)

(*a*) For (**7**). [Equivalent carbons in the two disordered orientations differ in serial number by 100.]

Mo(1)–C(1)	2.276(19)	Mo(1)–C(101)	2.370(14)	C(1)–C(2)	1.327(16)	C(101)–C(102)	1.331(16)
Mo(1)–C(2)	2.321(18)	Mo(1)–C(102)	2.333(18)	C(2)–C(3)	1.425(16)	C(102)–C(103)	1.402(15)
Mo(1)–C(3)	2.262(20)	Mo(1)–C(103)	2.310(15)	C(3)–C(4)	1.354(16)	C(103)–C(104)	1.382(15)
Mo(1)–C(4)	2.318(16)	Mo(1)–C(104)	2.281(18)	C(4)–C(5)	1.401(16)	C(104)–C(105)	1.396(15)
Mo(1)–C(5)	2.354(19)	Mo(1)–C(105)	2.369(17)	C(5)–C(6)	1.329(17)	C(105)–C(106)	1.323(16)
Mo(1)–C(6)	2.373(20)	Mo(1)–C(106)	2.318(23)	C(6)–C(7)	1.494(16)	C(106)–C(107)	1.498(17)
				C(7)–C(1)	1.484(16)	C(107)–C(101)	1.501(16)

C(7)–C(1)–C(2)	129.1(15)	C(3)–C(4)–C(5)	126.4(11)	C(107)–C(101)–C(102)	131.1(13)	C(103)–C(104)–C(105)	128.0(12)
C(1)–C(2)–C(3)	129.4(13)	C(4)–C(5)–C(6)	130.0(10)	C(101)–C(102)–C(103)	130.2(12)	C(104)–C(105)–C(106)	127.9(13)
C(2)–C(3)–C(4)	129.0(10)	C(5)–C(6)–C(7)	133.0(10)	C(102)–C(103)–C(104)	128.2(11)	C(105)–C(106)–C(107)	133.2(12)
		C(6)–C(7)–C(1)	115.7(14)			C(106)–C(107)–C(101)	115.8(14)

(*b*) For (**8**)

Mo(1)–C(1)	2.359(7)	Mo(1)–C(11)	2.244(8)	C(1)–C(2)	1.396(12)	C(11)–C(12)	1.385(16)
Mo(1)–C(2)	2.302(6)	Mo(1)–C(12)	2.279(8)	C(2)–C(3)	1.412(11)	C(12)–C(13)	1.384(15)
Mo(1)–C(3)	2.298(7)	Mo(1)–C(13)	2.262(7)	C(3)–C(4)	1.413(11)	C(13)–C(14)	1.390(15)
Mo(1)–C(4)	2.281(8)	Mo(1)–C(14)	2.249(7)	C(4)–C(5)	1.362(11)	C(14)–C(15)	1.409(17)
Mo(1)–C(5)	2.370(7)	Mo(1)–C(15)	2.257(9)	C(5)–C(6)	1.506(11)	C(15)–C(16)	1.403(18)
		Mo(1)–C(16)	2.254(10)	C(6)–C(7)	1.500(13)	C(16)–C(17)	1.361(19)
		Mo(1)–C(17)	2.242(10)	C(7)–C(1)	1.503(12)	C(17)–C(11)	1.384(19)

C(7)–C(1)–C(2)	129.1(7)	C(4)–C(5)–C(6)	122.6(6)	C(17)–C(11)–C(12)	127.2(10)	C(14)–C(15)–C(16)	126.9(10)
C(1)–C(2)–C(3)	127.6(7)	C(5)–C(6)–C(7)	113.6(7)	C(11)–C(12)–C(13)	129.2(9)	C(15)–C(16)–C(17)	130.0(10)
C(2)–C(3)–C(4)	124.8(7)	C(6)–C(7)–C(1)	112.8(7)	C(12)–C(13)–C(14)	129.4(9)	C(16)–C(17)–C(11)	129.5(10)
C(3)–C(4)–C(5)	121.1(7)			C(13)–C(14)–C(15)	127.6(9)		

(*c*) For (**9**)

Mo(1)–C(1)	2.375(6)	Mo(1)–C(5)	2.371(6)	C(1)–C(1′)	1.379(9)	C(5)–C(5′)	1.395(9)
Mo(1)–C(2)	2.327(5)	Mo(1)–C(6)	2.315(5)	C(1)–C(2)	1.393(7)	C(5)–C(6)	1.388(7)
Mo(1)–C(3)	2.289(5)	Mo(1)–C(7)	2.337(6)	C(2)–C(3)	1.382(7)	C(6)–C(7)	1.396(7)
Mo(1)–C(4)	2.349(9)	Mo(1)–C(8)	2.293(9)	C(3)–C(4)	1.395(6)	C(7)–C(8)	1.392(7)

C(1′)–C(1)–C(2)	129.1(3)	C(2)–C(3)–C(4)	128.4(6)	C(5′)–C(5)–C(6)	128.6(4)	C(6)–C(7)–C(8)	128.4(7)
C(1)–C(2)–C(3)	127.8(6)	C(3)–C(4)–C(3′)	128.4(8)	C(5)–C(6)–C(7)	128.4(6)	C(7)–C(8)–C(7′)	128.4(9)

B(1)–F(1)	1.351(9)	B(1)–F(3)	1.349(8)	B(1)–F(11)	1.371(9)	B(1)–F(13)	1.358(9)
B(1)–F(2)	1.376(9)			B(1)–F(12)	1.345(9)		

F(1)–B(1)–F(2)	110.2(5)	F(2)–B(1)–F(3)	109.7(4)	F(11)–B(1)–F(12)	109.8(5)	F(12)–B(1)–F(13)	110.6(5)
F(1)–B(1)–F(3)	111.4(4)	F(3)–B(1)–F(3′)	104.2(9)	F(11)–B(1)–F(13)	109.8(4)	F(13)–B(1)–F(13′)	106.2(12)

Atoms denoted by primes are generated by symmetry operator $x, \frac{1}{2} - y, z$; equivalent fluorines in the disordered $[BF_4]^-$ differ in serial number by 10.

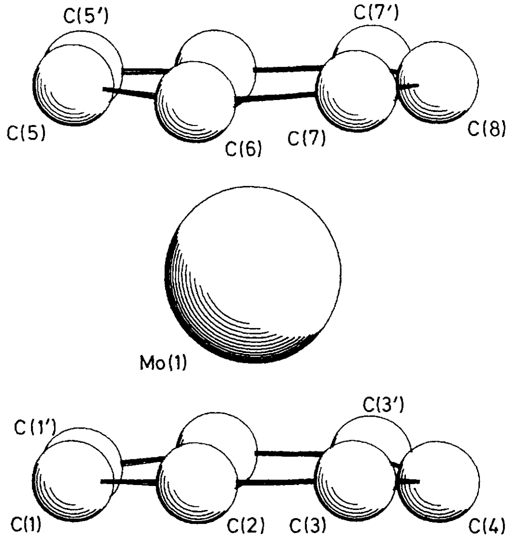


Figure 5. The molecular structure of the cation (**9**)

with the perpendicular distances to Mo(1) being 1.70 Å for the two rings, respectively. It is not possible to say from our results whether the removal of one electron from the $Mo(C_7H_8)_2$ system has resulted in geometrical changes (see below).

Bearing in mind the disorder observed for (**7**) and (**9**), we observe no intermolecular contacts for (**7**), (**8**), or (**9**) shorter than the sum of van der Waals radii. For (**9**) the closest cation–anion separation is 3.075 Å to the $[BF_4]^-$ anion generated from that in the asymmetric unit by the operator $x, y, z - 1$.

Kinetic Studies.—The thermal rearrangement of (**7**) to give the hydrogen-migrated compound (**8**) was monitored by ^1H n.m.r. spectroscopy. This showed that the reaction is indeed quantitative, and that no intermediates (in particular, metal–hydride species) are detected. Similarly, $[Mo(\eta\text{-}C_7H_8)_2][BF_4]$, (**9**) rearranges correspondingly in 1,2-dichloroethane solutions to give $[Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_7H_9)][BF_4]$, (**10**) and the visible absorption spectrum of the product (450—800 nm) is identical, within experimental error, to that of pure (**10**).

