Some η^1- and η^3-Allylic and Metallocyclobutane Derivatives of Molybdenum and Tungsten

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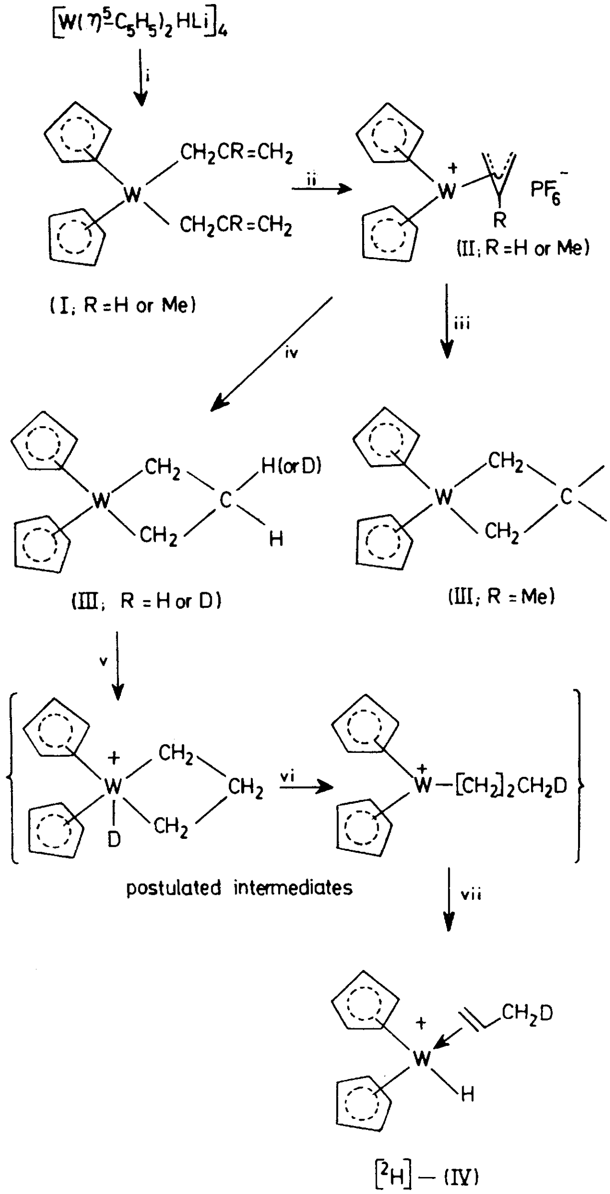
Summary Nucleophilic attack by $R^- = H^-$ or Me^- on $[W(\eta^5\text{-}C_5H_5)_2(\eta^3\text{-}CH_2CHCH_2)]^+PF_6^-$ occurs on the central carbon of the η^3-allylic group giving the metallocyclobutane compounds $[W(\eta^5\text{-}C_5H_5)_2(CH_2CHRCH_2)]$ which, for R=H, undergo deuteriation giving $[W(\eta^5\text{-}C_5H_5)_2H(CH_2CHCH_2D)]^+PF_6^-$; similar attack occurs on the analogous molybdenum compounds.

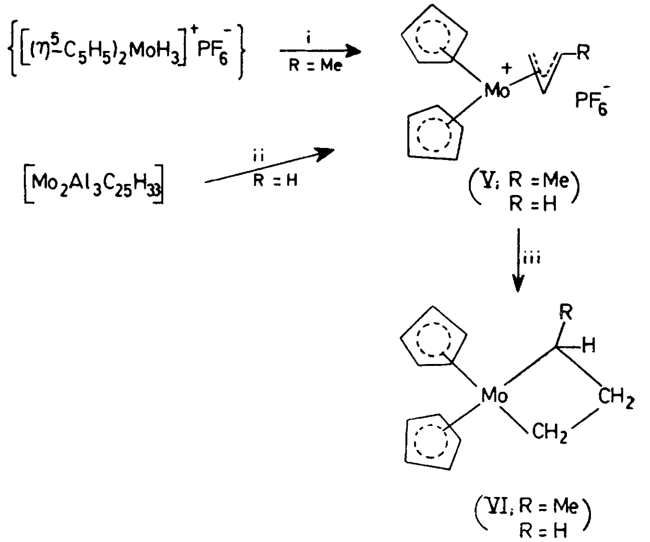
TREATMENT of the tetramer $[\{W(\eta^5\text{-}C_5H_5)_2HLi\}_4]$[1] with the allylic halides $CH_2{=}CRCH_2Cl$ gives the bis-η^1-allyl compounds $[W(\eta^5\text{-}C_5H_5)_2(CH_2CR{=}CH_2)_2]$ (I; R=H or Me). These react with dilute acid giving the η^3-allylic compounds $[W(\eta^5\text{-}C_5H_5)_2(\eta^3\text{-}CH_2CRCH_2)]^+PF_6^-$ (II; R=H or Me) respectively. The analogous 1-methylallyl compound $[W(\eta^5\text{-}C_5H_5)_2(\eta^3\text{-}MeCHCHCH_2)]^+PF_6^-$ may be made by treatment of the tetramer $[\{W(\eta^5\text{-}C_5H_5)_2HLi\}_4]$ with butadiene or with 1-chlorobut-2-ene.



