Preparation and Properties of Metallacyclopentane and Dineopentyl Derivatives of Molybdenocene and Tungstenocene. *X*-Ray Crystal and Molecular Structure of Bis(η-cyclopentadienyl)molybdenacyclopentane *

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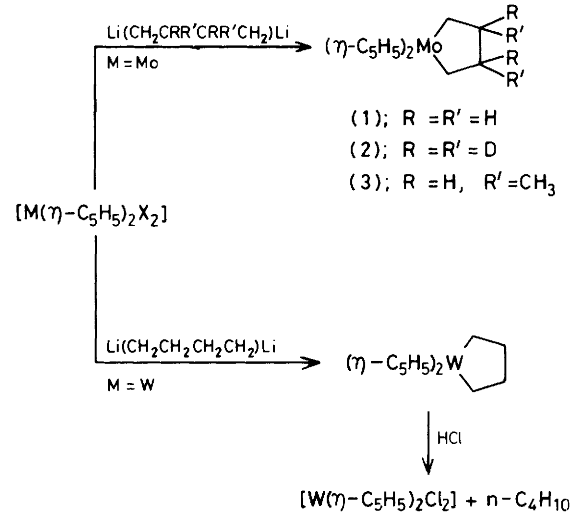
The interaction of $[Mo(\eta\text{-}C_5H_5)_2I_2]$ with the appropriate dilithium reagents yields the metallacyclopentane derivatives $[\overline{Mo(CH_2CH_2CH_2CH_2})(\eta\text{-}C_5H_5)_2]$ (1), $[\overline{Mo\{CH_2(CD_2)_2CH_2}\}(\eta\text{-}C_5H_5)_2]$ (2), and $[\overline{Mo(CH_2CHMeCHMeCH_2})(\eta\text{-}C_5H_5)_2]$ (3). Structures for these compounds are proposed on the basis of elemental analysis, n.m.r. and mass spectrometry. The crystal structure of the molybdenum parent compound (1) has been determined from *X*-ray diffractometer data and refined by least squares. Crystals of (1) are Monoclinic, space group $P2_1/c$, with unit-cell parameters a = 11.352(2), b = 7.665(1), c = 16.111(3) Å, β = 121.37(2)°, and Z = 4; R = 0.047 based on 1 272 observed reflections. The structural details are discussed also in terms of their chemical significance. Carbonylation of (1) yields cyclopentanone; compounds (1)—(3) give, by thermal decomposition, the corresponding olefins as the major products in addition to small amounts of olefins derived from metallacycle fragmentation. The dineopentyl derivatives $[M(CH_2CMe_3)_2(\eta\text{-}C_5H_5)_2]$ (M = Mo or W) have been prepared and their thermal decomposition has been investigated. No isolable metallacyclobutane has been obtained.

Metallacycloalkane derivatives of molybdenum and tungsten are relatively rare, in spite of their mechanistic relevance to the metathesis reaction catalyzed by compounds of these metals.[1]

The only reports on Group 6A metallacyclopentanes are those by Grubbs and Brunck [2] and Levisalles *et al.*[3] who have tested the intermediacy of these compounds in olefin metathesis, by reacting WCl_6 with 1,4-dilithio- or 1,4-dihalogenomagnesium butanes and studying the nature of the decomposition products; however, no tungstenacycle has been isolated. On the other hand, some metallacyclobutane derivatives of molybdenum and tungsten have been elegantly obtained by Green and co-workers [4] by addition of nucleophiles to η^3-allyl compounds.

During our continuing study [5] of the chemistry of metallacycloalkanes, we set out to prepare stable metallacyclopentane derivatives of molybdenocene and tungstenocene. We have also started the preparation of the corresponding neopentyl derivatives in order to test the possibility of their conversion to metallacyclobutanes *via* a γ-hydrogen elimination reaction; examples of this reaction have been recently reported [6-9] for Group 8A metals. These studies are described below.



Scheme 1.

Results and Discussion

Preparation of Metallacyclopentanes.—Treatment of molybdenocene dihalides $[Mo(\eta\text{-}C_5H_5)_2X_2]$ (X = Cl, Br, or I) with an excess of 1,4-dilithiobutane in diethyl ether followed by chromatographic purification of the pentane-soluble materials, yields orange-red crystals of bis(η-cyclopentadienyl)-molybdenacyclopentane (1) (Scheme 1). The yields are strongly dependent on the nature of the starting dihalide, being poorest for the dichloride, and highest for the di-iodide (*ca.* 40%). Also, the alkylating reagent : molybdenum molar ratio is found to be critical; the highest yields are observed when the ratio is about 2.5 : 3. Compound (1) was not obtained when a ' 1,4-diGrignard ' was used as the alkylating reagent; similarly, the formation of $[Mo(\eta\text{-}C_5H_5)_2Me_2]$ was found to be critically dependent on the nature of the alkylating reagent.[10,11]

Surprisingly, all the efforts made in order to isolate the tungstenacyclopentane analogue, starting from $[W(\eta\text{-}C_5H_5)_2X_2]$ (X = Cl, Br, or I) and ' 1,4-diGrignard ' or 1,4-dilithiobutane, were frustrated; however, by using 1,4-dilithiobutane and following the same work-up adopted for (1), small

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* *Supplementary data available* (No. SUP 23540; 14 pp.): structure factors, thermal parameters. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Non-S.I. units employed: 1 atm = 101 325 Pa; 1 mmHg = (101 325/760) Pa.