The rearrangements of (**7**) and (**9**) were most conveniently monitored quantitatively by visible absorption spectroscopy because, for both reactions, the spectra of starting material and

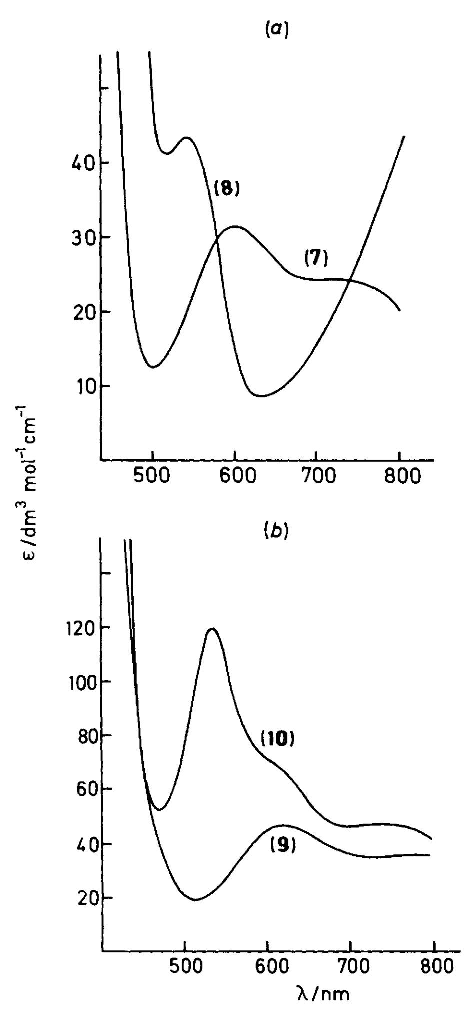


Figure 6. Visible absorption spectra of (*a*) (**7**) and (**8**) in cyclohexane, and (*b*) (**9**) and (**10**) in 1,2-dichloroethane

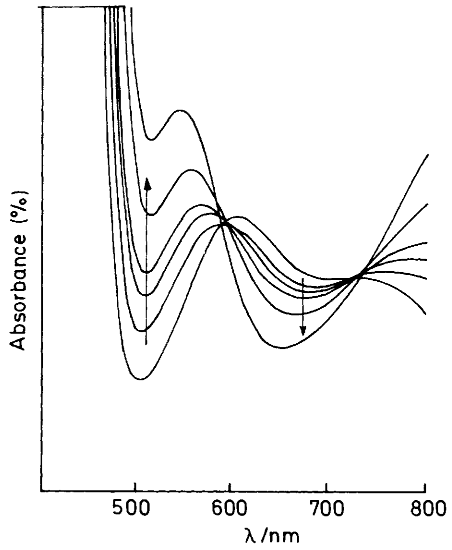


Figure 7. Successive visible absorption spectra during conversion of (**7**) to (**8**), at 40.5 °C in toluene

Table 2. Rate data for the isomerization of (*a*) (**7**) in toluene, and (*b*) (**9**) in 1,2-dichloroethane

T/°C	k/min^{-1}
(*a*)	
40.5	$(1.16 \pm 0.02) \times 10^{-3}$
54.4	$(5.6 \pm 0.1) \times 10^{-3}$
68.9	$(2.83 \pm 0.05) \times 10^{-2}$
73.1	$(3.97 \pm 0.09) \times 10^{-2}$
81.6	0.107 ± 0.007
(*b*)	
44.0	$(9.8 \pm 0.3) \times 10^{-5}$
50.0	$(2.2 \pm 0.05) \times 10^{-4}$
59.6	$(8.1 \pm 0.2) \times 10^{-4}$
69.3	$(2.4 \pm 0.08) \times 10^{-3}$
83.2	$(1.18 \pm 0.03) \times 10^{-2}$

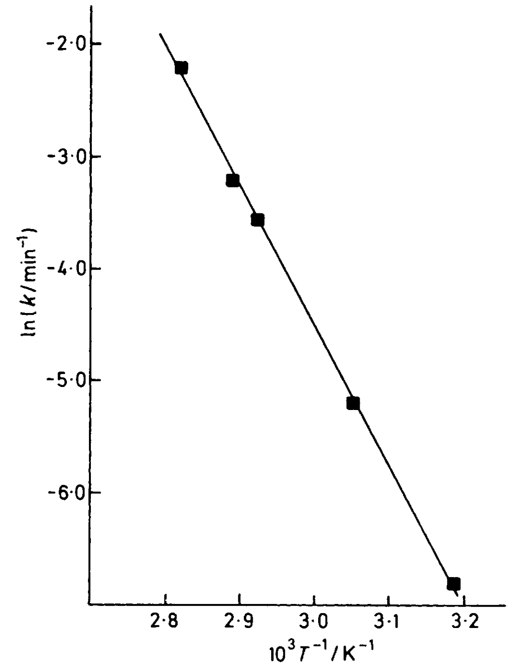


Figure 8. Arrhenius plot for the rates of conversion of (**7**) to (**8**) in toluene

product are well differentiated (Figure 6). In Figure 7 are shown successive spectra recorded during the isomerization of (**7**) in toluene. Isosbestic points occur at 590 and 730 nm. These were maintained throughout the course of the reactions provided conditions were rigorously anaerobic. The inference is that the concentration of any intermediates formed during the isomerization is too low to be spectroscopically significant.

In the temperature range *ca.* 40—80 °C the conversion of (**7**) into (**8**) was kinetically first order. Rate constants derived from these experiments are summarized in Table 2(*a*). The Arrhenius plot corresponding to these data was linear (Figure 8), and gave the activation parameters, $E_{\text{act.}} = 101.3 \pm 1.8$ kJ mol^{-1} and $\ln(A/\text{min}^{-1}) = 32.0 \pm 0.4$. From these it can be calculated that: $\Delta H^{\ddagger} = 99 \pm 2$ kJ mol^{-1}, $\Delta S^{\ddagger} = -13 \pm 5$ J K^{-1} mol^{-1}, and $\Delta G^{\ddagger} = 103 \pm 3$ kJ mol^{-1} at 50 °C.

The rate of reaction when the sample was irradiated [$k = (4.1 \pm 0.1) \times 10^{-3}$ min^{-1} at 51.2 °C] was equal, within experimental error, to the rate in the absence of photolysis ($k_{51.2} =$

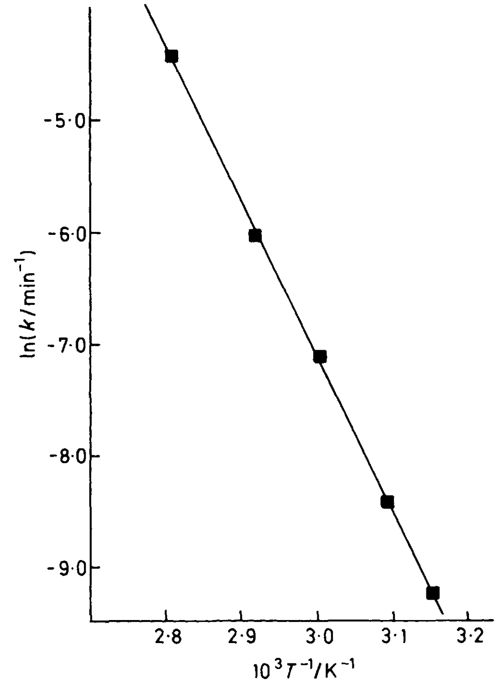


Figure 9. Arrhenius plot for the rates of conversion of (**9**) to (**10**) in 1,2-dichloroethane

4.0×10^{-3} min^{-1}). The isomerization cannot, therefore, be appreciably photocatalysed. The rate determined in cyclohexane [$k = (3.78 \pm 0.07) \times 10^{-1}$ min^{-1} at 54.5 °C] was only marginally slower than the corresponding value in toluene. The dielectric constants of these two solvents are 1.9 and 4.2 respectively, so this comparison involves only a rather modest change in the medium. The observation is nevertheless consistent with there being only a small degree of charge separation in the rate-limiting transition state for hydrogen migration.