Scheme 1. *Reagents:* i, $CH_2{=}CRCH_2Cl$, toluene, −78 °C (R=H or Me, 35% yield); ii, dilute HCl, NH_4PF_6(aq.) (R = H or Me, 80%); iii, LiMe in Et_2O, when R = H, or, when R = Me, $NaBH_4$ in tetrahydrofuran (THF), 70%; iv, $NaBH_4$ (or $NaBD_4$) in THF (70%) or $NaAlH_2(OCH_2CH_2OMe)_2$ in benzene; v, DBF_4 (aq.) (80%); vi, proposed reductive elimination step; vii, proposed β-elimination step.

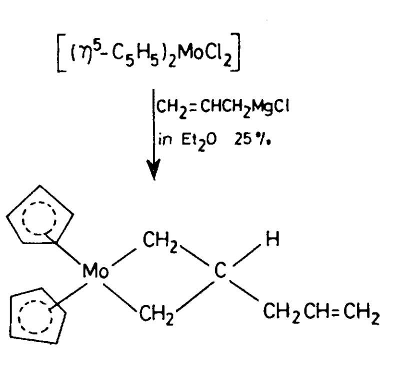
Treatment of the trihydride $[Mo(\eta^5\text{-}C_5H_5)_2H_3]^+PF_6^-$ in acetone with an excess of butadiene gives red crystals of $[Mo(\eta^5\text{-}C_5H_5)_2(\eta^3\text{-}RCHCHCH_2)]^+PF_6^-$ (V; R=Me). The compound $[Mo(\eta^5\text{-}C_5H_5)_2(\eta^3\text{-}RCHCHCH_2)]^+PF_6^-$ (V; R=H) is best prepared by addition of 1-chloro-prop-2-ene to the compound $[Mo_2Al_3C_{25}H_{33}]$.[2]

The η^3-allylic compounds (II) and (V) with sodium borohydride or $NaAlH_2(OCH_2CH_2OMe)_2$ give the metallocyclobutane compounds $[W(\eta^5\text{-}C_5H_5)_2(CH_2CHRCH_2)]$ (III; R=H or Me) and $[Mo(\eta^5\text{-}C_5H_5)_2(RCHCH_2CH_2)]$ (VI; R = Me or R=H) respectively (Schemes 1 and 2). Treatment of (II; R = H) with methyl-lithium also gives (III; R = Me). Further, reduction of (II; R = H) with sodium borodeuteride gives $[W(\eta^5\text{-}C_5H_5)_2(CH_2CHDCH_2)]$ (III; R = D). Thus it is clear that the formation of the metallocyclobutane compounds from the η^3-allylic precursors proceeds *via* nucleophilic attack exclusively on the central carbon atom of the η^3-allylic group. This may seem unexpected, especially since nucleophilic attack at the terminal carbon atom of (II; R = H) would give the known, stable η^2-propene compound $[W(\eta^5\text{-}C_5H_5)_2(MeCHCH_2)]$. However, the observed attack on the central η^3-allylic carbon atom is consistent with our previous observation that the products of nucleophilic attack on other electron-rich, polyfunctional organometallic cations proceeds with retention of the valence state of the metal.[3]



Scheme 2. *Reagents:* i, butadiene, Me_2CO, 60 °C for 6 h (R = Me, 40% yield); ii, $CH_2{=}CHCH_2Cl$, toluene, −78 °C, (R=H, 20%); iii, $NaAlH_2(OCH_2CH_2OMe)_2$ in THF (R = H or Me, 60%).

We have also observed that treatment of $[Mo(\eta^5\text{-}C_5H_5)Cl_2]$ with an excess of allylmagnesium chloride gives $[Mo(\eta^5\text{-}C_5H_5)_2CH_2CH(CH_2CHCH_2)CH_2]$ (VII) and in view of the above it seems reasonable that (VII) is formed *via* attack of $CH_2{=}CHCH_2^-$ on the intermediate (V; R = H).

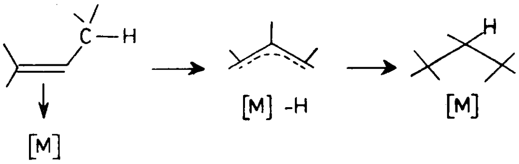


(VII)

Protonation of (III; R = H) with aqueous tetrafluoroboric acid gives the previously described[4] propene-hydride $[W(\eta^5\text{-}C_5H_5)_2H(MeCHCH_2)]^+ BF_4^-$ (IV) and when deuteriotetrafluorobic acid in D_2O is added to (III; R = H) the product is $[W(\eta^5\text{-}C_5H_5)_2H\{CH(CH_2D)CH_2\}]^+ BF_4^-$ [^{2}H]-(IV). We propose the mechanism for the formation of [^{2}H]-(IV) given in the Scheme 1.

Finally, we note that it has been observed, for example with propene,[5] that the β-hydrogen atoms of co-ordinated olefins may migrate to the metal giving η^3-allylic hydrides. This observation, when taken together with our discovery that η^3-allylic ligands may undergo addition to the central carbon atom, suggests the mechanism in Scheme 3 for the formation of metallocyclobutane derivatives. This mechanism may be relevant as an initiation mechanism for olefin metathesis reactions, especially where there is no apparent mechanism for the formation of intermediate hydrides by interaction of the catalyst components.

The compounds (I)—(VII) and $[W(\eta^5\text{-}C_5H_5)_2(\eta^3\text{-}MeCHCHCH_2)]^+PF_6^-$ have been characterised by their ^{1}H n.m.r., i.r., and mass spectra (where appropriate) and by elemental analysis.



SCHEME 3

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