Bis(η-cyclopentadienyl)-molybdenum and -tungsten Chemistry: σ- and η-Allylic and Metallacyclobutane Derivatives

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Treatment of $[\{W(\eta\text{-}C_5H_5)_2HLi\}_4]$ with $CH_2{=}CR{-}CH_2Cl$ (R = H or Me) gives $[W(\eta\text{-}C_5H_5)_2(CH_2CR{=}CH_2)_2]$. These react with aqueous HPF_6 giving the η-allylic salts $[W(\eta\text{-}C_5H_5)_2(\eta^3\text{-}CH_2CRCH_2)][PF_6]$. The salts $[M(\eta\text{-}C_5H_5)_2(\eta\text{-}CH_2CHCH_2)][PF_6]$ (M = Mo or W) with $Na[BH_4]$ give the metallacyclobutane compounds $[M(\eta\text{-}C_5H_5)_2\{(CH_2)_3\}]$. Treatment of $[W(\eta\text{-}C_5H_5)_2(\eta\text{-}CH_2CHCH_2)][PF_6]$ with allyl-lithium gives the compound $[M(\eta\text{-}C_5H_5)_2\{CH_2CH(CH_2CH{=}CH_2)CH_2\}]$ (M = W); the molybdenum analogue (M = Mo) is prepared by reaction of $[Mo(\eta\text{-}C_5H_5)_2Cl_2]$ with allylmagnesium chloride.

THE olefin metathesis reaction is thought to proceed *via* metallacyclobutane compounds as intermediates.[1] Isolated metallacyclic derivatives of transition metals are rare, being limited to platinum compounds.[2]

During our continuing study of the chemistry of the system $[M(\eta\text{-}C_5H_5)_2]$ (M = Mo or W) we set out to prepare σ- and η-allylic derivatives. We have found that η-allyl compounds lead to the synthesis of stable metallacyclobutane derivatives of molybdenum and tungsten. These studies are described below.

RESULTS

Chemical Studies.—Treatment of the tungsten–lithium tetramer $[\{W(\eta\text{-}C_5H_5)_2HLi\}_4]$ (1) [3] with allyl chloride gave orange crystals which the data in the Table show to be the bis(σ-allyl) derivative $[W(\eta\text{-}C_5H_5)_2(CH_2CH{=}CH_2)_2]$ (2). This is soluble in benzene and diethyl ether and the solutions are thermally stable at room temperature but are rapidly decomposed on exposure to air. Compound (1) reacted similarly with 2-methylallyl chloride giving $[W(\eta\text{-}C_5H_5)_2(CH_2CMe{=}CH_2)_2]$ (3) which has a similar solubility and stability to (2). Both (2) and (3) reacted readily with acids such as hexafluorophosphoric acid. The initial precipitates evolved a gas which has been shown to be propene (g.l.c.) in the case of (2). After gas evolution, the products were shown to be the η-allylic compounds $[W(\eta\text{-}C_5H_5)_2(\eta^3\text{-}CH_2CRCH_2)][PF_6]$ (4; R = H or Me).

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[1] N. Calderon, E. A. Ofstead, and W. A. Judy, *Angew. Chem. Internat. Edn.*, 1976, **15**, 401.

[2] P. W. Hall, R. J. Puddephatt, and C. F. H. Tipper, *J. Organometallic Chem.*, 1974, **71**, 145; F. J. McQuillin and K. G. Powell, *J.C.S. Dalton*, 1972, 2123.

[3] R. A. Forder and C. K. Prout, *Acta Cryst.*, 1974, **B30**, 2318.

Compounds (4) are unambiguously characterised by the data in the Table. They are well crystalline, moderately stable in air, and they are soluble in more polar solvents such as tetrahydrofuran or acetone.