The rate of isomerization of the perdeuterio analogue of (7), *viz*. [Mo(η-C_7D_8)$_2$], at 40.5 °C was $(4.4 \pm 0.3) \times 10^{-1}$ min^{-1}. This gives a value for the isotope effect, k_H/k_D, of 2.16 ± 0.3 (uncorrected for the small effect of incomplete deuteration in [$^2H_{16}$](M)). The kinetics of isomerization of [Mo(η-C_7H_8)$_2$][BF_4] (**9**) in 1,2-dichloroethane were determined in an essentially analogous manner as for the isomerization of (7).

Kinetics of the conversion of (**9**) into (**10**) were first order in the temperature range *ca*. 45—85 °C [see Table 2(*b*)]. The absence of kinetic complication and the appearance of a satisfactorily maintained isosbestic point imply, once again, that the relative concentration of intermediates formed during the isomerization must be very low: these criteria establish a likely upper bound of *ca*. 5%. The Arrhenius plot, given in Figure 9 provides the activation parameters, $E_{act.} = 114.7 \pm 1.8$ kJ mol^{-1} and $\ln(A/\text{min}^{-1}) = 34.0 \pm 0.5$. These lead to the values: $\Delta H^{\ddagger} = 112 \pm 2$ kJ mol^{-1}, $\Delta S^{\ddagger} = 3 \pm 4$ J K^{-1} mol^{-1}, and $\Delta G^{\ddagger} = 111 \pm 3$ kJ mol^{-1} at 50 °C.

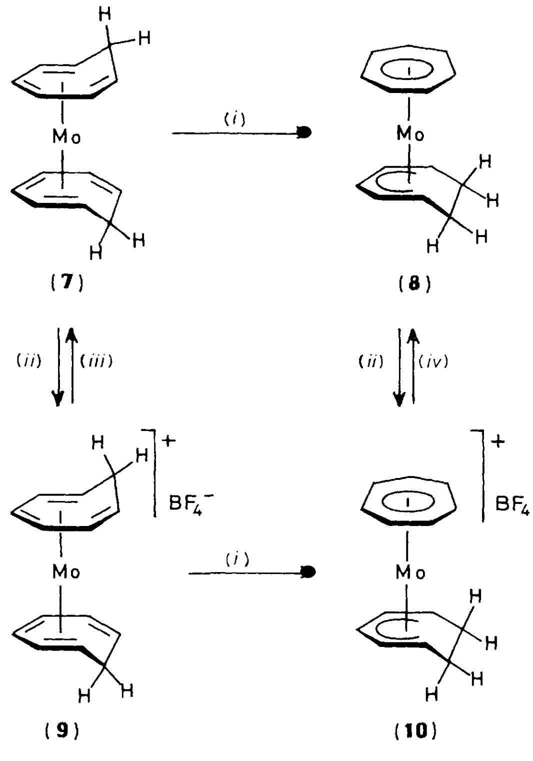
The rate of reaction in 1,2-dichloroethane when the sample was irradiated [$k = (1.82 \pm 0.06) \times 10^{-1}$ min^{-1} at 67.3 °C] was equal, within experimental uncertainty, to the rate in the absence of irradiation ($k = 1.92 \times 10^{-1}$ min^{-1}). A change of solvent, to the less polar medium, tetrahydrofuran—1,2-dichloroethane (2:1; v/v), caused only a negligible change in reaction rate [$k = (2.8 \pm 0.1) \times 10^{-1}$ min^{-1} at 69.3 °C]. Comparisons involving more radical changes in solvent were precluded because of the instability of (**9**) in more polar media such as acetone. A change of the counter ion of (**9**) to [PF_6]$^-$ similarly brought about only a very slight change in reactivity [$k_{PF_6} = (2.6 \pm 0.1) \times 10^{-3}$ min^{-1} at 69.3 °C], suggesting that the counter ion is entirely 'innocent' in the isomerization. The rate of isomerization of the perdeuterio analogue of (**9**), [Mo(η-C_7D_8)$_2$][BF_4], was $(4.8 \pm 0.4) \times 10^{-3}$ min^{-1} at 83.2 °C, which implies a value for the hydrogen isotope effect, k_H/k_D, of 2.5 ± 0.3.

In order to establish whether the isomerization reactions were inter- or intra-molecular, crossover experiments were carried out. Comparison of the electron-impact mass spectrum of the hydrogen-migrated neutral compound, formed from the thermal rearrangement of (7), with the theoretical spectrum for $C_{14}H_{16}Mo$ shows that much of (**8**) survives electron impact as the molecular ion, but that there is a degree of fragmentation involving loss of hydrogen to give $[M - H]^+$ and $[M - 2H]^+$, amongst others. The mass spectrum of the material obtained from thermal rearrangement of ostensibly perdeuterated (7) shows that no scrambling of deuterium into (**8**), or of protium into [$^2H_{16}$](**8**) has occurred. This implies that the hydrogen migration reaction is intramolecular.

The conclusion is valid despite the incomplete deuteration of nominally perdeuterio-(7), because the proportion of the [$^2H_{16}$] isotopomer is high enough to guarantee detectable crossover.

A corresponding crossover experiment involving (**9**) and [$^2H_{16}$](**9**) gave an entirely similar result. The field-desorption mass spectrum of the rearrangement products of (**10**) and [$^2H_{16}$](**10**) showed there had been no intermolecular scrambling of the label. The presence of any [$^2H_{16}$](**10**), which would indicate an intermolecular migration, would be very obvious and was not detectable. The rearrangement of (**9**) is therefore an intramolecular process.

Discussion.—The relationships between the compounds (7), (**8**), (**9**), and (**10**) are shown in the Scheme.



Scheme. (*i*) In toluene at 70 °C for 6 h, >99%; (*ii*) $AgBF_4$ in thf at r.t., 80%; (*iii*) Na/Hg (1%) in thf for 3 h, 65%; (*iv*) Na/Hg (1%) in thf for 3 h, 40%

Despite the fact that hydrogen-migration processes are so very widespread in transition-metal chemistry, studies in which they have been directly identified and examined kinetically have arisen only rarely. Even less often has the opportunity existed to examine the effect of removing an electron from the substrate on its migration reaction.

The above studies show that the molecules $[Mo(\eta\text{-}C_7H_8)_2]^{n+}$, $n = 0$ or 1, undergo intramolecular rearrangements involving ring-to-ring hydrogen migration to give $[Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_7H_9)]^{n+}$. Qualitatively, these reactions are remarkably similar in form: both are completely intramolecular and kinetically first order; both are insensitive in rate to changes of solvent and to irradiation. Furthermore, the two reactions have values of hydrogen kinetic isotope effect that are equal within experimental error. [When extrapolated to a standard temperature, 50 °C, $k_H/k_D = 2.5 \pm 0.3$ for (**7**), 2.7 ± 0.3 for (**9**)]. These observations are strong support for the assertion that correspondingly similar mechanisms operate in the two systems. We propose, on the basis of the results of this study and available analogies, that ring-to-ring migration of hydrogen proceeds *via* the intermediate formation of a metal–hydrogen bond. Implicit is the presumption that it is the *endo* hydrogen which is transferred to the metal, because the overall shift is an intramolecular one. Various hypothetical structures can be formulated for such a metal–hydride; the kinetic data do not distinguish between these possibilities, nor do spectroscopic techniques help, because, certainly, no intermediates can be detected during the rearrangements. The electron count of the metal remains at 18, in the case of (**7**), or 17 in the case of (**9**), only if formation of the Mo–H bond is accompanied by a reduction in ring hapticity: this might involve an incipient $\eta^5\text{-}C_7H_7$ ring or an $\eta^4\text{-}C_7H_8$ ring. The generation of co-ordination sites by 'ring-slipping' is a feature invoked frequently in the substitution reactions of η-cyclopentadienyl- and η-arene-metal complexes.[32] The formation of the metal–hydride species could be rate determining; or it could occur in a fast equilibrium prior to slow hydrogen transfer from the metal to the remaining C_7H_8 ring, in the product-forming step, *i.e.*,

$$[Mo(\eta\text{-}C_7H_8)_2]^{n+} \xrightarrow{\text{slow}} [Mo\text{-}H] \xrightarrow{\text{fast}} [Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_7H_9)]^{n+}$$

or

$$[Mo(\eta\text{-}C_7H_8)_2]^{n+} \xrightarrow{\text{fast}} [Mo\text{-}H] \xrightarrow{\text{slow}} [Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_7H_9)]^{n+}.$$

