Studies on Cyclic Bis(η^5:σ-2-cyclopentadienylidene-ethyl)- and Bis(η^5:σ-4-cyclopentadienylidenebutyl)-molybdenum Compounds

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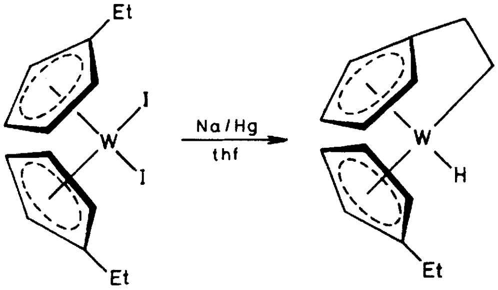
Co-condensation of molybdenum atoms with spiro[4.4]nona-1,3-diene gives the compound $[Mo\{\eta^5:\sigma\text{-}C_5H_4(CH_2)_3CH_2\}_2]$ (**1**). Protonation of (**1**) causes the cleavage of only one Mo–C bond and following a β-elimination reaction a mixture of *exo*- and *endo*-$[Mo(\eta^5\text{-}C_5H_4Bu^n)(\eta^5:\eta^2\text{-}C_5H_4CH_2CH_2CH{=}CH_2)H]PF_6$ (**2**) is formed. Treatment of (**2**) with NaOH gives $[Mo(\eta^5\text{-}C_5H_4Bu^n)(\eta^5:\eta^2\text{-}C_5H_4CH_2CH_2CH{=}CH_2)]$ (**3**). Compound (**1**) with iodine gives $[Mo(\eta^5\text{-}C_5H_4Bu^n)(\eta^5\text{-}C_5H_4CH_2CH_2CH{=}CH_2)I_2]$ (**4**). Treatment of $[Mo(\eta^5:\sigma\text{-}C_5H_4CH_2CH_2)_2]$ with benzoic acid forms $[Mo(\eta^5\text{-}C_5H_4Et)(\eta^5:\sigma\text{-}C_5H_4CH_2CH_2)(O_2CPh)]$ (**5**), which with $SiMe_3Cl$ forms $[Mo(\eta^5\text{-}C_5H_4Et)_2Cl_2]$ (**6**) and $[Mo(\eta^5\text{-}C_5H_4Et)(\eta^5:\sigma\text{-}C_5H_4CH_2CH_2)Cl]$ (**7**). Compound (**7**) reacts with PMe_2Ph giving the cation $[Mo(\eta^5\text{-}C_5H_4Et)(\eta^5:\sigma\text{-}C_5H_4CH_2CH_2)(PMe_2Ph)]^+$ (**8**).

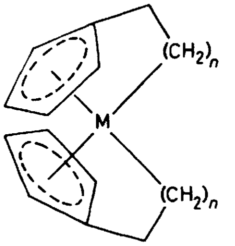
Previous studies on the bis(η-cyclopentadienyl)-molybdenum and -tungsten systems have elucidated features of general interest to transition metal–hydrocarbon chemistry. These include the activation of carbon–hydrogen bonds,[1] reversible 1,2-hydrogen shift processes,[2] and photochemically induced η^5- to η^3-cyclopentadienyl ring-shift processes.[3]

We have recently described the synthesis and chemistry of some cyclic bis(2-η-cyclopentadienylidene-ethyl)-molybdenum[4] and -tungsten[5] compounds. These systems have provided an opportunity to examine the proximity effects arising between a substituent group on the η-cyclopentadienyl ring and the metal centre. For example, we have shown that ring-closure reactions of the type symbolised in equation (1) (thf = tetrahydrofuran) are highly favoured.[5]



(1)

It was in the context of the above that we set out further to explore the chemistry of 'tucked-in'[5] cyclic η^5:σ-cyclopentadienylidenealkyl–transition metal compounds. A general representation of this system is shown below.



Results and Discussion

Eilbracht and Dahler[6] have shown that spiro[4.4]nona-1,3-diene reacts with $[Fe_2(CO)_9]$ to give the compound $[Fe\{\eta^5:\sigma\text{-}C_5H_4(CH_2)_3CH_2\}(CO)_3]$. We set out to prepare the compound $[Mo\{\eta^5:\sigma\text{-}C_5H_4(CH_2)_3CH_2\}_2]$, by analogy with $[Mo(\eta^5:\sigma\text{-}C_5H_4CH_2CH_2)_2]$, and to compare the chemistry of the two apparently closely related systems.

Spiro[4.4]nona-1,3-diene was co-condensed with molybdenum vapour at −196 °C, using the apparatus as described elsewhere,[7,8] giving red crystalline $[Mo\{\eta^5:\sigma\text{-}C_5H_4(CH_2)_3CH_2\}_2]$ (**1**). This compound is moderately air-sensitive and highly soluble in hydrocarbon solvents.