Table 1. Analytical and spectroscopic data

Compound	Colour	Analysis (%) [a] C	Analysis (%) [a] H	m/e [b]	^{1}H N.m.r.[c]
(1) $\overline{Mo(CH_2CH_2CH_2CH_2)}(\eta\text{-}C_5H_5)_2]$ [d]	Orange-red	59.8 (59.6)	6.55 (6.45)	284	4.14, **10** (s), C_5H_5; 1.8, **8** (cm), $-(CH_2)_4-$
(2) $[\overline{Mo\{CH_2(CD_2)_2CH_2\}}(\eta\text{-}C_5H_5)_2]$	Orange-red			288	4.14, **10** (s), C_5H_5; 1.7, **4** (bs), $MoCH_2$
(3) $[\overline{Mo\{CH_2(CHMe)_2CH_2\}}(\eta\text{-}C_5H_5)_2]$	Red	61.85 (61.95)	6.9 (7.15)	312	4.18, **10** (s), C_5H_5; 2.1—0.9, **12** (cm), $-CH_2(CHMe)_2CH_2-$
(4) $[Mo(CH_2CMe_3)_2(\eta\text{-}C_5H_5)_2]$	Orange-yellow	65.05 (65.2)	8.9 (8.75)	370	4.37, **10** (s), C_5H_5; 1.1, **18** (s), Me; 0.65, **4** (s), CH_2
(5) $[W(CH_2CMe_3)_2(\eta\text{-}C_5H_5)_2]$	Orange	52.55 (52.65)	6.55 (7.05)	456	4.26, **10** (s), C_5H_5; 1.1, **18** (s), Me; 0.89 and 1.3, **4** (cm), CH_2
(6) $[\{Mo(CH_2CMe_3)(\eta\text{-}C_5H_5)\}_2(\mu\text{-}\sigma : \eta^5\text{-}C_5H_4)_2]$	Yellow-green	60.5 (60.8)	6.2 (6.8)		5.58, 4.03, 2.98, and 2.32, **8** (cm), C_5H_4; 4.40, **10** (s), C_5H_5; 0.91, **18** (s), CH_3; 0.37, **4** (s), CH_2
(7) $[W(CH_2CMe_3)_2(\eta\text{-}C_5H_5)_2][PF_6]$ [e]	Violet	53.55 (52.65)	6.55 (7.05)		

[a] Calculated values are given in parentheses. [b] Mass spectra; parent ions only are given for ^{98}Mo and ^{184}W. For (1)—(3) the fragmentation patterns at values lower than 230 $[Mo(C_5H_5)_2^+$, base peak] are identical, and resemble that reported[11] for $[Mo(\eta\text{-}C_5H_5)_2Me_2]$. [c] In C_6D_6 solution referenced to the $SiMe_4$ as internal standard; given as chemical shift (δ), **relative intensity** (multiplicity), assignment; bs = broad singlet, cm = complex multiplet. [d] Carbon-13 n.m.r. (C_6D_6, δ/p.p.m. from $SiMe_4$): 88.3 (C_5H_5), 37.3 (Mo-β-CH_2), 14.5 (Mo-α-CH_2). [e] I.r. (KBr disc) 3 120s (C_5H_5); 2 950s, 2 865m, 850s (CH_3); 535s cm^{-1} (PF_6).

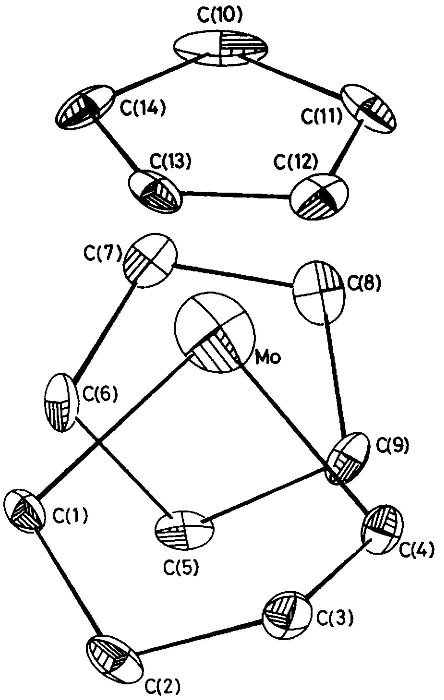


Figure. ORTEP drawing of (1), viewed along the *b* axis

Table 2. Selected bond distances (Å), angles (°), and torsion angles * for (1) with estimated standard deviations in parentheses

Mo–C(1)	2.267(12)	C(1)–C(2)	1.48(2)
Mo–C(4)	2.270(16)	C(2)–C(3)	1.44(3)
Mo–C(5)	2.255(12)	C(3)–C(4)	1.54(2)
Mo–C(6)	2.324(12)	C(5)–C(6)	1.41(3)
Mo–C(7)	2.322(15)	C(5)–C(9)	1.41(2)
Mo–C(8)	2.297(12)	C(6)–C(7)	1.37(2)
Mo–C(9)	2.293(15)	C(7)–C(8)	1.36(3)
Mo–C(10)	2.254(13)	C(8)–C(9)	1.34(3)
Mo–C(11)	2.257(13)	C(10)–C(11)	1.40(3)
Mo–C(12)	2.304(14)	C(10)–C(14)	1.39([illegible]
Mo–C(13)	2.320(18)	C(11)–C(12)	1.32(2)
Mo–C(14)	2.277(19)	C(12)–C(13)	1.27(3)
		C(13)–C(14)	1.35(2)
C(1)–Mo–C(4)	74.9(5)	C–C–C (C_5H_5 ring 1, av.)	108.0(11)
Mo–C(1)–C(2)	112.0(9)		
Mo–C(4)–C(3)	112.9(10)	C–C–C (C_5H_5 ring 2 av.)	108.0(11)
C(1)–C(2)–C(3)	111.1(12)		
C(2)–C(3)–C(4)	111.4(11)		
Mo–C(1)–C(2)–C(3)	−44(2)	C(2)–C(1)–Mo–C(4)	21(2)
Mo–C(4)–C(3)–C(2)	−26(2)	C(1)–C(2)–C(3)–C(4)	46(2)
C(1)–Mo–C(4)–C(3)	2(2)		

* The angle A–B–C–D has positive sign if, looking along the B–C bond, the near bond is rotated clockwise with respect to the far bond.

amounts of an impure oily product were obtained, which gave n-butane and $[W(\eta\text{-}C_5H_5)_2Cl_2]$ on reaction with dry HCl, and cyclopentanone on reaction with carbon monoxide.