In the latter case, the pre-equilibrium would clearly have to favour the starting compound, since the build-up of any intermediates has been ruled out; the kinetic form would nevertheless still be first order and therefore indistinguishable from that of the former case. The kinetic isotope effects, because of their magnitudes, also do not distinguish between these possibilities. Rate-limiting transfer of the *endo*-H to the metal would give rise to an isotope effect composed of a primary effect, from C–H bond breaking, and a secondary one, from rehybridization of the methylene carbon. The pre-equilibrium path, on the other hand, would have an isotope effect composed of an equilibrium effect, and a primary kinetic one, due to Mo–H bond breaking. In the absence of suitable model reactions from which to make reasonable estimates of these various components, it is not possible to draw meaningful conclusions from the value of the isotope effects. We note, however, that low primary effects ($k_H/k_D \sim 2$—3) are not unexpected when the transition state for hydrogen transfer is highly non-linear.[33]

Some important analogies can be drawn between the hydrogen migrations in (**7**) and (**9**), and the reversible ring-to-metal hydrogen transfer that occurs in the tricarbonyl complex, $[Mo(\eta\text{-}C_7H_8)(CO)_3]$ (**11**). It is known that thermolysis of (**11**) induces degenerate sigmatropic shifts of the *endo*-methylene hydrogen around the cycloheptatriene ring.[34,35] That it is the *endo*-hydrogen that migrates has been deduced unequivocally from deuterium-labelling studies.[34] The involvement of the metal–hydride intermediate, $[MoH(\eta^5\text{-}C_7H_7)(CO)_3]$, has been proposed since it provides the most logical explanation for the stereochemistry, and indeed the facility, of migration. Moreover, Brown *et al.*[35] have shown, by using a ^{13}C-labelled ring in (**11**), that the migration takes place by stereospecific [1,5]-hydride shifts. This implies that return of the hydrogen to the ring in (**11**) occurs only to the terminal positions of the η^5-unit (*viz.* C^4 and C^7). Hydride return must, then, also be faster than any fluxional process of the η^5-trienyl ring, which would destroy the integrity of the labelling, and lead merely to random shifts. Evidence for the formation of $[MoH(\eta^5\text{-}C_7H_7)(CO)_3]$ from (**11**) has been obtained additionally by infrared spectroscopic studies of low-temperature matrices formed by condensation of (**11**) with an inert gas onto a cold probe.[36] All these observations add support to the mechanistic picture proposed for the migration reactions in (**7**) and (**9**), and reassert the possibility that, in these systems, reversal of the initial ring-to-metal hydrogen transfer may be competitive with the product-forming shift.

The most important difference between the migration reactions of (**7**) and (**9**) is that of reactivity: the rearrangement of (**9**) is considerably slower than that of (**7**) (by a factor of 16 at 50 °C), as is reflected in the activation-energy difference of 14 kJ mol^{-1}. The entropies of activation also differ slightly, though the large error limits on these parameters diminish the significance of this observation. For intramolecular rearrangements, we expect values of $\Delta S^\ddagger$ that are relatively small in magnitude, as is certainly the case for both (**7**) and (**9**). Clearly, the 17-electron cation, (**9**), is only slightly less reactive than its 18-electron analogue, (**7**). Yet this result contrasts completely with the normal pattern: studies on a wide range of rearrangement reactions show that, in general, 17-electron compounds have greatly enhanced reactivity (often by many orders of magnitude) relative to the corresponding 18-electron species. Catalysis of reactions by electron transfer (e.t.c.), which is based on this phenomenon, is being utilized increasingly in synthesis, in order to effect transformations thermally inaccessible to 18-electron molecules themselves.[37] Thus the 17-electron complexes, *fac*-$[Mo(CO)_3P_3]^+$ [P = $P(OPh)_3$, PMe_2Ph, or $PPh_2(CH_2Ph)$] rapidly undergo intramolecular isomerization to give *mer*-$[Mo(CO)_3P_3]^+$, whereas interconversion between the corresponding 18-electron compounds is either very slow or does not occur at all.[38] Entirely analogous observations of the effect of oxidation on lability have arisen from studies on the *cis–trans* isomerizations of $[M(CO)_2(P\text{–}P)_2]$ [M = Cr, Mo, or W; P–P = $Ph_2P(CH_2)_nPPh_2$, $n = 1$, 2, or 3],[39] $[Mo(CO)_4(PR_3)_2]$ (R = alkyl or aryl),[40] $[Mo(CO)_4(\text{carbene})_2]$,[41] $[Mo(CO)_2(CNR)_4]$,[42] and $[Mo(CO)_2(CNR)_2(PR_3)]$(R = alkyl or aryl),[42] as well as on the *mer–fac* interconversion of $[Cr(NO)(CNR)_3(P\text{–}P)]^{n+}$ [$n = 1$ or 2; P–P = $Ph_2P(CH_2)_mPPh_2$, $m = 1$ or 2, R = alkyl or aryl].[43] In each of these cases, thermodynamic and kinetic measurements suggest that the isomerizations occur by an intramolecular, non-dissociative twist mechanism, involving trigonal-prismatic transitions states. Extended Hückel calculations[44] also demonstrate that, by such a mechanism, the barrier to *mer–fac* isomerization in the model $[Mo(CO)_3(PH_3)_3]$ system is lower in the 17-electron than in the 18-electron case. Furthermore, there are also, well established examples of ligand-substitution[45] and migratory-insertion[46] reactions in which rates are enormously increased by one-electron oxidation of the substrate.

Attempts to account for the enhanced reactivity of 17-electron complexes generally make reference to (or assume implicitly) the effect of depopulating a bonding molecular orbital on the facility of stereochemical change or of ligand dissociation. It is intuitive that removal of a bonding electron from a molecule will weaken bonds between atoms, to a degree dependent upon the contribution of those atoms to the molecular orbital involved. Thus, the metal–carbon distances[47] in $V(CO)_6$ are *ca.* 0.08 Å longer than those in $[V(CO)_6]^-$, in accordance with the fact that the highest occupied molecular orbital (h.o.m.o.) in this system is involved strongly in metal-to-ligand π-back-bonding. Such a tendency appears generally to outweigh the opposing effect of metal-orbital contraction that is also associated with oxidation. Bond weakening can lead to increased lability in carbonyl complexes by making transition states for ligand reorganization, such as trigonal-prismatic configurations, energetically more accessible.

Although differential effects of orbital depopulations on ground- and transition-state energies must be very much more complex than is suggested by this argument, and will depend specifically on the particular reaction mechanism, the bond-weakening argument is one that at least does not necessarily conflict with the initially surprising results of the present study. Removal of an electron (albeit a weakly bonding one) from **(7)** to give **(9)** would be expected to be accompanied by a slight increase in the metal-to-ring distances. This would be manifest as diminished, rather than enhanced, reactivity because, all else being equal, hydrogen transfer over the slightly greater distances in **(9)** would be less favourable than **(7)**. Such bond lengthening is observable in ferrocene, for which the h.o.m.o. is also only weakly bonding: the average Fe–C distance, *viz.* 2.033 Å, in the neutral molecule[48] is *ca.* 0.04 Å shorter than that in $[Fe(\eta\text{-}C_5H_5)_2][FeCl_4]$ (2.075 Å).[49] It is also observable in decamethylferrocene [$Fe\text{–}C_{av}$ = 2.050(2) Å[50]] compared to 2.090(7) Å in $[Fe(\eta\text{-}C_5Me_5)_2][tcnq]_2$ (tcnq = tetracyanoquinodimethane radical anion).[51] The effect is apparently negligibly small in bis(benzene)chromium,[52] though the *X*-ray structural data for $[Cr(C_6H_6)_2]^+$ are of poor quality. A direct comparison between **(7)** and **(9)** themselves is unfortunately ruled out because of the positional disorder encountered in their crystal-structure determinations.