The analytical and spectroscopic data characterising this compound, and all the other new compounds described in this paper are given in Table 1. These data are only discussed where the interpretation is not straightforward. The ^1H n.m.r. spectrum of (**1**) at ambient temperature showed broad featureless bands centred at 4.7, 4.3, 3.3, 2.1, 1.6, 1.4, and 1.3 p.p.m. However, at −60 °C the spectrum was well resolved and showed much more detail. For example, the four signals each of relative intensity 2, in the region 3.0—4.5 p.p.m., could be assigned to two $\eta\text{-}C_5H_5$ groups. Eight further multiplets, each with relative intensity 2, are associated with the two $(\text{–}CH_2\text{–})_4$ groups. The assignment of the latter required detailed double-resonance studies, which showed their connectivity. The data and assignments are given in Table 1. Not every coupling between adjacent hydrogens was observed and some must be presumed to be too small to be resolved. On the basis of this information (Table 2), it was concluded that the spectra were most consistent with there being only one type of cyclopentadienyl ring and four linearly linked CH_2 units. Therefore, a structure analogous to the compound $[Mo(\eta^5:\sigma\text{-}C_5H_4CH_2CH_2)_2]$ is proposed (Scheme 1). We attribute the temperature sensitivity of the n.m.r. spectra to the occurrence of fluxional rearrangements (one could envisage the two η^5-cyclopentadienyl rings swinging to and fro, tethered to the metal centre by the C_4 chains.)

Compound (**1**) was dissolved in dilute aqueous hydrochloric acid giving, after the addition of hexafluorophosphate (NH_4PF_6), red crystals of (**2**). Treatment of (**2**) with aqueous base gives a neutral, hydrocarbon-soluble compound, (**3**). The mass spectrum of (**3**) shows a parent ion at m/e = 338.

The ^1H n.m.r. spectrum of (**3**) is consistent with only one compound being present, with the eight cyclopentadienyl hydrogens appearing as eight multiplets each of relative

Table 1. Analytical and spectroscopic data

Compound	Colour	Analysis[a] (%)		N.m.r. data[b]
		C	H	
(**1**)	Red	64.0 (64.3)	7.1 (7.2)	^{1}H n.m.r. at −60 °C:[c] 4.3 [2 H, c, 4 lines, CH (cp)], 3.8 [2 H, c, 4 lines, CH (cp)], 3.3 [2 H, c, 4 lines, CH (cp)], 3.2 [2 H, c, 4 lines, CH (cp)], 2.72 [2 H, dd, *J* 13.9 and 9.0, –CH], 2.7 [2 H, d, *J* 14.2, –CH], 1.9 [2 H, m, 5 lines, –CH], 1.7 [2 H, q, *J* 6.0, –CH], 1.5 [2 H, q, *J* 5.9, –CH], 1.3 [2 H, dd, *J* 3.0 and 11.5, –CH], 1.1 [2 H, tq, *J* 3.9 and 12.8, –CH], 0.6 [2 H, dt, *J* 12.0 and 2.6, –CH]. ^{13}C n.m.r. at −20 °C:[d] −37 [t, Mo–CH_2], 18.3 [t, 3 CH_2], 29.0 [t, 3 CH_2], 75.2 [d, CH (cp)], 77.1 [d, CH (cp)], 79.5 [d, CH (cp)], 98.8 [d, CH (cp)], 99.0 [s, $-\overset{\mid}{C}-$ (cp)]
(**2**)[e]	Red	46.6 (46.3)	5.7 (6.0)	[f]
(**3**)[g]	Red			^{1}H n.m.r.:[h] 4.8 [1 H, m, 4 lines, CH (cp)], 4.6 [1 H, m, 4 lines, CH (cp)], 4.5 [1 H, m, 4 lines, CH (cp)], 4.1 [1 H, m, 4 lines, CH (cp)], 4.0 [1 H, m, 4 lines, CH (cp)], 3.7 [1 H, m, 4 lines, CH (cp)], 3.6 [1 H, m, 4 lines, CH (cp)], 3.3 [1 H, m, 4 lines, CH (cp)], 2.9 [1 H, c, 6 lines, CH], 2.6 [2 H, t, *J* 7.0, $C_5H_4C\mathit{H}_2$], 2.1[2 H, m, 6 lines, CH_2], 1.8 [2 H, m, 8 lines, CH=$C\mathit{H}_2$], 1.4 [2H, quintet, *J* 7.0, CH_2(Bu^n)], 1.3 [4 H, m, 10 lines, 2 CH_2(Bu^n)], 0.83 [3 H, t, *J* 7.7, CH_3]
(**4**)[i]	Green	36.6 (35.7)	4.1 (3.9)	^{1}H n.m.r.:[j] 5.8 [1 H, c, 6 lines, $C\mathit{H}$=CH_2], 5.5 [2 H, m, 3 lines, CH (cp)], 5.4 [2 H, m, 3 lines, CH (cp)], 5.25 [4 H, c, 4 lines, CH (cp)], 5.0 [2 H, c, 3 lines, CH=$C\mathit{H}_2$], 2.3 [4 H, quintet, *J* 6.2, 2CH_2], 2.1 [2 H, t, *J* 7.2, $C_5H_4C\mathit{H}_2$], 1.5 [2 H, q, *J* 5.6, CH_2], 1.4 [2 H, sextet, *J* 7.2, $C\mathit{H}_2CH_3$], 1.0 [3 H, t, *J* 7.2, CH_3]
(**5**)[k]	Red			^{1}H n.m.r.:[h] 8.4 [2 H, c, 5 lines, Ph], 7.2 [1 H, c, 4 lines, Ph], 7.1 [2 H, c, 3 lines, Ph], 6.3 [1 H, m, 3 lines, CH (cp)], 5.4 [1 H, m, 3 lines, CH (cp)], 4.6 [1 H, m, 3 lines, CH (cp)], 4.5 [1 H, m, 3 lines, CH (cp)], 4.3 [1 H, m, 3 lines, CH (cp)], 4.0 [1 H, m, 3 lines, CH (cp)], 3.7 [1 H, m, 3 lines, CH (cp)], 3.5 [1 H, m, 3 lines, CH (cp)], 2.8 [2 H, ddd, *J* 13.0, 12.5, 5.3, $C_5H_4C\mathit{H}_2CH_2$], 1.8 [2 H, m, 12 lines, CH_2 of Et], 0.9 [3 H, t, *J* 8.0, Me of Et], −0.25 [1 H, ddd, *J* 12.0, 6.2, 6.2, Mo–CH_2], −0.8 [1 H, ddd, *J* 12.0, 6.2, 3.6, Mo–CH_2]
(**6**)	Green	47.0 (47.3)	5.3 (5.2)	^{1}H n.m.r.:[j] 5.2 [4 H, m, 3 lines, CH (cp)], 5.1 [4 H, m, 3 lines, CH (cp)], 2.3 [4 H, q, *J* 7.5, 2 CH_2], 1.1 [6 H, t, *J* 7.5, 2 CH_3]
(**7**)	Red	53.1 (53.5)	5.3 (5.3)	^{1}H n.m.r.:[l] 4.9 [1 H, c, 5 lines, CH (cp)], 4.7 [1 H, c, 5 lines, CH (cp)], 4.2 [1 H, c, 5 lines, CH (cp)], 4.0 [1 H, c, 5 lines, CH (cp)], 3.7 [2 H, c, 7 lines, CH (cp)], 3.2 [1 H, c, 5 lines, CH (cp)], 3.0 [1 H, c, 5 lines, CH (cp)], 2.3 [2 H, m, 10 lines, CH_2], 1.7 [2 H, m, 9 lines, CH_2 of Et], 0.69 [3 H, t, *J* 7.4, Me of Et], −0.8 [1 H, ddd, *J* 4.4, 4.4, 9.6, Mo–CH_2], −0.9 [1 H, ddd, *J* 4.3, 6.5, 7.6, Mo–CH_2]
(**8**)	Red	46.2 (45.6)	5.1 (4.8)	^{1}H n.m.r.:[l] 7.7 [2 H, c, 6 lines, Ph], 7.5 [3 H, c, 6 lines, Ph], 5.5 [1 H, m, 3 lines, CH (cp)], 5.4 [1 H, m, 3 lines, CH (cp)], 5.2 [1 H, m, 3 lines, CH (cp)], 5.1 [1 H, m, 3 lines, CH (cp)], 5.0 [1 H, m, 3 lines, CH (cp)], 4.9 [1 H, m, 3 lines, CH (cp)], 4.8 [1 H, m, 6 lines, *J*(P–H) 11.5, CH (cp)], 4.7 [1 H, m, 3 lines, CH (cp)], 2.71 [1 H, ddd, *J* 4.0, 14.0, 15.0, $C_5H_4C\mathit{H}_2CH_2$], 2.31 [1 H, ddd, *J* 7.5, 12.0, 14.0, $C_5H_4C\mathit{H}_2CH_2$], 2.1 [2 H, c, 10 lines, $C\mathit{H}_2CH_3$], 2.0 [3 H, d, *J* 3.9, PMe], 1.9 [3 H, d, *J* 4.4, PMe], 1.1 [3 H, t, *J* 5.9, CH_3], −0.7 [1 H, dddd, *J* 4.5, 6.5, 10.0, *J*(P–H) 14.0, Mo–CH_2], −0.8 [1 H, dddd, *J* 6.5, 6.5, 13.0, *J*(P–H) 2.0, Mo–CH_2]