Treatment of compound (1) with 1-chlorobut-2-ene followed by addition of aqueous HPF_6 to the unisolated intermediate gave the 1-methylallyl analogue of (4), namely $[W(\eta\text{-}C_5H_5)_2(\eta^3\text{-}MeCH{=}CH\text{-}CH_2)][PF_6]$ (5). The syntheses of the compounds $[Mo(\eta\text{-}C_5H_5)_2(\eta\text{-}CH_2CHCH_2)][PF_6]$ (6) and $[Mo(\eta\text{-}C_5H_5)_2(\eta^3\text{-}MeCHCHCH_2)][PF_6]$ (7) have been described elsewhere.[4,5]

TABLE

Analytical and spectroscopic data

Compound	Colour	Analysis (%)[a]		m/e[b]	^{1}H N.m.r.[c]
		C	H		
$[W(\eta\text{-}C_5H_5)_2(CH_2CH{=}CH_2)_2]$	Red	47.3 (48.5)	5.80 (5.35)	396	4.02, *2*, ***c***, CH=; 5.43, *2*, ***c***, 5.65, *2*, ***c***, $=CH_2$; 6.0, *10*, ***s***, C_5H_5; 8.77, *4*, ***d***, CH_2 [d,e]
$[W(\eta\text{-}C_5H_5)_2(CH_2CMe{=}CH_2)_2]$	Red	50.6 (50.9)	5.8 (5.7)	424	5.50, *4*, ***c***, $=CH_2$; 6.02, *10*, ***s***, C_5H_5; 8.27, *6*, ***s***, CH_3; 8.70, *4*, ***s***, CH_2 [d,e]
$[W(\eta\text{-}C_5H_5)_2(\eta^3\text{-}CH_2CMeCH_2)][PF_6]$	Red	32.2 (32.7)	3.5 (3.3)		4.13, *5*, ***s***, 4.49, *5*, ***s***, C_5H_5; 5.98, *2*, ***d*** (7), H(*syn*); 7.14, *3*, ***s***, CH_3; 7.43, *2*, ***d*** (7), H(*anti*) [f]
$[W(\eta\text{-}C_5H_5)_2(\eta^3\text{-}MeCHCHCH_2)][PF_6]$	Orange	32.7 (32.7)	3.3 (3.3)		4.15, *5*, ***s***, 4.42, *5*, ***s***, C_5H_5; 5.6—5.9, *2*, ***c***, H(*central*), H(*syn*); 7.55, *3*, ***d***, CH_3; 7.9—8.5, *2*, ***c***, H(*anti*)
$[W(\eta\text{-}C_5H_5)_2\{(CH_2)_3\}]$	Orange	43.7 (43.7)	4.7 (4.7)	356	5.79, *10*, ***s***, C_5H_5; 6.13, *2*, ***q*** (8), C^2H_2; 8.98, *4*, ***t*** (8), C^1H_2, C^3H_2 [d]
$[Mo(\eta\text{-}C_5H_5)_2\{(CH_2)_3\}]$	Orange	58.6 (58.2)	5.6 (6.0)	270	5.81, *10*, ***s***, C_5H_5; 6.45, *2*, ***q*** (8), CH_2; 9.31, *4*, ***t*** (8), C^1H_2, C^3H_2 [d]
$[W(\eta\text{-}C_5H_5)_2(CH_2CHDCH_2)]$	Orange				5.79, *10*, ***s***, C_5H_5; 6.1, *1*, ***c***, C^2H; 8.98, *4*, ***d*** (8), C^1H_2, C^3H_2 [d]
$[W(\eta\text{-}C_5H_5)_2\{CH_2CH(CH_2CH{=}CH_2)CH_2\}]$	Orange			396	3.8, *1*, ***c***, H^e; 4.7, *2*, ***c***, H^f, and H^g; 5.65, *5*, ***s***; 5.80, *5*, ***s***, C_5H_5; 7.5, *3*, ***c***, H^c, $2H^d$; 8.8, *2*, ***c***, H^a or H^b; 9.4, *2*, ***c***, H^a or H^b [d]
$[Mo(\eta\text{-}C_5H_5)_2\{CH_2CH(CH_2CH{=}CH_2)CH_2\}]$	Orange	62.3 (62.4)	6.7 (6.5)	310	3.8, *1*, ***c***, H^e; 4.7, *2*, ***c***, H^f, H^g; 5.65, *5*, ***s***; 5.80, *5*, ***s***, C_5H_5; 7.30, *1*, ***c***, H^c; 7.80, *2*, ***c***, $2H^d$; 8.8, *2*, ***c***, $2H^a$ or $2H^b$; 9.7, *2*, ***c***; H^a or $2H^b$ [d]