Following the above general procedure, the molybdenacyclopentanes (2) and (3) were also prepared by reaction of $[Mo(\eta\text{-}C_5H_5)_2I_2]$ with the appropriate substituted 1,4-dilithiobutane (Scheme 1).

Compounds (1)—(3) are orange-red crystalline compounds soluble in most organic solvents. Solutions in air show signs of decomposition almost immediately whilst the crystals decompose more slowly. In Table 1 are reported the analytical and spectroscopic data. It is interesting to note that in the ^{1}H n.m.r. of (1) the chemical shift of the α-methylene protons is similar to that of the β-methylene protons; analogous results are reported[5c,12] for pallada- and platina-cyclopentane complexes. In the case of (3) the interpretation of the aliphatic region of the spectrum, which consists of a super-imposition of resonances, is further complicated by the presence of a mixture of stereoisomers, therefore no unequivocal assignment can be made.

Crystal and Molecular Structure of (1).—The crystal structure of (1) is based on the packing of $[\overline{Mo(CH_2CH_2CH_2CH_2)}(\eta\text{-}$

Table 3. Results of one-factor variance analysis on C–C distances (Å) of metallacyclopentane derivatives[a]

	$[Ir(CH_2CH_2CH_2CH_2)(\eta\text{-}C_5Me_5)(PPh_3)]$[b]	$[Co(CH_2CH_2CH_2CH_2)(\eta\text{-}C_5H_5)(PPh_3)]$[b]	$[Mo(CH_2CH_2CH_2CH_2)(\eta\text{-}C_5H_5)_2]$[c]
C(1)–C(2)	1.51	1.51	1.48
C(2)–C(3)	1.32	1.45	1.44
C(3)–C(4)	1.55	1.54	1.54

[a] The *F* value (8.03), computed on the basis of all the C–C distances in the three rows, is larger than 7.26, *i.e.*, $F_{0.025}$ (2,6). The *F* value (15.58), computed on the basis of the C–C distances in rows 1 and 3, is larger than 12.22, *i.e.*, $F_{0.025}$ (1,4). For tables of *F* values see ref. 18. When the computed *F* value exceeds the tabled value F_α $(r - 1, n - r)$, where *n* is the number of observations and *r* is the number of the rows in the Table, the data are consistent with the null hypothesis that the means within the rows are all equal only at the level of significance α. [b] Ref. 5(*e*). [c] Present work.

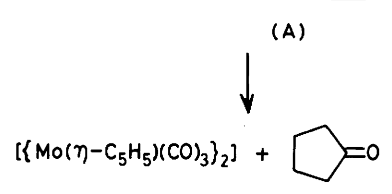
$C_5H_5)_2]$ molecules, each having approximate C_s symmetry with the pseudo-mirror plane passing through the Mo atom and the centres of gravity of the two cyclopentadienyl rings. Actually, the symmetry of the metallacyclic moiety, in view of its puckering, is better described as C_2 with the Mo atom and the midpoint of the C(2)–C(3) bond (Figure) lying on the pseudo-rotation axis. Selected bond distances, angles, and torsion angles in the molecule are given in Table 2. The average value of the Mo–C σ bonds (2.269 Å) is comparable with similar distances found in $[Mo(\eta^5\text{-}C_5H_4\text{-}CH_2CH_2)_2]$ (2.27 Å)[13] and in $[Mo(\eta^5\text{-}C_5H_5)_2(Et)Cl]$ (2.28 Å)[14] for Mo^{IV}–C σ bonds and should be considered relatively long in view of the value of 2.29 Å found[15] for a Mo^{III}–C σ bond and in view of the Mo–C(cyclopentadienyl) distances found in the present structure (average value 2.29 Å) as well as in the above cited[13,14] complexes. Indeed, a probable value for the Mo^{IV} radius can be derived (1.48 Å) from the average Mo–Cl distance (2.471 Å)[14] in $[Mo(\eta^5\text{-}C_5H_5)_2Cl_2]$ on the basis of the accepted value of 0.99 Å for the radius of Cl,[16] thereby obtaining a value of 2.25 Å for the expected Mo^{IV}–C σ bond length. In view of this reasoning, the Mo–C σ bonds in the two already cited[13,14] complexes should be considered also relatively long. While in the former complex[13] this feature can be correlated with the strained conformation of the hydrocarbon ligand, in the latter[14] the apparent lengthening of the Mo–C(ethyl) distance may be attributed to the electron-withdrawing action of the Cl atom in the co-ordination sphere.

The angle C–Mo–C in the metallacycle (75°) is smaller than the minimum value (76°) expected[17] on theoretical grounds for a d^2 complex. This result can be attributed to the steric requirements of the ring and may be correlated with the above discussed lengthening of the Mo–C σ bonds. All these results describe a structural situation fairly close to that expected for the metallacyclic moiety in a transition state in the thermal decomposition reaction leading to n-C_4 olefins (see next section).