Certainly, more complex, and more highly speculative explanations for the reactivity difference can be put forward, that are equally consistent with the experimental facts. It is conceivable, for example, that the change in rate reflects a more general effect of h.o.m.o. occupancy on the facility of oxidative addition (in this case, of a C–H bond) to a metal centre. The highest occupied (d_{z^2}) orbital in the present system, though it is essentially non-bonding in the ground state, may correlate with a more strongly bonding m.o. in the metal–hydride intermediate proposed for the ring-to-ring shift. Bonding interactions in the transition state leading to this metal hydride would then be weakened unfavourably by removal of an electron. We nevertheless still favour the explanation involving differences in the metal-to-ring distances in **(7)** and **(9)**, on the grounds of its relative simplicity, and of the fact that it fits in with the wider body of experimental observations.

Experimental

All reactions and manipulations were performed under nitrogen either by standard Schlenk and vacuum-line techniques or in an inert-atmosphere glove box.

All solvents were thoroughly de-oxygenated prior to use by repeatedly shaking them under an active vacuum then admitting nitrogen to the vessel. Generally solvents were pre-dried over molecular sieves and then distilled, under an atmosphere of nitrogen, from potassium (toluene, cyclohexane, thf), sodium–potassium alloy [diethyl ether, light petroleum (b.p. 40—60 °C)], or phosphorus pentoxide (dichloromethane).

1,2-Dichloroethane for kinetic experiments was purified by first shaking it with concentrated sulphuric acid, then washing it with aqueous $Na(HCO_3)$ and finally with water. It was dried over anhydrous $MgSO_4$, then heated under reflux for 10 h over P_2O_5, from which it was finally distilled, with fractionation, b.p. 82—83 °C. Deuterated solvents for use in n.m.r. spectroscopy were stored over molecular sieves in ampoules sealed with Teflon taps. They were de-oxygenated by repeated freeze–pump–thaw cycles, and were transferred by vacuum distillation.

Cycloheptatriene (Fluka) was fractionally distilled through a Vigreux column, under nitrogen at atmospheric pressure, b.p. 115—116 °C (central fraction). It was stored at −80 °C, and was vacuum distilled immediately before use in metal vapour synthesis (m.v.s.) experiments. Tetrabutylammonium hexafluorophosphate (Fluka) for cyclic voltammetry experiments was recrystallized from thf, then dried *in vacuo* for 6 h at 100 °C. Alumina (Fluka) for column chromatography was dried at 180 °C for 20 h, then deactivated by shaking it with water (4% w/w). Silver tetrafluoroborate (Aldrich) and *N*-methyl-*N*-nitroso-*p*-toluenesulphonamide (Aldrich) were used without further purification.

Microanalyses were performed by the Analysis Department of the Inorganic Chemistry Laboratory, Oxford, or, in the case of very air-sensitive materials, by Analytische Laboratorien, 5270 Gummersbach 1 Elbach, West Germany.

Infrared spectra were recorded by using a Pye Unicam SP2000 double-beam, grating spectrometer. Visible–ultra-violet absorption spectra were recorded by using a Perkin-Elmer 552 u.v.–visible spectrophotometer. A pair of matched Quartz spectral cells (path length 1.00 cm) of an ampoule construction, sealed with Teflon taps, was used. In kinetic experiments, reactions were run directly in the cells, which, for temperature control, were immersed in a circulating-water bath. Constant temperature was maintained, to within ±0.05 °C, with a Tecam C-100 circulator. Reactions under photolysis were performed by placing the reaction cell next to a 500-W medium-pressure mercury-arc lamp, immersed in the thermostatted water bath.

Cyclic voltammetry measurements were made with the use of an in-house triangular-wave generator. The working electrode was a platinum disc (2.5 mm in diameter), and the counter, or current-carrying, electrode a cylinder of platinum gauze. The reference electrode was a platinum pigtail, simply immersed in the solvent system of the experiment (typically thf|0.19 mol dm^{-3} $[NBu_4]PF_6$) and brought close to the surface of the working electrode by means of a low-porosity glass frit. Though the potential of this electrode is constant and reproducible, it is not possible to determine its value relative to, say, the saturated calomel electrode (s.c.e.) without introducing an unknown junction potential. Instead, in accordance with the recommendations on reporting electrode potentials in non-aqueous solvents given by Gritzner and Kuta,[53] values of $E_{\frac{1}{2}}$ are quoted relative to the reference redox system, $[Fe(\eta\text{-}C_5H_5)_2]$–$[Fe(\eta\text{-}C_5H_5)_2]^+$ which occurs at +0.62 V relative to Pt|thf, 0.19 mol dm^{-3} $[NBu_4]PF_6$. Substrate concentrations in these experiments were typically 10^{-3} mol dm^{-3}.

Electron spin resonance spectra were measured at r.t. on solutions in silica sample tubes, using a JEOL JES-PE spectrometer; they were calibrated externally with a standard sample of manganese oxide.

Nuclear magnetic resonance spectra were recorded with the following instruments: ^1H n.m.r., 60 MHz, JEOL PMX-60, 300 MHz, Bruker WH-300; ^{13}C n.m.r., 62.9 MHz, Bruker AM-250. Spectra were referenced internally to either the residual protio-solvent resonance (^1H), or the solvent carbon resonance (^{13}C), both relative to tetramethylsilane (δ = 0 p.p.m.). All chemical shifts are quoted in p.p.m.; signals are expressed as position, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), relative integration, and assignment respectively. Variable-temperature spectra were measured with the use of the WH-300 temperature controller. Temperatures quoted are accurate to ±1 °C, and were calibrated by using the linewidth of a standard methanol sample.

Solid-state ^{13}C n.m.r. spectra were measured with cross-polarization and magic-angle spinning, by use of a Bruker CPX 200 instrument; spinners were constructed of deuterated perspex.

Electron-impact mass spectra were obtained by using a VG-Analytical MM30F spectrometer, and field-desorption spectra were measured with a VG-Analytical ZAB1F instrument. In the f.d. technique, spectra show only the parent ion (with associated isotope envelope) and no fragmentation pattern.

Metal vapour syntheses were performed on either the 10-kW metal-atom reactor[54] or, in the case of reactions with [$^2H_8$]-cycloheptatriene, on the 1.5-kW small-hearth apparatus;[55] the latter is more suitable when only small quantities of ligand are being used. Both machines were operated in the positive-hearth mode. Reactions were carried out with a pre-melted ingot of molybdenum. The metal was evaporated, and the ligand introduced during runs, at such rates as to allow a vacuum better than 5×10^{-5} Torr to be maintained by the system. Typically, 1—2 g of molybdenum atoms per hour could be generated. When co-condensation was complete, the cooling shroud of liquid nitrogen was emptied, and the apparatus filled with nitrogen, then allowed to warm up to r.t. The product was then washed off the walls of the apparatus with an appropriate solvent and collected.

Bis(η-*cycloheptatriene*)*molybdenum*, (**7**).—Molybdenum vapour (8 g, 8.3×10^{-2} mol), generated from a molten ingot (*ca.* 20 g), was condensed with pure cycloheptatriene (100 cm^3, 0.96 mol) over a period of 4 h. The input power to the positive-hearth electron-gun was 2 kW throughout. At the end of the run, the dark brown matrix was washed out of the apparatus with thf (800 cm^3) and filtered through a bed of Celite. The solvent and excess cycloheptatriene were removed under reduced pressure at r.t. to give a dark green solid (*ca.* 15 g); since the product was thermally unstable, precautions were taken to ensure that it was not, at any stage of work-up, heated above r.t. The crude product was purified portionwise, as follows, by chromatography on alumina. The crude product (*ca.* 8 g) was dissolved in toluene (30 cm^3) and added to alumina (15 g). Removal of the solvent under reduced pressure gave a black powder, which was then transferred to the top of an alumina column (40 × 2 cm diameter) prepared with light petroleum (b.p. 40—60 °C). Elution with this solvent gave a green first band, which was collected (*ca.* 300 cm^3) and evaporated under reduced pressure to 50 cm^3, whereupon green crystals separated out. Crystallization of the product, [Mo(η-C_7H_8)$_2$], was achieved by cooling to −80 °C; the crystals (suitable for *X*-ray diffraction study) were filtered off, washed with light petroleum (b.p. 40—60 °C) at −80 °C, and dried *in vacuo*; yield 4 g. Further elution of the column led, slowly, to an orange second band containing [Mo(η-C_7H_7)(η-C_7H_9)].