[a] Calculated values are given in parentheses. [b] Mass spectra; parent ions only are given. [c] Given as chemical shift (τ), *relative intensity*, **multiplicity** (J in Hz), assignment, *etc.* [d] In C_6D_6, for labelling see Scheme 1. [e] The i.r. spectrum shows a strong band at 1 610 cm^{-1} assignable to ν(C=C). [f] In $(CD_3)_2SO$.

Treatment of the η-allylic compounds (4; R = H) and (6) with sodium tetrahydroborate gave the metallacyclobutane compounds $[M(\eta\text{-}C_5H_5)_2\{(CH_2)_3\}]$ [M = W (8) or Mo (9)] respectively. Compounds (8) and (9) are soluble in light petroleum, the solutions showing signs of decomposition after exposure to air for a few minutes. They decompose in vacuum at *ca.* 80 °C. The structures of compounds (8) and (9) are based on the data in the Table. The ^{1}H n.m.r. spectra show the two $\eta\text{-}C_5H_5$ rings to be equivalent. This would arise if the metallacyclobutane ring was planar, but if it were bent, as is customary for cyclobutane compounds, then it is necessary to postulate a fluxional inversion about the axis through the C^1 and C^3 carbons which is rapid on the n.m.r. time scale.

The resonances assigned to the $C^1H_2C^2H_2C^3H_2$ groups appeared, at lower resolution, as a 1 : 4 : 6 : 4 : 1 quintet of relative intensity two assignable to the C^2H_2 hydrogens, whilst the C^1H_2 and C^3H_2 hydrogens gave a clear 1 : 2 : 1 triplet. At higher resolution, the components of the quintet and triplet showed further fine structure. These spectra are closely analogous to those of other $CH_2CH_2CH_2$ moieties, for example, some indane systems,[6] and are comparable to the spectrum of $[Pt(C_5H_5N)_2Cl_2\{(CH_2)_3\}]$.[2,7] The spectrum of these cyclic $C^1H_2C^2H_2C^3H_2$ systems should in principle be assignable in terms of an $(AB)_2XX'$ group but to first approximation they appear as an A_4X_2 system. The formation of (8) and (9) from (4) and (6) appears to proceed *via* H^- attack on the central carbon of the η-allylic group. In order to confirm this, (4; R = H) was treated with $Na[BD_4]$ giving the monodeuteriated product (8d) for which the ^{1}H n.m.r. spectrum clearly shows the deuterium to be located on the 2-carbon methylene group.

The i.r. spectra of (8) and (9) show medium-strong bands at 2 775 and 2 786 cm^{-1} respectively which are reminiscent of the relatively intense low-frequency bands near 2 750 cm^{-1} assigned to *exo*-C–H stretching modes of η^4-cyclopentadiene and η^5-cyclohexadienyl hydrogens. The reaction between $[Mo(\eta\text{-}C_5H_5)_2Cl_2]$ and excess of allylmagnesium chloride gave orange crystals for which the data clearly indicate the stoicheiometry $[Mo(\eta\text{-}C_5H_5)_2\{CH_2CH(CH_2CH{=}CH_2)CH_2\}]$ (10; M = Mo) with the structure shown in Scheme 2. We propose a mechanism for the formation of (10; M = Mo) from $[Mo(\eta\text{-}C_5H_5)_2Cl_2]$ which proceeds *via* attack of the allyl anion on intermediate (6), as shown in Scheme 2. Strong support for this proposal arises from the observation that treatment of (4) with allyllithium gives an orange compound characterised as (10; M = W) which closely resembles the molybdenum analogue. Compounds (10; M = Mo or W) are soluble in light