The C(2)–C(3) distance is shorter than the average (1.51 Å) of the other two C–C distances in the ring by >2σ, indicating a trend which has been observed[5e] by us in two other metallacyclopentane derivatives of cobalt(III) and iridium(III). This trend can be substantiated using conventional analysis of variance[18] as shown in Table 3.

The two η^5 co-ordinated C_5H_5 rings are planar and staggered to each other. The normals to these rings form an angle of *ca.* 139° and the average distance from their centres to the metal atom is 1.977 Å. The range of Mo–C(cyclopentadienyl) distances is 2.25—2.32 Å. While in ring 1 [atoms C(5)—C(9)] only Mo–C(5) is significantly shorter than the average of the other four Mo–C distances (2.309 Å), in ring 2 [C(10)—C(14)] three distances, symmetrically distributed with respect to the pseudo-mirror plane of the approximate C_s symmetry, average to 2.263 Å; this value is significantly shorter than the average of the other two distances (2.312 Å). The latter result may be indicative of a trend in ring 2 towards a change from η^5 to η^3 co-ordination.

Chemical Studies.—(*a*) *Reaction with carbon monoxide.* The carbonylation of (1) (1 atm, room temperature) in various solvents [*e.g.* pentane, tetrahydrofuran (thf), or benzene] yields cyclopentanone. The reaction proceeds slowly (48 h) in poor yields; the recovered organometallic product, insoluble in common organic solvents, exhibits no i.r. acyl or carbonyl absorptions. The same results are obtained when the reaction is carried out under CO pressure (50 atm) at room temperature. On the other hand, cyclopentanone is obtained in almost quantitative yields, in addition to $[\{Mo(\eta\text{-}C_5H_5)(CO)_3\}_2]$, when (1) is carbonylated in toluene at 80 °C under 50 atm CO pressure (Scheme 2).

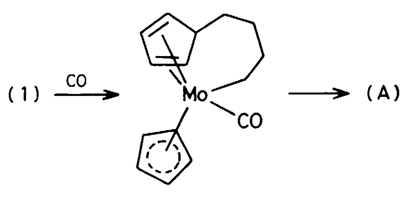


Scheme 2.

Considering that (1) is a 18-electron system, the formation of the intermediate compound (A) *via* the CO insertion into the Mo–C bond, which is the key step for the formation of cyclopentanone, is puzzling. Apart from the intervention of a rather exceptional external CO attack, a plausible explanation is a rearrangement of the $\eta^5\text{-}C_5H_5$ to a $\eta^3\text{-}C_5H_5$ moiety in the intermediate, which is substantiated by the above discussed structural features of (1). Such a mode of bonding has been recently recognised[19] in $[W(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_5H_5)(CO)_2]$.

However, it is interesting to note that, under similar conditions, $[Mo(\eta\text{-}C_5H_5)_2Me_2]$ reacts[10] with CO to give $[Mo(CO)_6]$ and MeC_5H_5, the latter being derived from two successive methyl-to-ring steps giving an intermediate *endo*-methylcyclopentadiene species. On this basis a reasonable mechanism could involve an analogous migration of one of the ends of the tetramethylene moiety, followed by CO co-ordination, according to Scheme 3.

The different results found in the carbonylation of (1) compared with the carbonylation[10] of $[Mo(\eta\text{-}C_5H_5)_2Me_2]$ are



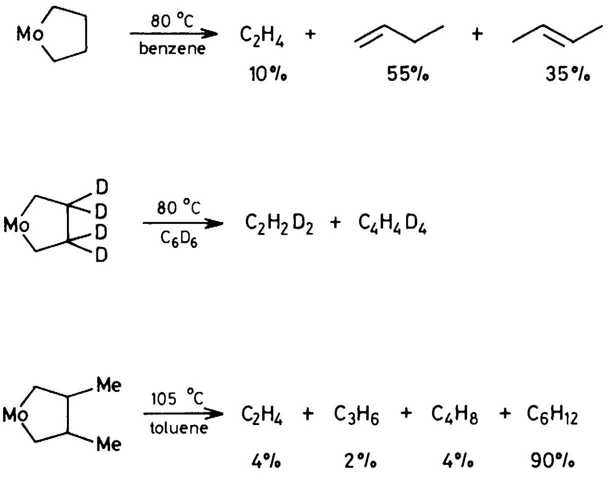
Scheme 3.

probably a consequence of the particular structure of the chelating tetramethylene moiety.

(*b*) *Thermal decomposition.* Metallacycles have been found to thermally decompose, exhibiting a variety of degradation patterns including most fundamental organometallic elimination reaction types.[20] Thermal decomposition of several transition metal metallacycles has been studied following pioneering studies by Whitesides and co-workers.[12,21,22]

So far, the absence of well characterized compounds has prohibited such a study on Group 6A metallacycles. We have therefore studied the thermal decomposition of (1) along with that of the related substituted molybdenacyclopentanes (2) and (3).

The thermal decomposition of (1)—(3) has been carried out by heating benzene solutions at 80 °C, and analyzing the organic volatile products by g.l.c.-mass spectrometry combined techniques (Scheme 4).

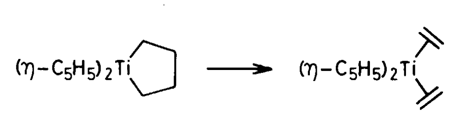


Scheme 4.