[Mo(η-C_7H_8)$_2$] is very soluble in hydrocarbon and ether solvents, but decomposes rapidly in halogenated solvents such as dichloromethane. It was stored at −80 °C. Total yield from 6 g molybdenum: 8 g (44%) (Found, C, 59.7; H, 5.7. $C_{14}H_{16}Mo$ requires C, 60.0; H, 5.7%). ^1H N.m.r. (300 MHz, [$^2H_8$]toluene, *J* in Hz): at 20 °C, 1.28 [d, 1 H, *J*(H^7-*exo*, H^7-*endo*) 13, H^7-*exo*], 1.78 [dt, 1 H, *J*(H^7-*endo*, H^7-*exo*) 13, *J*(H^7-*endo*, $H^{1,6}$) 6, H^7-*endo*], 2.90 (br, t, 2 H, $H^{1,6}$), 4.43 (br s, 2 H, $H^{2,5}$), 5.92 (br s, 2 H, $H^{3,4}$); at −60 °C, 1.42 [d, 1 H, *J*(H^7-*exo*, H^7-*endo*) 12.9, H^7-*exo*], 1.87 [dt, 1 H, *J*(H^7-*endo*, H^7-*exo*) 12.9, *J*(H^7-*endo*, H^1) = *J*(H^7-*endo*, H^6) 7.7, H^7-*endo*], 2.82 [td, 1 H, *J*(H^1, H^7-*endo*) = *J*(H^1,H^2) 7.8, *J*[H^1, H^7-*exo*) 2.7, H^1], 3.11 [td, 1 H, *J*(H^6, H^7-*endo*) = *J*(H^6, H^5) 7.6, *J*(H^6, H^7-*exo*) 1.9, H^6], 3.65 [t, 1 H, *J*(H^5, H^6) = *J*(H^5, H^4) 7.1, H^5], 5.25 (t, 1 H, *J*(H^4, H^5) = *J*(H^4, H^3) 6.9, H^4], 5.32 [t, 1 H, *J*(H^2, H^3) = *J*(H^2, H^1) 7.3, H^2], 6.71 [t, 1 H, *J*(H^3, H^4) = *J*(H^3, H^2) 6.8, H^3]. ^{13}C-{^1H} n.m.r. (62.9 MHz, [$^2H_8$]toluene): at 30 °C, 28.0 (s, C^7), 52.6 (br s, $C^{1,6}$), 95.7 (br s, $C^{2,5}$ or $C^{3,4}$), 105.9 (br s, $C^{3,4}$ or $C^{2,5}$); at −50 °C (off-resonance decoupled), 27.7 (t, C^7), 45.6 (d, C^1 or C^6), 58.8 (d, C^6 or C^1), 90.2 (d, C^2, C^5, C^3, or C^4), 100.7 (d, C^5, C^2, C^4, or C^3), 102.9 (d, C^3, C^4, C^2, or C^5), 108.6 (d, C^4, C^3, C^5, or C^2).

(η-*Cycloheptadienyl*)(η-*cycloheptatrienyl*)*molybdenum*, (**8**).—[Mo(η-C_7H_8)$_2$], (**7**), (0.5 g) in toluene (50 cm^3) was heated at 70 °C for 6 h. The solvent was then removed under reduced pressure to give the product as a red crystalline solid, which was recrystallized from light petroleum (b.p. 40—60 °C); yield 0.45 g (90%). Crystals suitable for *X*-ray diffraction study were grown from light petroleum (b.p. 40—60 °C) at −25 °C. ^1H N.m.r. (300 MHz, [$^2H_6$]benzene): at r.t. 1.55 (m, 2 H, H^1-*exo* or -*endo*), 1.81 (m, 2 H, H^1-*endo* or -*exo*), 4.17 (m, 2 H, H^2), 4.68 (s, 7 H, C_7H_7), 4.78 (t, 1 H, H^4), 5.06 (dd, 2 H, H^3). Photoelectron spectrum: first ionization potential, 5.62 eV.

[$^2H_8$]*Cycloheptatriene*.—This was prepared from the reaction of C_6D_6 with [$^2H_2$]diazomethane, catalysed by copper(I) chloride. CD_2N_2 was prepared in a greaseless distillation apparatus, by a modification of the method for preparation of the protio-analogue.[56] A solution of *N*-methyl-*N*-nitroso-*p*-toluenesulphonamide (21.8 g, 0.10 mol) in diethyl ether (200 cm^3) was added dropwise, over 30 min, to a rapidly stirred mixture of 40% Na(OD) in D_2O (20 g of solution), [$^2H_1$]-2-(2-ethoxyethoxy)ethanol (45 cm^3), and diethyl ether (10 cm^3), all of which was maintained at 70 °C. The yellow ethereal solution of CD_2N_2, which immediately began distilling over, was collected in a flask cooled by immersion in a solid CO_2–acetone bath. When distillation was complete and the yellow solution had been allowed to warm up to r.t., the CD_2N_2 was swept out by the passage of a slow stream of nitrogen, and passed into a stirred mixture of [$^2H_6$]benzene (20 g) and CuCl (0.2 g) maintained at 60 °C. The outlet of the apparatus was passed through a −80 °C cold trap, and occasionally the material that accumulated (diethyl ether and some CD_2N_2) was run back into the reaction mixture. The passage of nitrogen was maintained for 6 h, after which time all the CD_2N_2 had been swept over, and the benzene–CuCl mixture had become black. This mixture was then cooled and filtered; the colourless filtrate (20 cm^3) was fractionally distilled with a Perkin-Elmer M131-T spinning-band column, at a reflux ratio of *ca.* 10. The first two fractions (diethyl ether and [$^2H_6$]benzene respectively) were discarded; [$^2H_8$]cycloheptatriene was collected as the third fraction (b.p. range 114—117 °C); yield 2.1 g, 21%. Mass spectrum: *m*/*z* (relative abundance) 100 (39.4), 99 (14.6), 98 (100.0%). The degree of deuteration was estimated assuming the parent-ion intensities gauge the proportion of the isotopomers in the sample as $C_7D_8:C_7D_7H = 85:15$.

[$^2H_{16}$]*Bis*(η-*cycloheptatriene*)*molybdenum*.—This was prepared in a manner analogous to that for the protio-compound. Molybdenum vapour (0.6 g, 6×10^{-3} mol), generated at a power of 1 kW from a molten ingot (*ca.* 6 g), was condensed with a solution of [$^2H_8$]cycloheptatriene (2.1 g, 2.1×10^{-2} mol) in light petroleum (b.p. 40—60 °C, 10 cm^3) over a period of 45 min. The crude product was purified by chromatography on a short column of alumina (10 × 2 cm diameter), with light petroleum as eluant. From the green, first band were obtained crystals of [Mo(η-C_7D_8)$_2$]; yield 0.06 g (3%).

The visible absorption spectrum of this compound was identical to that of its protio-analogue.