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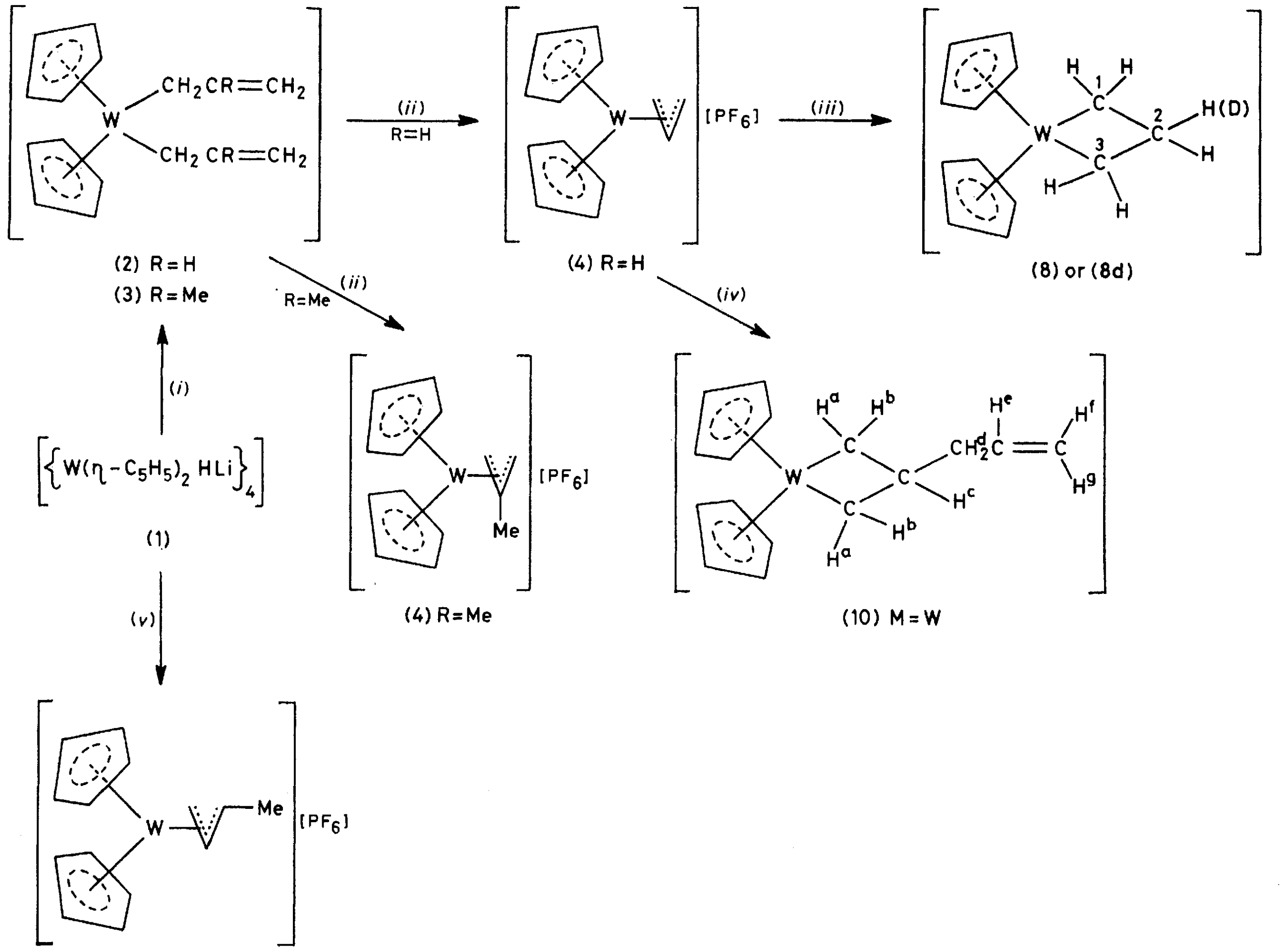
[4] R. A. Forder, M. L. H. Green, R. E. Mackenzie, J. S. Poland, and C. K. Prout, *J.C.S. Chem. Comm.*, 1973, 426; M. L. H. Green, R. E. Mackenzie, and J. S. Poland, *J.C.S. Dalton*, 1976, 1993.