In all cases the major products are those expected from hydrogen β-elimination reactions, *i.e.* C_4 olefins [or C_6 in the case of (3)]. However, substantial amounts of ethylene have been found in the decomposition of (1) and (2). In particular, in the case of the deuterium-substituted molybdenacyclopentane (2), the $[^2H_2]$ethylene is the only C_2 product detected. Apparently, β-C–C cleavage is involved; this is in agreement with the data of Grubbs and Brunck [2] who found predominantly $[^2H_1]$ethylene in the decomposition of a tungstenacyclopentane of the type $W(\overline{CH_2CHDCHDCH_2})$ formed *in situ.*

The results of the thermal decomposition of (3) are, on the contrary, not so easily interpreted. In fact, in addition to the C_6H_{12} olefins (90%) probably derived from a β-hydrogen elimination, small amounts of C_2, C_3, and C_4 olefins have been found. Assuming for (3) a decomposition pattern analogous to that observed for (2), the formation of propylene only would be expected. The fact that ethylene and C_4 olefins are also observed in roughly equimolar amounts could be interpreted in terms of a migration of the metal along the heterocycle skeleton.

The formation of ethylene from metallacyclopentanes has been studied theoretically by Hoffmann and co-workers [17,23] and it was found to be a symmetry-allowed reaction for titaniacyclopentanes (see below). On the contrary, the corresponding molybdenum bis(ethylene) complex would not be expected from the degradation of (1), since it would lead to a 20-electron species with occupied antibonding orbitals. Accordingly, the major products are those expected from the β-hydrogen elimination reaction which does not suffer such restrictions. On the other hand, the formation of some ethylene could be easily explained if a rearrangement of the C_5H_5 moiety from an η^5 to an η^3 bonding mode is envisaged (see previous discussion on the carbonylation reaction).



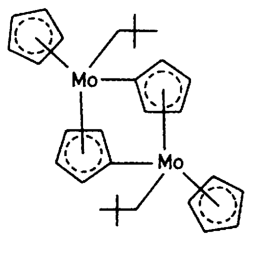
Finally, (1) does not exchange on reaction with propylene; neither substituted molybdenacyclopentanes nor the corresponding decomposition products have been detected in the reaction, the starting (1) being recovered unchanged.

Neopentyl Derivatives.—The metallocene dihalides $[M(\eta\text{-}C_5H_5)_2X_2]$ ($M = Mo$, $X = I$; $M = W$, $X = Cl$ or Br) react slowly with an excess of $Mg(CH_2CMe_3)X$ or $Li(CH_2CMe_3)$ in diethyl ether to give the yellow-orange crystalline complexes $[M(CH_2CMe_3)_2(\eta\text{-}C_5H_5)_2]$ [$M = Mo$, (4); $M = W$, (5)]. Compounds (4) and (5) are relatively stable to air in the solid state and can be kept indefinitely at low temperature under a nitrogen atmosphere. In Table 1 are reported the analytical and spectroscopic data. The mass spectra confirm the structural assignment, showing, in addition to the isotopic cluster of the parent peak, molecular ions corresponding to the loss of one and then of both the neopentyl groups.

A noticeable feature of (4) and (5) is that the ^1H n.m.r. spectra of freshly prepared solutions invariably showed considerable line broadening. When the tubes were left to stand a few hours, the linewidths reduced to normal values. The line-broadening effect varied considerably for different resonances, *e.g.* the η-C_5H_5 absorptions were markedly broader than the methyl absorptions. Probably, the line broadening is due to the presence of trace amounts of paramagnetic impurities which slowly decompose to non-interfering species. In the case of (4) the CH_2 attached to the metal atom is visible only when the sharp line spectrum is recorded, completely disappearing when a broad resonance for the cyclopentadienyl moiety is observed. In the case of (5), the bands assignable to the methylene groups appear as two broad signals. This behaviour could be attributed to steric overcrowding due to the bulky neopentyl groups which cause the CH_2 hydrogens to become non-equivalent on the time-scale of the experiment.

In the preparation of (4) using lithium neopentyl as the alkylating reagent, a second yellow-green band was eluted with pentane–diethyl ether (10 : 1). This minor product (10% yield) shows in the ^1H n.m.r. spectrum, in addition to the methyl and the cyclopentadienyl signals, a very characteristic pattern (four signals at δ 5.58, 4.03, 2.98, and 2.32 p.p.m. in the ratio 1 : 1 : 1 : 1). This spectroscopic behaviour strongly resembles that found by Green and co-workers [24] in binuclear molybdenocene derivatives containing two equivalent η^5-C_5H_5

groups and two equivalent μ-σ : η^5-C_5H_4 groups. On this basis this compound has been tentatively assigned the structure (6).



(6)

In order to test whether (4) and (5) could be induced to lose neopentane and give metallacyclobutane derivatives, we studied their thermal decomposition. Benzene solutions of (4) or (5) were heated at temperatures of 40—90 °C and the reactions followed by ^{1}H n.m.r. spectroscopy. The tungstenocene dineopentyl compound was found to be remarkably stable even at 90 °C for a long time (after 60 h of heating no new signals were observed). The molybdenocene dineopentyl compound was less stable, showing even at 40 °C a slow formation of neopentane and dineopentyl and a new unidentified organometallic compound, which does not correspond to the expected metallacyclobutane derivative. Also compound (6), which in principle could be prepared from an elimination of neopentane from (4) followed by a rearrangement of the fragment so obtained, was absent.

Why is thermal intramolecular C–H activation to give metallacyclobutane derivatives apparently unfavourable? Our view is that, assuming that such a reaction occurs *via* internal oxidative addition, a successful γ-abstraction reaction requires that in the 18-electron systems (4) and (5), the η^5-C_5H_5 rearranges to a η^3-C_5H_5 moiety, which is thermally very unlikely.