[a] Found (required). [b] Given as follows: chemical shift (relative intensity, multiplicity, *J* in Hz, assignment); cp = cyclopentadienyl protons; c = complex; at room temperature unless otherwise stated. [c] In $C_6D_5CD_3$. [d] In CD_2Cl_2. [e] I.r. data (hcbd mull): 1 900m, br, 1 570s, 1 480s, 1 450s cm^{-1}. [f] ^{1}H N.m.r. at −60 °C in $(CD_3)_2CO$: region 6.5—4.0 p.p.m. shows 8 lines due to major isomer and 8 lines due to minor isomer; region 4.0—0.0 p.p.m. has 17 multiplets; −5.09 [s, Mo–H (**2a**)], −5.10 [s, Mo–H (**2b**)]. [g] Mass spectrum: *m/e* = 338 [P^+]. [h] In C_6D_6. [i] I = 43.1 (45.7)%. [j] In $CDCl_3$. [k] Not analysed due to sensitivity. [l] In $(CD_3)_2CO$.

intensity 1. These correspond to the two ABCD spin systems of the different η-cyclopentadienyl rings. In the region 3.0—0.0 p.p.m. another seven distinct multiplets were observed. Decoupling experiments were required to establish the connectivity between these multiplets. The multiplet at 2.9 p.p.m. is characteristic of a co-ordinated vinylic group, implying an η^2-but-1-ene ligand.