Bis(η-*cycloheptatriene*)*molybdenum Tetrafluoroborate*, (**9**).—The compound [Mo(η-C_7H_8)$_2$] (0.21 g, 7.5×10^{-4} mol) in thf

Table 3. Crystal data, collection and refinement details for (**7**), (**8**), and (**9**)

	$[Mo(\eta\text{-}C_7H_8)_2]$, (**7**)	$[Mo(\eta\text{-}C_7H_7)(\eta^5\text{-}C_7H_9)]$, (**8**)	$[Mo(C_7H_8)_2][BF_4]$, (**9**)
Formula	$C_{14}H_{16}Mo$	$C_{14}H_{16}Mo$	$C_{14}H_{16}BF_4Mo$
M	280.2	280.2	367.0
System	Monoclinic	Monoclinic	Orthorhombic
a/Å	6.844(2)	11.948(3)	16.666(2)
b/Å	8.219(2)	8.011(2)	10.397(2)
c/Å	10.211(2)	12.954(5)	8.137(1)
β/°	94.78(2)	115.20(2)	
U/Å^3	572.4	1 121.9	1 410.0
Space group	$P2_1/n$	$P2_1/n$	*Pnma*
Z	2	4	4
D_c/Mg m^{-3}	1.63	1.66	1.73
F(000)	284	568	732
Radiation	Cu-K_α	Cu-K_α	Mo-K_α
λ/Å	1.5418	1.5418	0.710 69
μ/cm^{-1}	92.24	94.12	9.37
Crystal size/mm	0.75 × 0.33 × 0.33	0.5 × 0.2 × 0.19	0.5 × 0.42 × 0.64
Colour	dark green	red	bright green
$\theta_{max.}$/°	75	75	30
Scan	ω—2θ	ω—2θ	ω—2θ
Scan angle/°	1.1 + 0.14 tan θ	1.2 + 0.14 tan θ	0.9 + 0.35 tan θ
Horizontal aperture/mm	4.5	4.5	4.5
Zone	$+h, +k, \pm l$	$+h, +k, \pm l$	$+h, +k, +l$
R_{merge}	0.0553	0.0375	0.0126
Absorption (min., max.)	1.0, 7.32	1.0, 1.48	1.0, 1.06
N_{tot}	1 181	2 291	2 156
$N_{obs.}[I > 3\sigma(I)]$	754	1 827	1 356
$N_{par.}$	111	187	122
R,R'*	0.055, 0.066	0.049, 0.064	0.049, 0.06
Weighting scheme parameters	261.6, −312.9, 308.3, −105.4, 57.2	86.01, 77.95, −12.78, −8.59, 7.19	24.39, −19.36, 26.45, −8.00, 4.88

* $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$.

(15 cm^3) was treated with $AgBF_4$ (0.16 g, 8.3 × 10^{-4} mol) in thf (5 cm^3). A fine black precipitate formed immediately and the supernatant solution became colourless. The solid was filtered off and washed with thf, then extracted exhaustively with dichloromethane (5 × 15 cm^3). The green extract was concentrated under reduced pressure to 10 cm^3 and cooled to −80 °C, whereupon the product formed as grass green crystals. These were filtered off, washed with thf (in which the product is only sparingly soluble), and dried *in vacuo*; yield 0.22 g (80%).

The product is moderately air stable, but thermally sensitive and so was stored at −80 °C. Crystals suitable for *X*-ray diffraction study were grown by allowing diethyl ether to diffuse slowly into a 1,2-dichloroethane solution of (**9**) (Found: C, 45.4; H, 4.4. $C_{14}H_{16}BF_4Mo$ requires C, 45.8; H, 4.4%). Field-desorption mass spectrum: *m/z* 282 (100%), M^+. E.s.r. spectrum (*ca.* 10^{-5} mol dm^{-3} in thf): $\langle g \rangle$ = 1.976 [singlet superposed on sextet, $A(^{95}Mo) = A(^{97}Mo)$ = 220 MHz].

Bis(η-*cycloheptatriene*)*molybdenum Hexafluorophosphate*.—The compound $[Mo(\eta\text{-}C_7H_8)_2][BF_4]$ (0.10 g) in dichloromethane (10 cm^3) was treated with tetrabutylammonium hexafluorophosphate (0.20 g) in dichloromethane (5 cm^3). The mixture was concentrated to 5 cm^3 under reduced pressure, and cooled to −80 °C for 3 d, giving green crystals. These were filtered off, washed (thf), and dried *in vacuo*; yield 0.07 g (Found C, 39.6; H, 3.8. $C_{14}H_{16}F_6MoP$ requires C, 39.6; H, 3.8%).

(η-*Cycloheptadienyl*)(η-*cycloheptatrienyl*)*molybdenum Tetrafluoroborate*, (**10**).—This compound was prepared in a manner exactly analogous to that for oxidation of $[Mo(\eta\text{-}C_7H_8)_2]$. The fine black solid, formed on treatment of $[Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_7H_9)]$ with $AgBF_4$ in thf, was extracted with dichloromethane exhaustively. The purple extract (50 cm^3) was concentrated under reduced pressure to 5 cm^3, and cooled to −80 °C for 1 d, giving purple crystals. These were filtered off, washed (thf), and dried *in vacuo*; yield 80% (Found: C, 45.6; H, 4.4. $C_{14}H_{16}BF_4Mo$ requires C, 45.8; H, 4.4%). Field-desorption mass spectrum: *m/z* 282 (100%), M^+. E.s.r. spectrum (10^{-3} mol dm^{-3} in thf): $\langle g \rangle$ = 1.971 [singlet superposed on sextet, $A(^{95}Mo) = A(^{97}Mo)$ = 220 MHz].

Reduction of $[Mo(\eta\text{-}C_7H_8)_2][BF_4]$ *with Sodium Amalgam*.—A suspension of $[Mo(\eta\text{-}C_7H_8)_2][BF_4]$ (0.20 g) in thf (30 cm^3) was treated with 1% sodium amalgam (10 g), with vigorous stirring. After 3 h, all of the green solid had dissolved, and the supernatant solution was green. It was decanted and evaporated to dryness under reduced pressure, to give a green crystalline solid. This was found, by ^1H n.m.r. (300 MHz, [$^2H_6$]benzene), to be essentially pure $[Mo(\eta\text{-}C_7H_8)_2]$, contaminated only by some thf and paraffin oil. Yield *ca.* 0.10 g (65%).

Reduction of $[Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_7H_9)][BF_4]$ *with Sodium Amalgam*.—Treatment of $[Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_7H_9)][BF_4]$ with 1% sodium amalgam, in a manner analogous to that for the reduction of $[Mo(\eta\text{-}C_7H_8)_2]BF_4$, gave a brown crystalline solid as product (*ca.* 40%). The ^1H n.m.r. spectrum of this material indicated the presence, in addition to $[Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_7H_9)]$, of much free cycloheptatriene and a small proportion of unidentifiable species.

Crystal Structure Determination.—Crystal data, and collection and processing parameters are given in Table 3.

Data collection and processing. Crystals sealed under nitrogen in Lindemann glass capillaries, mounted on an Enraf-Nonius CAD4 diffractometer. Cell dimensions obtained by least-

Table 4. Fractional atomic co-ordinates with estimated standard deviations in parentheses

Atom	X/a	Y/b	Z/c
(*a*) For [Mo(η-$C_7H_8)_2$], (**7**)			
Mo(1)	0.5000	0.0000	0.0000
C(1)	0.422(3)	−0.069(3)	0.205(2)
C(2)	0.609(3)	−0.024(2)	0.221(2)
C(3)	0.764(2)	−0.059(3)	0.140(2)
C(4)	0.769(2)	−0.169(2)	0.042(2)
C(5)	0.615(3)	−0.270(2)	−0.007(2)
C(6)	0.433(3)	−0.281(2)	0.027(2)
C(7)	0.334(3)	−0.217(3)	0.142(2)
C(101)	0.699(2)	−0.029(2)	0.200(2)
C(102)	0.791(2)	−0.101(2)	0.105(2)
C(103)	0.721(2)	−0.213(2)	0.009(1)
C(104)	0.533(3)	−0.276(2)	−0.013(1)
C(105)	0.374(3)	−0.254(2)	0.063(2)
C(106)	0.358(2)	−0.150(3)	0.159(2)
C(107)	0.504(3)	−0.063(3)	0.252(2)
(*b*) For [Mo(η-C_7H_7)(η-C_7H_9)], (**8**)			
Mo(1)	0.023 91(5)	0.039 69(6)	0.260 92(4)
C(1)	−0.189 4(7)	0.003(1)	0.207 4(8)
C(2)	−0.122 4(7)	−0.053(1)	0.319 2(7)
C(3)	−0.022 6(7)	−0.166 9(9)	0.359 5(6)
C(4)	0.029 7(7)	−0.241(1)	0.291 3(7)
C(5)	−0.026 0(7)	−0.228 0(9)	0.175 6(7)
C(6)	−0.163 1(8)	−0.251(1)	0.107 0(7)
C(7)	−0.236 8(8)	−0.095(1)	0.098 1(8)
C(11)	0.175(1)	0.178(2)	0.402 8(8)
C(12)	0.231 7(8)	0.088(1)	0.348(1)
C(13)	0.196 7(8)	0.068(1)	0.232(1)
C(14)	0.098(1)	0.139(1)	0.140 0(8)
C(15)	0.011(1)	0.255(2)	0.144(1)
C(16)	0.004(1)	0.319(1)	0.241(2)
C(17)	0.074(1)	0.284(2)	0.354(1)
(*c*) For [Mo(η-$C_7H_8)_2$][BF_4], (**9**)			
Mo(1)	0.134 75(4)	0.2500	0.261 62(6)
C(1)	0.132 8(4)	0.316 3(4)	−0.017 6(8)
C(2)	0.086 3(4)	0.400 8(6)	0.075 1(8)
C(3)	0.026 1(4)	0.370 8(6)	0.185 4(8)
C(4)	−0.005 0(5)	0.2500	0.224(1)
C(5)	0.269 93(4)	0.317 1(4)	0.301(1)
C(6)	0.218 1(4)	0.400 3(6)	0.383 7(9)
C(7)	0.158 9(5)	0.370 6(6)	0.499 0(8)
C(8)	0.129 7(6)	0.2500	0.543(1)
B(1)	0.393 5(4)	0.2500	0.836 8(9)
F(1)	0.428(1)	0.2500	0.686(2)
F(2)	0.311 3(5)	0.2500	0.823(3)
F(3)	0.417 4(9)	0.352 4(7)	0.926(2)
F(11)	0.350(1)	0.2500	0.693(2)
F(12)	0.343(1)	0.2500	0.966(3)
F(13)	0.442 4(8)	0.354(1)	0.842(2)