[5] B. R. Francis, M. L. H. Green, N. T. Luong-Thi, and G. Moser, *J.C.S. Dalton*, 1976, 1339; M. L. H. Green, N. T. Luong-Thi, G. Moser, I. Packer, F. Pettit, and D. M. Roe, *ibid.*, p. 1988.

[6] W. R. Jackson, C. H. McMullen, R. Spratt, and P. Bladen, *J. Organometallic Chem.*, 1965, **4**, 392.

[7] D. M. Adams, J. Chatt, R. G. Guy, and N. Sheppard, *J. Chem. Soc.*, 1961, 738.

petroleum and are quite rapidly oxidised by oxygen; they do not have bands near 2 700 cm^{-1} in the i.r. spectra.



SCHEME 1 (*i*) CH$_2$=CRCH$_2$Cl in toluene, 0 °C, R = H or Me, 40%; (*ii*) dilute HPF$_6$ at room temperature, 90%; (*iii*) Na[BH$_4$] (or Na[BD$_4$]) in tetrahydrofuran (thf) or acetone, 80%; (*iv*) Mg(CH$_2$CH=CH$_2$)Cl in OEt$_2$, excess, 70%; (*v*) MeCH=CHCH$_2$Cl in toluene at 0 °C then dilute HPF$_6$, 70%

DISCUSSION

We wish to draw attention to the observation that nucleophilic attack by the ions H$^-$, D$^-$, and CH$_2$=CHCH$_2^-$ on the η-allyl cations described above proceeds exclusively on the central 2-carbon of the η-allylic group. In fact, from the literature, there are two other possible positions for nucleophilic addition to compounds (4). Attack by H$^-$ on the terminal carbons of (4; R = H) would give rise to the η^2-propene compound [W(η-C$_5$H$_5$)(η^2-MeCH=CH$_2$)], which has been isolated and is thermally stable,[8] whilst H$^-$ addition to the η-C$_5$H$_5$ ring would give the (unknown) 18-electron compound [W(η-C$_5$H$_5$)(η^4-C$_5$H$_6$)(η^3-C$_3$H$_5$)].

It is interesting to enquire what factors may control the observed but unexpected regiospecificity of nucleophilic attack on (4; R = H) and (6). First, we note that nucleophilic attack of H$^-$ on the cation [Mo(η-C$_7$H$_7$)(η-C$_6$H$_6$)]$^+$ proceeds exclusively on the η-C$_6$H$_6$ ring giving the compound [Mo(η-C$_7$H$_7$)(η^5-C$_6$H$_7$)].[9] The alternative apparently reasonable product of H$^-$ addition to the η-C$_7$H$_7$ ring, namely [Mo(η^6-C$_7$H$_8$)(η-C$_6$H$_6$)], is not observed. Other related examples of regiospecific attack include H$^-$ addition to [Mo(η-C$_5$H$_5$)(η^4-C$_5$H$_6$)(dppe)][PF$_6$] giving [Mo(η-C$_5$H$_5$)(η^3-C$_5$H$_7$)(dppe)][10] rather than [Mo(η^4-C$_5$H$_6$)$_2$(dppe)], and H$^-$ addition to [Mo(η-C$_6$H$_6$)(η-C$_3$H$_5$)(dppe)][PF$_6$] giving [Mo(η^5-C$_6$H$_7$)(η-C$_3$H$_5$)(dppe)][11] rather than [Mo(η-C$_6$H$_6$)(η^2-MeCH=CH$_2$)(dppe)] (dppe = Ph$_2$P[CH$_2$]$_2$PPh$_2$).

We propose the following general explanation concerning the position of nucleophilic addition to organometallic cations which have two (or more) positions at which the addition might reasonably be expected to occur. We refer to such cations as ‘polyfunctional

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[8] F. W. S. Benfield, B. R. Francis, and M. L. H. Green, *J. Organometallic Chem.*, 1972, **44**, C13.