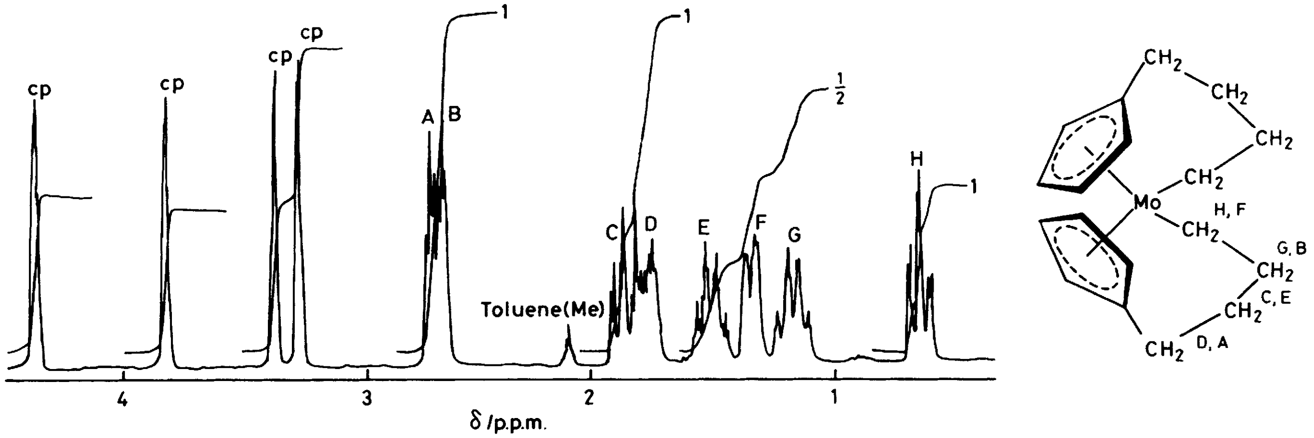
On the basis of the above n.m.r. data we assign to (**3**) the structure [Mo(η^5-$C_5H_4Bu^n$)(η^5:η^2-$C_5H_4CH_2CH_2CH$=CH_2)] (Scheme 1).

Treatment of (**3**) with dilute aqueous hydrochloric acid followed by hexafluorophosphate reformed (**2**). The i.r. spectrum of (**2**) showed a broad band at 1 900 cm^{-1} characteristic of a terminal Mo–H stretch[9] and a band at 1 570 cm^{-1} which can be tentatively assigned to ν(C=C) of a but-1-ene ligand. The room temperature ^{1}H n.m.r. spectrum in $(CD_3)_2CO$ was consistent with the presence in solution of two closely related compounds. Two signals were observed at −4.85 and −4.86 p.p.m. with relative intensities in the ratio 5:3 assigned as two molybdenum hydrides. Sixteen signals were observed in the region normally associated with cyclopentadienyl protons, 4.5—3.0 p.p.m. These sixteen signals can be divided into two groups, also with relative intensities in a 5:3 ratio. The complexity of the region 3.5—0.0 p.p.m. made it impossible to assign fully even with 400 MHz n.m.r. data.

Evidence for the presence of two isomers in equilibrium arises from the observation that, lowering the temperature to −60 °C, caused a slight change in the relative proportions of the two isomers, the ratio now being 2:1. Also, changing the solvent to CD_3OD caused the relative intensities of the signals assignable to the two isomers to alter to a ratio of 1:1. The fact that deprotonation of (**2**) reforms pure (**3**) indicates that each isomer separately deprotonates. In the light of the structure shown for (**3**), the ^{1}H n.m.r. spectrum of (**2**) may be interpreted in terms of *exo* and *endo* isomers of the compound [Mo(η^5:σ-C_5H_4-Bu^n)(η^5:η^2-$C_5H_4CH_2CH_2CH$=CH_2)H]PF_6 (**2**). The proposed isomers are shown in Scheme 1.

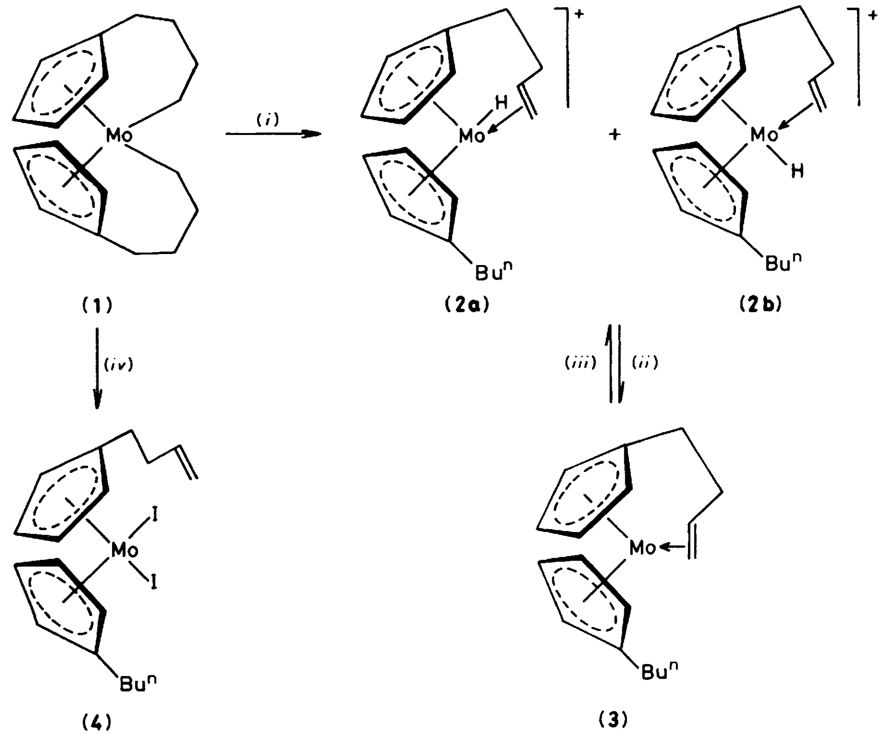
Treatment of [Mo{η^5:σ-$C_5H_4(CH_2)_3CH_2$}$_2$] (**1**) with iodine gave green crystals of (**4**). The ^{1}H n.m.r. spectrum showed three bands characteristic of the presence of two η^5-C_5H_4 groups. In