In an attempt to overcome this difficulty we investigated the synthesis of neopentyl halide ionizable systems. However, we could not prepare such complexes *via* the reaction of $[M(\eta\text{-}C_5H_5)_2X_2]$ with equimolar amounts of alkylating reagent: under these conditions no reaction occurs.

We also tried the reaction of (4) and (5) with iodine. Treatment with equimolar amounts of iodine gave, in *ca.* 1 : 1 ratio, $[M(\eta\text{-}C_5H_5)_2I_2]$ and the unchanged dineopentyl complex. By increasing the molar ratio of metal complex : iodine to 2 : 1, it is possible, in the case of W, to isolate, after conversion into the hexafluorophosphate salt, $[W(CH_2CMe_3)_2(\eta\text{-}C_5H_5)_2][PF_6]$ (7). In the case of Mo a similar compound has been obtained, but we were not able to prepare samples giving satisfactory elemental analysis. Such one-electron oxidation to a dialkyl tungsten(V) cationic complex has been previously observed by Green and co-workers [25] for $[W(\eta\text{-}C_5H_5)_2Me_2]$.

Experimental

All operations were carried out under nitrogen or argon by Schlenk techniques. Diethyl ether and thf first were refluxed and distilled from sodium, and then from lithium aluminium hydride. Pentane and benzene were washed free of olefins or thiophene with concentrated sulphuric acid, dried on calcium chloride, and then distilled from lithium aluminium hydride. Unless otherwise stated, other solvents were reagent grade, and were degassed under vacuum and dried on molecular sieves before use.

Hydrogen-1 n.m.r. spectra were run at 60 MHz on a Varian T60 instrument by using $SiMe_4$ as internal standard. Carbon-13 n.m.r. spectra were run on a Varian XL 100 instrument. Mass spectra were obtained with a Varian MAT CH7 spectrometer. Infrared spectra were run on a Perkin-Elmer 283-B instrument. G.l.c. analyses were performed on a Carlo Erba Fractovap GT or a Perkin-Elmer F30 instrument equipped with flame ionization detector. Melting or decomposition points were determined with a Kofler hot-stage apparatus and are uncorrected. Microanalyses were performed by the Laboratorio di Microanalisi of the Istituto di Chimica Organica, Facoltà di Farmacia, Università di Pisa.

$[M(\eta\text{-}C_5H_5)_2H_2]$ (M = Mo or W) were prepared following a modification [26] of the previously reported method.[27] $[M(\eta\text{-}C_5H_5)_2X_2]$ (M = Mo or W; X = Cl, Br, or I) were prepared from the dihydrides by the literature method.[28] $BrMg(CH_2)_4MgBr$,[29] $Mg(CH_2CMe_3)Cl$,[30] $Li(CH_2CMe_3)$,[30] and $Li(CH_2)_4Li$ [12] were prepared as described previously.

Preparation of $Li(CH_2CD_2CD_2CH_2)Li$.—[$^2H_4$]Dimethyl succinate $CH_3OC(O)CD_2CD_2C(O)OCH_3$, was prepared in 98% yield from $CH_3OC(O)CCC(O)OCH_3$ (Fluka) by catalytic deuteriation (10 atm) with PtO_2.[31] $HOCH_2CD_2CD_2CH_2OH$ [b.p. 132—136 °C (17 mmHg)] was obtained in 64% yield after treatment of [$^2H_4$]dimethyl succinate with $LiAlH_4$ in diethyl ether.[31] $ClCH_2CD_2CD_2CH_2Cl$ [b.p. 56—61 °C (17 mmHg); ^{1}H n.m.r. δ 3.58 (s) p.p.m.; isotopic purity 99%] was obtained in 42% yield after treatment of the corresponding alcohol with $SOCl_2$ in benzene. Reaction of the dichloride with lithium in diethyl ether at 0 °C yielded the title compound (47%).

Preparation of $Li(CH_2CHMeCHMeCH_2)Li$.—1,2-Diethyl 2,3-dimethylsuccinate [b.p. 109—110 °C (20 mmHg)] was prepared in 97% yield from 2,3-dimethylsuccinic acid (Merck, mixture of *meso* and DL forms) using the Vogel azeotropic mixture method.[32a] $HOCH_2CHMeCHMeCH_2OH$ [b.p. 140—141 °C (20 mmHg)] was isolated in 94% yield after treatment of 1,2-diethyl 2,3-dimethyl succinate with $LiAlH_4$ in diethyl ether.[32b] $ClCH_2CHMeCHMeCH_2Cl$ [b.p. 75—76 °C (20 mmHg); ^{1}H n.m.r. consistent with the literature report for a mixture of *meso* and DL forms [33]] was isolated in 90% yield after treatment of the alcohol with $SOCl_2$ and pyridine (2.5 cm^3), using the procedure described by Vogel.[32c] Reaction of the dichloride with lithium in diethyl ether at 0 °C yielded the title compound (85%).

$[\overline{Mo(CH_2CH_2CH_2CH_2})(\eta\text{-}C_5H_5)_2]$ (1).—The compound $[Mo(\eta\text{-}C_5H_5)_2I_2]$ (1.14 g, 2.3 mmol) suspended in diethyl ether (80 cm^3) was treated with 1,4-dilithiobutane (7.0 mmol; 16 cm^3 of a 0.44 mol dm^{-3} diethyl ether solution). The resulting mixture was stirred at room temperature for 24 h and then filtered. A red solution was obtained which, after removal of solvent under reduced pressure, gave a residue that was extracted with pentane (2 × 70 cm^3). The combined pentane extracts were concentrated to 15 cm^3 and chromatographed on a column of neutral alumina (Merck, diameter 1.5 cm, height 15 cm) using diethyl ether–pentane (1 : 6) as eluant. The first yellow-orange band eluted, containing a mixture of (1) and 1,4-dichlorobutane, was discharged and the second orange band was collected; this gave orange-red crystals of (1) (0.25 g, 39%) which were recrystallized from pentane at −30 °C.