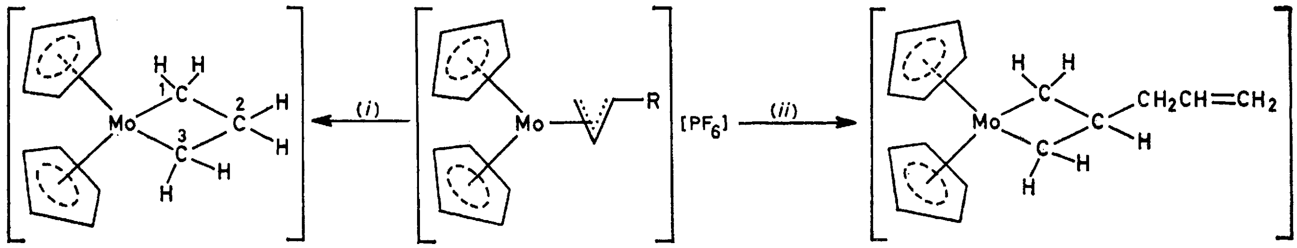
[9] J. A. Segal, J. Knight, and M. L. H. Green, *J.C.S. Chem. Comm.*, 1976, 766.

[10] C. Romao, T. Aviles-Perea, A. R. Dias, and M. L. H. Green, personal communication.

[11] M. L. H. Green, L. C. Mitchard, and W. E. Silverthorn, *J.C.S. Dalton*, 1973, 2177.

cations.' Where the metal centre of the polyfunctional cation is very electron rich then, in the absence of marked steric effects, nucleophilic addition occurs so that the electron density at the metal centre of the product is either reduced or subjected to the minimal increase. The reverse of this is that, for cations with electron-poor metal centres, nucleophilic addition normally occurs at that position which will cause the maximum increase of electron density at the metal centre. It is assumed that the initial polyfunctional cations and the product of nucleophilic attack are 18-electron compounds.

A normal consequence of these trends is that nucleophilic addition on electron-rich polyfunctional cations will proceed with *retention* of the formal valency state of the metal, whilst for electron-poor metal cations nucleophilic attack causes reduction of the formal valence (or formal oxidation state) of the metal by two. Clearly, when the metal centre of a polyfunctional cation is neither very rich nor very poor, then regiospecificity to nucleophilic attack is not to be expected. We note, for example, that hydride-ion addition to $[Ru(\eta\text{-}C_6H_6)(\eta^5\text{-}C_6H_7)]^+$ gives both divalent $[Ru(\eta^5\text{-}C_6H_7)_2]$ and zerovalent $[Ru(\eta\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)]$.[12]



SCHEME 2 (*i*) $Na[BH_4]$ in thf, 70%; (*ii*) $Mg(CH_2CH{=}CH_2)Cl$ in OEt_2, 60%

If these ' rules ' are to be useful for predictions then it is necessary to have independent criteria of whether a metal centre in a polyfunctional cation is relatively rich or poor in electron density. There is no direct or absolute criterion of the partial charge at a metal centre. However, it is possible to approximately classify ligands in order of their ability to donate or withdraw electrons from a metal centre. For example, $\eta\text{-}C_6H_6$ and $\eta\text{-}C_5H_5$ ligands give relatively electron-rich metal centres compared to the isoelectronic $(CO)_3$ or (NO)(CO) systems. This statement is based on data such as a comparison of the first ionisation potentials [13] of $[Cr(\eta\text{-}C_6H_6)_2]$ (5.40),[13] $[Cr(\eta\text{-}C_6H_6)(CO)_3]$ (7.35), and $[Cr(CO)_6]$ (8.40 eV).* Clearly, the molybdenum in $[Mo(\eta\text{-}C_6H_6)_2]$ is a more electron-rich centre than in $[Mo(CO)_6]$. Also, the position of ν(CO) in a series of isoelectronic compounds $[M(CO)_xL_y]$ can be indicative of the relative ability of L to donate or withdraw electrons from the metal. Chemical criteria of electron richness may also be used; for example the greater nucleophilicity of the $[Fe(\eta\text{-}C_5H_5)(CO)_2]^-$ anion compared with $[Mn(CO)_5]^-$ anion suggests that the $\eta\text{-}C_5H_5$ ligand withdraws relatively less electron density from the metal than a $(CO)_3$ group.