Table 2. Spin decoupling experiment[a] on $[Mo\{\eta^5:\sigma\text{-}C_5H_4(CH_2)_3CH_2\}_2]$



A,B	C	D	E	F	G	H
↑	d(*J* 14.0)	d(*J* 14.0)	*c*	*b*	*d*	*b*
c	↑	*b*	t(*J* 13.5)	*b*	*b*	*b*
s	*d*	↑	*d*	*b*	*b*	*b*
c	s	d(*J* 6.5)	↑	*b*	*d*	*b*
b	*b*	*b*	*b*	↑	*b*	d(*J* 14.5)
d(*J* 9.0)	*b*	*c*	*d*	*b*	↑	d(*J* 13.9)
b	*c*	*c*	*b*	s	t(*J* 13.9)	↑

[a] cp = Cyclopentadienyl protons; *J* values are in Hz; s = singlet, d = doublet, t = triplet; ↑ = position of irradiation. [b] Essentially no change from original spectrum. [c] Slight change in appearance. [d] Poor resolution (inconclusive).

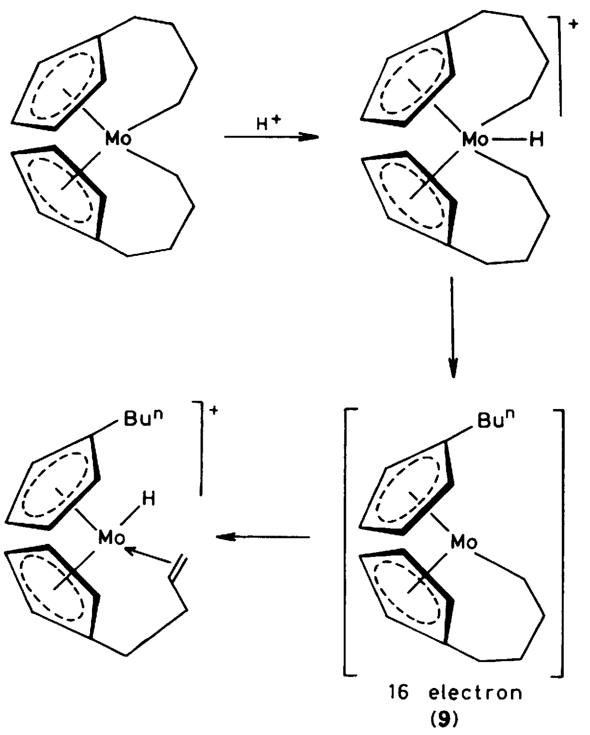


Scheme 1. (*i*) HCl (aq), NH_4PF_6, yield 80%, ratio (**2a**):(**2b**) = (5:3); (*ii*) NaOH (aq); (*iii*) HCl (aq), NH_4PF_6; (*iv*) I_2 in thf, yield > 70%

the region 6.0—0.0 p.p.m., another seven resonances were observed which were assigned with assistance from decoupling experiments. The data show (**4**) to be the compound $[Mo(\eta^5\text{-}C_5H_4Bu^n)(\eta^5\text{-}C_5H_4CH_2CH_2CH{=}CH_2)I_2]$.

The chemistry of the compound (**1**) differs markedly from that of $[Mo(\eta^5:\sigma\text{-}C_5H_4CH_2CH_2)_2]$, in quite unexpected ways. Treatment of $[Mo(\eta^5:\sigma\text{-}C_5H_4CH_2CH_2)_2]$ with proton acids causes rapid cleavage of both Mo–C bonds giving bis(η^5-

ethylcyclopentadienyl) derivatives. However, (**1**), when treated with dilute aqueous HCl, gives the olefin–hydride complex (**2**) and not the expected compound $[Mo(\eta^5\text{-}C_5H_4Bu^n)_2Cl_2]$. A likely mechanism for the formation of (**2**) is shown in Scheme 2. This proposes that the β-elimination reaction of the intermediate (**9**) proceeds more rapidly than the protonation of (**9**) and subsequent reductive elimination of a second n-butyl group. It seems probable that the reductive elimination step is enhanced by a favourable orientation of the β-C–H system arising from constraints within the system.