Treatment of a benzene solution of (1) with dry HCl gave $[Mo(\eta\text{-}C_5H_5)_2Cl_2]$ and n-butane (100%) (identified by g.l.c analysis).

Reaction of $[W(\eta\text{-}C_5H_5)_2I_2]$ *with* 1,4-*Dilithiobutane*.—Following the same procedure reported for (1), $[W(\eta\text{-}C_5H_5)_2I_2]$

(0.85 g, 1.5 mmol) suspended in diethyl ether (70 cm^3) was treated with 1,4-dilithiobutane (4.5 mmol; 10.3 cm^3 of a 0.44 mol dm^{-3} diethyl ether solution) to give 0.107 g of an orange-red oily product. Treatment of a benzene solution of this product with anhydrous HCl gave [$W(\eta\text{-}C_5H_5)_2Cl_2$] and n-butane (identified by g.l.c. analysis); treatment with CO (1 atm) at room temperature gave cyclopentanone (identified by g.l.c.).

Reaction of (1) *with Carbon Monoxide.*—(*a*) *At atmospheric pressure.* A benzene solution of (1) (0.102 g, 0.36 mmol) was placed under an atmosphere of CO and stirred at room temperature for 48 h. An unidentified green-black precipitate and an orange solution were obtained. The solution was flash-distilled under vacuum and the volatile products were trapped at −78 °C. G.l.c. analysis revealed the presence of cyclopentanone. The orange solid residue was identified as unreacted (1) (yield 75%). The same results were obtained using n-pentane or thf as solvents.

(*b*) *At* 50 *atm* CO *pressure.* A toluene solution of (1) (0.09 g, 0.32 mmol) was placed in a stainless-steel autoclave under 50 atm CO pressure and stirred at 90 °C for 12 h. The red solution obtained was flash-distilled under vacuum and the volatile products were trapped at −78 °C. G.l.c. analysis revealed the presence of cyclopentanone (yield 90%). The red-violet solid residue was identified as [$Mo(\eta\text{-}C_5H_5)(CO)_3$] (yield 83%).

[$\overline{Mo(CH_2CD_2CD_2CH_2})(\eta\text{-}C_5H_5)_2$] (2).—Following the same procedure reported for (1), [$Mo(\eta\text{-}C_5H_5)_2I_2$] (0.49 g, 1.03 mmol) suspended in diethyl ether (70 cm^3) was reacted with $Li(CH_2CD_2CD_2CH_2)Li$ (3.06 mmol; 8.5 cm^3 of a 0.36 mol dm^{-3} diethyl ether solution) to give 0.112 g (yield 38%) of orange-red crystals of (2).

[$\overline{Mo(CH_2CHMeCHMeCH_2})(\eta\text{-}C_5H_5)_2$] (3).—Following the same procedure reported for (1), [$Mo(\eta\text{-}C_5H_5)_2I_2$] (0.82 g, 1.71 mmol) suspended in diethyl ether (80 cm^3) was reacted with $Li(CH_2CHMeCHMeCH_2)Li$ (5.1 mmol; 10.3 cm^3 of a 0.5 mol dm^{-3} diethyl ether solution) to give 0.165 g (yield 31%) of orange-red crystals of (3).

Thermal Decomposition of Complexes (1)—(3).—A solution of (1) (0.052 g, 0.18 mmol) in benzene (2 cm^3) was heated in a sealed tube at 80 °C for 36 h. The volatile products were flash-distilled under vacuum and trapped at −190 °C. G.l.c. analysis on a 2-m squalane column revealed the presence of ethylene (10%), but-1-ene (55%), and *trans*-but-2-ene (35%). These results were confirmed by g.l.c.–mass spectrometry combined techniques.

The thermal decomposition of (2) was carried out following the same above procedure, starting from 0.035 g (0.127 mmol) of (2) in C_6D_6 (1.5 cm^3). G.l.c.–mass analysis revealed [$^2H_2$]-ethylene and [$^2H_4$]butenes as the only volatile products.

Compound (3) (0.05 g, 0.16 mmol) was thermally decomposed in toluene (2 cm^3) at 105 °C for 48 h giving rise to ethylene (4%), propylene (2%), C_4 olefins (4%), and C_6 olefins (90%).

[$Mo(CH_2CMe_3)_2(\eta\text{-}C_5H_5)_2$] (4).—(*a*) [$Mo(\eta\text{-}C_5H_5)_2I_2$] (0.178 g, 0.463 mmol) was added in portions to $Mg(CH_2CMe_3)Cl$ (2.8 cm^3 of a 0.45 mol dm^{-3} diethyl ether solution). The suspension was stirred at room temperature for 48 h. The solvent was then removed under reduced pressure, and the residue extracted with pentane (30 cm^3). The solution, after concentration, was chromatographed using a column of neutral alumina (Merck, 1.5 cm × 15 cm) and pentane as eluant. A yellow band was collected; by concentrating the solution to *ca.* 7 cm^3 and cooling at −40 °C, orange needles of (4) were obtained overnight (0.02 g, 14%).