From these qualitative criteria it is possible to make some assessment in advance as to the probability of a metal centre in a given compound being rich or poor. Thus, we have noted that nucleophilic addition to (6) proceeds on the 2-carbon of the η-allyl group. Since (CO)(NO) is more electron withdrawing than $\eta\text{-}C_5H_5$, it is therefore consistent with the rules that nucleophilic addition to $[Mo(\eta\text{-}C_5H_5)(\eta\text{-}C_3H_5)(CO)(NO)]^+$ occurs on the terminal carbon of the η-allyl group giving the compound $[Mo(\eta\text{-}C_5H_5)(\eta\text{-}MeCH{=}CH_2)(CO)(NO)]$ as is observed.[14] Clearly steric restrictions could change the position of attack from the electronically preferred position. We put these ' rules ' forward as a guidance and to stimulate further discussion.

EXPERIMENTAL

Operations were performed under dry nitrogen. Hydrogen-1 n.m.r. spectra were recorded on JEOL (60 MHz) or Varian spectrophotometers (100 MHz). All the solvents were dried and distilled before use. Light petroleum (b.p. 40—60 °C) was used. Low-resolution mass spectra were recorded on an MS9 spectrometer. Infrared spectra were obtained for mulls using a Perkin-Elmer 457 instrument. The compounds $[M(\eta\text{-}C_5H_5)_2H_2]$ (M = Mo or W) were prepared as described.[15]

Bis(η-allyl)bis(η-cyclopentadienyl)tungsten, (2).—The tetramer $[\{W(\eta\text{-}C_5H_5)_2HLi\}_4]$ (1), prepared as described from $[W(\eta\text{-}C_5H_5)_2H_2]$ (0.17 g, 2.3 mmol), was suspended in dry toluene. The mixture was cooled to 0 °C and treated with freshly distilled allyl chloride (0.4 cm³, 4.94 mmol). A clear orange solution formed and after 1 h water (1 cm³) was added. The benzene layer was separated and the solvent was removed under reduced pressure. The orange residue was extracted with warm light petroleum (50 cm³) and the extract was filtered, leaving some impure $[W(\eta\text{-}C_5H_5)_2H_2]$. The filtrate was concentrated and cooled giving

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* Throughout this paper: 1 eV ≈ 1.60×10^{-19} J.

[12] D. Jones, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1962, 4458.

[13] S. Evans, J. C. Green, S. E. Jackson, and B. Higginson, *J.C.S. Dalton*, 1974, 394; B. R. Higginson, R. Lloyd, P. Burroughs, D. H. Gibson, and A. F. Orchard, *J.C.S. Faraday II*, 1973, 1659.

[14] J. A. McCleverty and A. J. Murray, *Proc. 2nd Climax Internat. Conf. Chem. Uses Molybdenum*, 1976.

[15] M. L. H. Green and P. J. Knowles, *J.C.S. Perkin I*, 1973, 989.

orange needles. These were washed with a little cold light petroleum. The *product* was recrystallised a second time from cold light petroleum, *ca.* 40%. The analogue *bis(η-cyclopentadienyl)bis(η-2-methylallyl)tungsten*, (3), was similarly prepared as orange prisms using 2-methylallyl chloride, *ca.* 40%.

(η-Allyl)bis(η-cyclopentadienyl)tungsten Hexafluorophosphate, (4).—Bis(η-allyl)bis(η-cyclopentadienyl)tungsten (0.3 g) in acetone was treated with a small excess of aqueous hexafluorophosphoric acid (40%, 0.2 cm^3). The initially red solution became yellow. Water (5 cm^3) was added and the solution was slowly concentrated under reduced pressure giving pale yellow crystals. These slowly became orange and propene was evolved. The orange residue was recrystallised from aqueous acetone giving orange *crystals*[5] which were washed with water and dried under reduced pressure, *ca.* 90% (Found: C, 31.1; H, 3.25. Calc.: C, 31.2; H, 3.00%).