Scheme 2. Proposed mechanism for formation of (**2**)

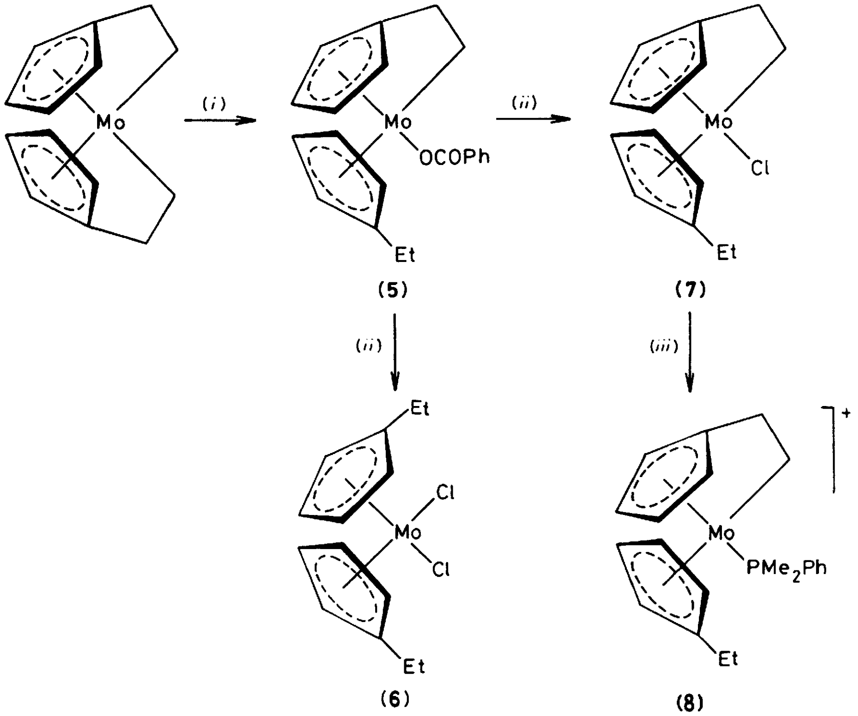
The rapid cleavage of both Mo–C bonds when $[Mo(\eta^5\text{:}\sigma\text{-}C_5H_4CH_2CH_2)_2]$ is treated with iodine, giving $[Mo(\eta^5\text{-}C_5H_4CH_2CH_2I)_2I_2]$,[6] contrasts markedly with the reaction of (**1**) with iodine, giving (**4**). This reaction may proceed *via* initial electron transfer, giving the 17-electron cation $[Mo\{\eta^5\text{:}\sigma\text{-}C_5H_4(CH_2)_3CH_2\}_2]^+$ {*cf.* $[W(\eta^5\text{:}\sigma\text{-}C_5H_4CH_2CH_2)_2]^+$ (ref. 10)}. Homolysis of an Mo–C bond follows, to give a butyl radical and subsequent abstraction by the radical of a β-hydrogen atom from the remaining $[Mo\{\eta^5\text{:}\sigma\text{-}C_5H_4(CH_2)_3\}]$ moiety occurs.

The compound $[Mo(\eta^5\text{-}C_5H_5)_2Et(Cl)]$ reacts in an interesting and unusual manner with tertiary phosphines PR_3 (R_3 = Et_3, $MePh_2$, or Me_2Ph). This results in the transfer of the ethyl group to an η^5-cyclopentadienyl ring, giving the 1-*endo*-ethylcyclopentadiene derivative $[Mo(\eta^5\text{-}C_5H_5)(\eta^4\text{-}1\text{-}endo\text{-}EtC_5H_5)(PR_3)Cl]$.[11]

We were interested to see whether a similar reaction with tertiary phosphine would occur for the closely related compound $[Mo(\eta^5\text{-}C_5H_4Et)(\eta^5\text{:}\sigma\text{-}C_5H_4CH_2CH_2)Cl]$ (**7**), giving the η^4-spiro[2.4]hepta-4,6-diene derivative $[Mo(\eta^5\text{-}C_5H_4Et)\{\eta^4\text{-}C_5H_4(CH_2)_2\}(PR_3)Cl]$. Compound (**7**) was synthesised by first a selective cleavage of one Mo–C σ-bond of $[Mo(\eta^5\text{:}\sigma\text{-}C_5H_4CH_2CH_2)_2]$ using benzoic acid. The red crystalline product of this reaction was $[Mo(\eta^5\text{-}C_5H_4Et)(\eta^5\text{:}\sigma\text{-}C_5H_4CH_2CH_2)(O_2CPh)]$ (**5**) (Scheme 3).

The favoured silicon–oxygen bond formation was then used to drive the exchange reaction between $SiMe_3Cl$ and (**5**) giving $[Mo(\eta^5\text{-}C_5H_4Et)(\eta^5\text{:}\sigma\text{-}C_5H_4CH_2CH_2)Cl]$ (**7**) in high yield.

In this reaction, a small amount of $[Mo(\eta^5\text{-}C_5H_4Et)_2Cl_2]$ (**6**) is also formed, presumably arising from the presence of traces of hydrogen chloride formed by hydrolysis of the chlorotrimethylsilane. This was identified by the ^1H n.m.r. spectrum, δ 5.2 (4 H, m, 3 lines, C_5H_4), 5.1 (4 H, m, 3 lines, C_5H_4), 2.3 (4 H, q, J 7.5, 2 CH_2), and 1.1 p.p.m. (6 H, t, J 7.5, 2



Scheme 3. (*i*) PhCOOH in thf, yield > 80%; (*ii*) $SiMe_3Cl$ in thf, yield of (**7**) 50%, (**6**) 16%; (*iii*) PMe_2Ph in toluene, yield 70%

CH_3), and confirmed by mass spectroscopy which showed a parent ion at $m/e = 354$.