squares methods from the positions of up to 25 carefully centred reflections. Any decay in intensity corrected during data reduction. Empirical absorption[57] [including, for (**7**) and (**9**) θ-dependence][58] and Lorentz polarization corrections applied.

Structure analysis and refinement. All structures were solved by the heavy-atom method. Refinement was by full matrix least squares and corrections were made for anomalous dispersion[59a] and isotropic extinction [(**9**), BF_4 salt only].[60]

For (**7**). Disorder of the cycloheptatriene ring was modelled using two partial occupancy conformations. Geometry was restrained[61] to values observed for [Mo(η-C_7H_8)$(CO)_3$].[31] Hydrogens were included in calculated positions, U[iso] = 0.1 Å^2, and refined with geometrical restraints. Molybdenum refined anisotropically, carbon isotropically.

For (**8**). Most hydrogens located by difference Fourier synthesis and included in calculated positions. Molybdenum and carbon refined anisotropically, hydrogens refined isotropically subject to geometrical restraints and thermal parameters in three groups.

For (**9**). Attempts to model disorder of rings gave poorer agreement than the single anisotropic model assuming the methylene group is disordered over all sites. Hydrogen atoms were not included. The $[BF_4]^-$ ion modelled with two partial occupancy orientations (occupancies refined to 0.26 and 0.24). All atoms refined anisotropically subject to soft geometrical restraints.

In all cases Chebyshev weighting schemes were applied[62] to give satisfactory agreement analyses, where $w = 1/\sum_{r=1}^{n} A_rT_r(X)$ and $X = F_o/|F_o|_{max.}$; T_r is the polynomial function with coefficients A_r given in Table 3. Solution and refinement used the Oxford CRYSTALS package[63] on the VAX 11/750 computer of the Chemical Crystallography Laboratory, Oxford University. Scattering factors were taken from International Tables for X-ray Crystallography.[59b]

Fractional atomic co-ordinates for (**7**), (**8**), and (**9**) are given in Table 4. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

Kinetic Measurements.—The rearrangement of [Mo(η-$C_7H_8)_2$], (**7**), in toluene to give [Mo(η-C_7H_7)(η-C_7H_9)], and of [Mo(η-$C_7H_8)_2$][BF_4], (**9**), in 1,2-dichloroethane to give [Mo(η-C_7H_7)(C_7H_9)][BF_4] were followed by visible absorption spectroscopy. For both reactions, the spectra of starting compound and product are well differentiated in the region 400—800 nm (see Figure 6).

The procedure for a kinetic run involved transferring a freshly prepared solution of pure starting compound in the appropriate solvent (typically 1—3 × 10^{-2} mol dm^{-3}) to a quartz cell and measuring the initial visible spectrum at r.t. The sample was then heated to the appropriate temperature in a thermostatted water bath to begin the reaction. At various times the reaction was quenched by removing the sample from the bath and shaking it vigorously in an ice–water slush until cold; the spectrum of the mixture was measured, then the sample was replaced in the bath. This procedure was satisfactory because the reaction of both (**7**) and (**9**) at r.t. was negligibly slow ($t_{\frac{1}{2}}$ > 200 h), and because the time taken for the sample to equilibrate upon replacement in the water bath (< 0.5 min) was short relative to the time scale of the reactions.

Kinetics for the two conversions were investigated in the temperature range 40—85 °C. The reactions were quantitative, and isosbestic points were maintained throughout, provided strict care was taken to exclude adventitious oxygen; kinetics were discarded in the few cases in which extraneous processes could be detected spectroscopically. The conversion of (**7**) into (**8**) was followed by monitoring the increase in absorbance at λ = 500 nm that accompanied the reaction; that of (**9**) into (**10**) was followed correspondingly at λ = 530 nm. Kinetics were cleanly first-order and, in all but the slowest conversions, were followed to *ca.* 3 half lives, with the infinity measurement being made only after at least 6 half lives. In the cases of slow reaction ($t_{\frac{1}{2}}$ > *ca.* 1 d), roughly 50% of the transformation was covered, then infinity spectra were obtained by heating the samples to *ca.* 80 °C in order to complete the process. When reactions were monitored additionally at other wavelengths [λ = 800 nm for (**7**), 740 nm for (**9**)], first-order rate constants agreed, within experimental error, with those from data at 500 and 530 nm respectively. Six to nine data points were measured in each run for the calculation of the rate constant; the associated error was taken to be the variance given by analysis of residuals from the least-squares line.[64]

Arrhenius plots of ln k *vs.* $1/T$ were constructed from all data for (**7**) and (**9**), which were then fitted by non-weighted least squares to the equation $\ln k = \ln A - E_a/RT$. $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were calculated from the equations, *viz.*, $\Delta H^\ddagger = E_a - RT$; $S^\ddagger = R\ln(NhA/RT)$; then $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$. Errors in activation parameters represent one standard deviation calculated by error propagation when the measured k values were varied within their uncertainty limits. Data from kinetic runs for both (**7**) and (**9**) are available in ref. 65.

The Crossover Experiments.—For $[\mathrm{Mo}(\eta\text{-}C_7H_8)_2] + [\mathrm{Mo}(\eta\text{-}C_7D_8)_2]$. A toluene solution containing the compounds $[\mathrm{Mo}(\eta\text{-}C_7H_8)_2]$ and $[\mathrm{Mo}(\eta\text{-}C_7D_8)_2]$ in the mole ratio 48:52 was prepared by mixing the required volumes of solutions of the individual reactants, whose relative concentrations had been estimated by visible spectrometry. The mixture was heated to 80 °C for 2 h to effect isomerization. The resulting red solution was evaporated to dryness and the electron-impact mass spectrum of the residual red solid was determined. Spectra were recorded also of the products of isomerization of pure $[\mathrm{Mo}(\eta\text{-}C_7H_8)_2]$ and of pure $[\mathrm{Mo}(\eta\text{-}C_7D_8)_2]$ obtained under the same conditions as the mixture.

For $[\mathrm{Mo}(\eta\text{-}C_7H_8)_2][BF_4] + [\mathrm{Mo}(\eta\text{-}C_7D_8)_2][BF_4]$. A solution containing the compounds $[\mathrm{Mo}(\eta\text{-}C_7H_8)_2][BF_4]$ and $[\mathrm{Mo}(\eta\text{-}C_7D_8)_2][BF_4]$ in the mole ratio 55:45 was prepared in 1,2-dichloroethane by mixing the required volumes of solutions of the individual reactants, whose relative concentrations had been estimated by visible spectrometry. The mixture was heated to 86 °C for 7 h to effect isomerization. The resulting purple-brown solution was evaporated to dryness, and the field-desorption mass spectrum of the residual brown solid was determined. Spectra were obtained similarly from the products given by pure protio- and by pure deuterio-compound under the same conditions.

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