Table 4. Crystal data collection and refinement

$C_{14}H_{18}Mo$, M = 282.24, Space group $P2_1/c$ (no. 14)

a = 11.352(2) Å	Z = 4
b = 7.665(1) Å	D_c = 1.566 g cm^{-3}
c = 16.111(3) Å	$F(000)$ = 576
β = 121.37(2)°	μ(Mo-K_α) = 10.41 cm^{-1}
U = 1 196.9 $Å^3$	λ(Mo-K_α) [a] = 0.7107 Å
Scan mode	ω—2θ
Scan width	1.2°
Scan speed	4.2° min^{-1}
Background time	2 × 17 s
Reciprocal space explored	$-h_{max.} \leqslant h \leqslant h_{max.}$ (with $k,l \geqslant 0$)
Measured reflections	1 661
Observed reflections [b]	1 272
θ range (d_{min})	2.5—23° (0.91)
Approximate crystal size	0.25 × 0.12 × 0.15 mm
Power used	45 kV, 30 mA

[a] Graphite monochromated. [b] $I \geqslant 2.5\sigma(I)$; $\sigma(I)$ = (peak counts + total background counts)$^{\frac{1}{2}}$.

(*b*) [$Mo(\eta\text{-}C_5H_5)_2I_2$] (1.04 g, 2.16 mmol) was treated with $Li(CH_2CMe_3)$ (0.44 g, 5.63 mmol) in 20 cm^3 of diethyl ether for 16 h at room temperature. Following the same work-up as above, chromatographic separation gave (4) in 52% yield. A second running band (yellow-green) was eluted which gave (6) as an oily residue (0.128 g, 10%).

[$W(CH_2CMe_3)_2(\eta\text{-}C_5H_5)_2$] (5).—[$W(\eta\text{-}C_5H_5)_2Cl_2$] (0.221 g, 0.575 mmol) was treated with $Mg(CH_2CMe_3)Cl$ (9.42 cm^3 of a 0.26 mol dm^{-3} diethyl ether solution). The resulting mixture was stirred at room temperature for 48 h. The solvent was then removed under reduced pressure, and the residue extracted with pentane (70 cm^3). The yellow solution, after concentration, was chromatographed using a column of neutral alumina (Merck, 1.5 cm × 10 cm) and using pentane as eluant. A yellow band was eluted, and (5) crystallized as orange needles by removing part of the solvent and cooling at −40 °C (15% yield); m.p. 159—160 °C (decomp.). Analogous results were obtained using $Li(CH_2CMe_3)$ as the alkylating reagent.

Thermal Decomposition of (4) *and* (5).—In the ^1H n.m.r. tubes was placed 0.7 cm^3 of a 0.05 mol dm^{-3} C_6D_6 solution. The thermolyses were run at 40 and 60 °C for (4) and at 40 and 90 °C for (5), and followed by ^1H n.m.r. investigation.

[$W(CH_2CMe_3)_2(\eta\text{-}C_5H_5)_2$][$PF_6$] (7).—Compound (5) (0.06 g, 0.13 mmol) in toluene (2 cm^3) was treated (with stirring) with I_2 (0.017 g, 0.066 mmol) in toluene (2 cm^3). A rapid reaction occurred: the yellow solution changed to red, and a solid was formed. The mixture was stirred for a further 15 min and extracted with water (20 cm^3). Addition of an excess of [NH_4][PF_6] precipitated a violet solid which was collected, washed with water, and dried under vacuum to give 0.033 g (60%) of (7).

X-*Ray Diffraction Study of* (1).—Crystals suitable for *X*-ray diffraction measurements were obtained by slow crystallization from pentane. They are stable at room temperature under an argon atmosphere and can be stored for months at −30 °C. Exposure to air over a short period did not cause appreciable chemical change.

The diffracted intensities were measured by means of a Philips PW 1100 four-circle diffractometer with randomly

Table 5. Fractional atomic co-ordinates ($\times 10^4$ for C, $\times 10^5$ for Mo) with estimated standard deviations in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Mo	27 531(10)	16 655(11)	2 656(7)
C(1)	715(12)	3 038(16)	−704(9)
C(2)	847(15)	4 474(21)	−1 266(11)
C(3)	1 670(18)	3 950(20)	−1 661(10)
C(4)	2 988(13)	2 997(18)	−899(9)
C(5)	1 914(15)	−444(15)	−877(9)
C(6)	1 290(13)	−734(16)	−327(11)
C(7)	2 325(17)	−1 130(16)	602(13)
C(8)	3 531(15)	−1 161(15)	620(12)
C(9)	3 327(14)	−794(15)	−256(11)
C(10)	4 210(22)	1 880(18)	1 885(10)
C(11)	4 728(13)	2 922(23)	1 431(11)
C(12)	3 859(16)	4 226(19)	1 015(10)
C(13)	2 833(16)	4 132(21)	1 128(11)
C(14)	2 993(19)	2 712(20)	1 668(10)

oriented crystals. For the accurate determination of the unit-cell parameters, the setting angles of 64 strong reflections were measured. The crystal data and working conditions are reported in Table 4.

Intensity data were corrected for decay (about 30% during the collection) for Lorentz and polarization effects, and also an experimental procedure for absorption correction [34] was applied (the variation of transmittance was calculated to be about 15%). The structure was solved by Fourier and Patterson methods and refined by least squares in the block-diagonal approximation. The atomic scattering factors given in the literature [35a] were used, taking into account real and imaginary dispersion corrections.[35b] In the final step of the refinement the thermal vibration parameters of the non-hydrogen atoms were refined anisotropically, giving a conventional *R* factor of 0.053. At this point a Fourier-difference map was calculated and 18 electron-density peaks were attributed to hydrogen atoms. Therefore, in the last three least-squares cycles the hydrogen-atom contribution to the structure factors was included to give a final conventional *R* factor of 0.047.

The atomic fractional co-ordinates of the non-hydrogen atoms are reported in Table 5.

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