Treatment of (7) with PMe_2Ph, and addition of hexafluorophosphate (NH_4PF_6) gave red crystals of $[Mo(\eta^5\text{-}C_5H_4\text{-}Et)(\eta^5\text{:}\sigma\text{-}C_5H_4CH_2CH_2)(PMe_2Ph)]PF_6$ (**8**). The ^1H n.m.r. spectrum of this compound is very similar to that of (7). In addition, signals due to a co-ordinated PMe_2Ph ligand are observed: δ 2.0 [3 H, d, J(P–H) 3.9, PMe], 1.9 [3 H, d, J(P–H) 4.4, PMe], 7.7 (2 H, c, 6 lines, Ph), 7.5 (3 H, c, 6 lines, Ph). As expected, the two Me groups on the PMe_2Ph ligand are inequivalent due to the presence of a chiral metal centre.

An interesting feature in the ^1H n.m.r. spectrum is that coupling of the ^{31}P nucleus to one of the cyclopentadienyl hydrogens was observed. This was confirmed by the $^1H\text{-}\{^{31}P\}$ n.m.r. spectrum, in which a one proton doublet of triplets collapses into a single triplet.

We therefore conclude that there is no evidence for a metal-to-ring migration reaction of (7).

In conclusion, there are striking differences between the reactivities of the compounds $[Mo\{\eta^5\text{:}\sigma\text{-}C_5H_4(CH_2)_nCH_2\}_2]$ where $n = 1$ or 3. We attribute these differences to the differing proximity of C–H groups to the metal centres.

Experimental

All reactions and manipulations were carried out in an inert atmosphere or *in vacuo*. Light petroleum (b.p. > 80 °C), toluene, and tetrahydrofuran (thf) were dried by refluxing over potassium metal under dinitrogen. Light petroleum of b.p. 30—40 and 40—60 °C was dried over sodium–potassium alloy. Solvents were distilled immediately prior to use. Dichloromethane was dried by refluxing over CaH_2 and stored over molecular sieves (type 4A).

Celite 545 Filter Aid was used as supplied by Koch-Light Laboratories Ltd. Alumina (100—120 mesh) supplied by East Anglia Chemicals was deactivated before use by the addition of 6% by weight of distilled water.

Infrared spectra were recorded on a Pye Unicam SP2000 spectrometer as mulls in either Nujol or hexachlorobutadiene (hcbd) between CsI or KBr plates and were calibrated using hcbd or Nujol. N.m.r. spectra were obtained on either JEOL JNM-PMX (60 MHz), Bruker WH90 (90 MHz), Bruker WH300 (300 MHz), or Bruker WH400 (400 MHz) instruments. Spectra were calibrated using residual solvent peaks as internal standards. All chemical shifts are given in p.p.m. relative to $\delta(SiMe_4) = 0$ p.p.m.; coupling constants are in Hz. Mass spectra were obtained on an AEI MS 902 mass spectrometer; parent ions are given as m/e assignments, for ^{98}Mo.

Spiro[4.4]*nona*-1,3-*diene*.—The following procedure, modified from the published method[12] was used. A 5-l three-necked flask, equipped with an addition funnel, a mechanical stirrer, and a dry-ice condenser was charged with NaH (300 g, 60% in mineral oil, 7.5 mol). After washing the NaH with light petroleum (b.p. 30—40 °C, 2 × 500 cm^3), thf (1.5 l) was added. A mixture of freshly cracked cyclopentadiene (285 cm^3, 3.51 mol) and 1,4-dibromobutane (375 cm^3, 3.13 mol) was added dropwise over 5 h. An exothermic reaction occurred and hydrogen was evolved. Excess of NaH was decomposed with a methanol–water mixture (2:1, 1 l). The two phases were separated, the aqueous phase washed with light petroleum (b.p. 30—40 °C, 2 × 100 cm^3) and the combined extracts dried with sodium sulphate. Finally, distillation under reduced pressure gave the product [b.p. 55 °C at 5 mmHg (*ca.* 670 Pa)]. Yield, 101 cm^3 (40%).

Bis(η^5:σ-4-*cyclopentadienylidenebutyl*)*molybdenum*, (**1**).—Spiro[4.4]nona-1,3-diene (100 cm^3, 0.8 mmol) was condensed with molybdenum atoms (*ca.* 6 g) at −196 °C during a period of 4 h. After warming to room temperature, the mixture was washed from the reaction chamber with thf (*ca.* 1 l). The mixture was then filtered through Celite and the solvent removed under reduced pressure. Extraction of the dried residue with light petroleum (b.p. 40—60 °C, 4 × 500 cm^3) gave a dark red solution which was filtered, concentrated, and chromatographed on an alumina column made up with light petroleum (b.p. 40—60 °C). Elution with light petroleum (b.p. 40—60 °C) gave an orange band, which was collected and concentrated to 30 cm^3. On cooling overnight to −78 °C, red crystalline plates separated. These were collected and dried *in vacuo*. Yield, 3.1 g (12%).

(η^5:η^2-*But*-3-*enylcyclopentadienyl*)(η^5-*butylcyclopentadienyl*)*hydridomolybdenum Hexafluorophosphate*, (**2**).—Compound (**1**) (0.25 g, 0.73 mmol) in toluene (50 cm^3) was treated with aqueous HCl (0.1 mol dm^{-3}, 40 cm^3). The mixture was shaken for 10 min and the two layers were allowed to separate. A saturated aqueous solution of NH_4PF_6 was added to the aqueous layer giving a fine precipitate which was collected and washed with water (2 × 15 cm^3). The isolated powder was recrystallised from an acetone–ethanol (1 : 1) mixture giving red crystals which were collected and dried *in vacuo*. Yield, 0.2 g (80%).