The analogue *bis(η-cyclopentadienyl)(1—3-η-2-methylallyl)-tungsten Hexafluorophosphate* was prepared similarly from compound (3). Recrystallisation of the product was from acetone–ethanol, after the initial acetone extract had been passed through a short alumina column made up in light petroleum in order to remove a black material, *ca.* 75%.

Bis(η-cyclopentadienyl)(1—3-η-1-methylallyl)tungsten Hexafluorophosphate, (5).—A suspension in toluene of the tungsten–lithium derivative prepared by addition of n-butyl-lithium (6.8 mmol in hexane) to the hydride $[W(\eta\text{-}C_5H_5)_2H_2]$ (2.14 g, 6.8 mmol in toluene) was treated at 0 °C with 1-chlorobut-2-ene (0.70 cm^3, 7.2 mmol). Immediate reaction gave a clear orange-red solution. After 30 min, water (5 cm^3) was added and the toluene layer was separated. The solvent was removed under reduced pressure giving a red oil containing the parent dihydride. This was extracted with light petroleum (50 cm^3) leaving most of the less-soluble dihydride (35%); the extract was separated and the solvent was removed under reduced pressure. The oily red residue was dissolved in acetone (10 cm^3) and treated with aqueous HPF_6 (40%, 0.5 cm^3). Addition of water (5 cm^3) followed by removal of solvent under reduced pressure gave orange crystals which were separated, washed with water, and dried *in vacuo*, *ca.* 40%.

1,1-*Bis(η-cyclopentadienyl)*-1-*tungstacyclobutane*, (8).—The compound $[W(\eta\text{-}C_5H_5)_2(\eta\text{-}C_3H_5)][PF_6]$ (300 mg) in acetone (30 cm^3) was treated with $Na[BH_4]$ (250 mg) in portions over 30 min, with stirring. The initially red solution became orange and after another 30 min the solvent was removed under reduced pressure. The residue was extracted with dry toluene and the extract was filtered then washed with water. The toluene layer was separated and evaporated to dryness. The residue was recrystallised from light petroleum giving orange crystals, *ca.* 80%.

1,1-*Bis(η-cyclopentadienyl)*-3-*deuterio*-1-*tungstacyclobutane* was prepared in an identical manner using $Na[BD_4]$ instead of $Na[BH_4]$. The analogous molybdenum compound 1,1-*bis(η-cyclopentadienyl)*-1-*molybdacyclobutane*, (9), was prepared in the same way as the tungsten derivative from $[Mo(\eta\text{-}C_5H_5)_2(\eta\text{-}C_3H_5)][PF_6]$. It was recrystallised from light petroleum giving red-orange crystals, *ca.* 80%.

3-*Allyl*-1,1-*bis(η-cyclopentadienyl)*-1-*molybdacyclobutane*, (10).—The compound $[Mo(\eta\text{-}C_5H_5)_2Cl_2]$ (9 g) was added slowly to a stirred solution of allylmagnesium chloride (0.25 mol in diethyl ether, 120 cm^3) with cooling in ice. The reaction was exothermic and produced a very clear deep orange solution. The solvent was then removed *in vacuo* and the residue was extracted into light petroleum (250 cm^3) with vigorous stirring for 1 h. The extract was filtered, leaving a powdery residue. The orange filtrate was concentrated *in vacuo* and placed on a short alumina column in light petroleum (5 in of alumina). A red band was quickly eluted using dry degassed diethyl ether and collected. Removal of solvent gave a viscous red oil which crystallised overnight as a solid mass on the bottom of the flask. The compound was recrystallised from light petroleum at −10 °C giving small orange needles, *ca.* 50%.

3-*Allyl*-1,1-*bis(η-cyclopentadienyl)*-1-*tungstacyclobutane*, (10).—A suspension of $[W(\eta\text{-}C_5H_5)_2(\eta\text{-}C_3H_5)][PF_6]$ (200 mg) in diethyl ether (50 cm^3) was treated with an excess of allyl-lithium dissolved in diethyl ether. After 10 min an orange solution was obtained which was hydrolysed with water. The diethyl ether solution was separated and evaporated to dryness. The residue was dissolved in light petroleum from which it was recrystallised as orange crystals, *ca.* 70%.

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