(η^5:η^2-*But*-3-*enylcyclopentadienyl*)(η^5-*butylcyclopentadienyl*)*molybdenum*, (**3**).—A solution of compound (**2**) (0.15 g, 0.44 mmol) in acetone (30 cm^3) was treated with sufficient dilute aqueous NaOH to make the solution basic. The mixture was shaken for 10 min and the solvent removed under reduced pressure. The red residue was extracted with hot light petroleum (b.p. 100—120 °C) (50 cm^3) and concentrated to 25 cm^3. After cooling to −78 °C overnight a red solid was obtained which was washed with cold light petroleum (b.p. 30—40 °C) and dried *in vacuo*. Yield, 0.1 g (70%).

(η^5-*But*-3-*enylcyclopentadienyl*)(η^5-*butylcyclopentadienyl*)-*di-iodomolybdenum*, (**4**).—A solution of compound (**1**) (0.44 g, 1.39 mmol) in thf (20 cm^3) was treated with iodine (0.36 g, 0.71 mmol) in thf (10 cm^3). Within 30 min green-black crystals separated which were collected, washed with diethyl ether (2 × 20 cm^3), and dried *in vacuo*. Yield, 0.57 g (71%).

Benzoato(η^5:σ-2-*cyclopentadienylidene-ethyl*)(η^5-*ethylcyclopentadienyl*)*molybdenum*, (**5**).—The compound $[Mo(\eta^5\text{:}\sigma\text{-}C_5H_4CH_2CH_2)_2]$ (0.651 g, 2.325 mmol) in toluene (50 cm^3) was treated with a stoicheiometric amount of PhCOOH (0.292 g, 2.326 mmol) in toluene (30 cm^3), and the mixture was refluxed for 5 h. The solution darkened. The toluene was removed under reduced pressure, and the resulting red oily residue recrystallised from toluene–light petroluem (b.p. 100—120 °C) (1 : 1, 70 cm^3) giving red crystals which were collected and dried *in vacuo*. Yield, 0.74 g (79%).

Dichlorobis(η^5-*ethylcyclopentadienyl*)*molybdenum*, (**6**), *and chloro*(η^5:σ-2-*cyclopentadienylidene-ethyl*)(η^5-*ethylcyclopentadienyl*)*molybdenum*, (**7**).—Compound (**5**) (0.35 g, 0.87 mmol) in toluene (20 cm^3) was treated with an excess of freshly distilled $SiMe_3Cl$ (0.2 cm^3, 1.8 mmol). Some green crystals slowly formed after 5—10 min, but the solution remained red. The solution was filtered and cooled to −78 °C for 24 h. The resulting green crystals of (**6**) were washed with cold light petroleum (b.p. 40—60 °C) (2 × 30 cm^3) and dried *in vacuo*. Yield, 0.15 g (16%).

(η^5:σ-2-*Cyclopentadienylidene-ethyl*)(*dimethylphenylphosphine*)(η^5-*ethylcyclopentadienyl*)*molybdenum Hexafluorophosphate*, (**8**).—Compound (**7**) (0.2 g, 0.62 mmol) in toluene (50 cm^3) was treated with PMe_2Ph (*ca.* 1 cm^3). The mixture was refluxed at *ca.* 110 °C in a sealed tube overnight. The solvent was removed under reduced pressure, and the residue was extracted with water (60 cm^3). The product was precipitated as the hexafluorophosphate salt by addition of a saturated solution of NH_4PF_6 in water (10 cm^3). The precipitate was isolated, washed with water (2 × 25 cm^3), and recrystallised from acetone–water (slow evaporation) to give red crystals. Yield, 1.55 g (61.0%).

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References

1 M. Berry, K. Elmitt, and M. L. H. Green, *J. Chem. Soc., Dalton Trans.*, 1979, 1950.

2 N. J. Cooper and M. L. H. Green, *J. Chem. Soc., Dalton Trans.*, 1979, 1121.

3 M. L. H. Green, *Pure Appl. Chem.*, 1978, **50**, 27.

4 A. Baretta, F. G. N. Cloke, A. Feiganbaum, A. Gourdon, K. Prout, and M. L. H. Green, *J. Chem. Soc., Chem. Commun.*, 1981, 157; A. Baretta, K. S. Chong, F. G. N. Cloke, A. Feiganbaum, and M. L. H. Green, *J. Chem. Soc., Dalton Trans.*, 1983, 861.

5 K. S. Chong and M. L. H. Green, *Organometallics*, 1982, **12**, 1586.

6 P. Eilbracht and P. Dahler, *J. Organomet. Chem.*, 1977, **135**, C26.

7 F. G. N. Cloke and M. L. H. Green, *J. Chem. Soc., Dalton Trans.*, 1981, 1938.

8 M. L. H. Green, 'IUPAC, Frontiers of Chemistry,' ed. K. J. Laidler, Pergamon Press, Oxford, 1982, p. 229.

9 H. D. Kaesz and R. B. Saillent, *Chem. Rev.*, 1972, **72**, 231.

10 K. S. Chong and M. L. H. Green, *J. Chem. Soc., Chem. Commun.*, 1982, 991.

11 F. W. S. Benfield and M. L. H. Green, *J. Chem. Soc., Dalton Trans.*, 1974, 1324.

12 C. F. Wilcox and E. R. Craig, *J. Am. Chem. Soc.*, 1961, **83**, 3866.

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