Evidence for the Base-promoted Conversion of Alkyl-substituted Molybdenum and Tungsten Alkylidyne Complexes into Anionic Vinylalkylidene Species

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Summary Addition of $\mathrm{Bu^nLi}$-tetrahydrofuran or $\mathrm{Et_2O}$ to $[\mathrm{M(CCH_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)}]$ (M = Mo, W) affords the anionic species $[\mathrm{M(CCHBu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)}]\mathrm{Li}$, which on quenching with $\mathrm{D_2O}$ affords a mixture of $[\mathrm{M(CCHDBu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)}]$ and $[\mathrm{M(CCD_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)}]$.

THE analogy between acetylenes and carbyne[1] or alkylidyne complexes has been placed on a firm basis by both experimental[2] and theoretical[3] work. However, one of the interesting and synthetically important reactions of acetylenes, the base-promoted reversible isomerisation into allenes,[4] has, so far, no parallel in transition metal alkylidyne chemistry. The recent[5] synthesis of the alkylidyne complexes $[\mathrm{M(CCH_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)}]$ (M = Mo, W) provided an opportunity to study whether such a reaction could occur.

Addition (−78 °C) of $\mathrm{Bu^nLi}$ to the yellow alkylidyne complex $[\mathrm{Mo(CCH_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)}]$ dissolved in $[^2\mathrm{H}_8]$tetrahydrofuran (THF) gave a deep-red solution. The $^{31}\mathrm{P}\{^1\mathrm{H}\}$ n.m.r. spectrum (−30 °C $[^2\mathrm{H}_8]$THF, rel. to $\mathrm{H_3PO_4}$) of the red solution showed a singlet† at 213·4 p.p.m., the corresponding signal for the alkylidyne complex occurring at 212·3 p.p.m. The $^{13}\mathrm{C}\{^1\mathrm{H}\}$ spectrum [−25 °C, THF, $\mathrm{Cr(acac)_3}$, rel. to $\mathrm{C_6D_6}$] was more revealing, showing resonances at δ (p.p.m.) 322·8 [t, $\mathrm{Mo}\mathit{C}\mathrm{CHBu^t}$, $^2J(\mathrm{CP})$ 17 (±3) Hz], 121·8 (s, $\mathrm{MoC}\mathit{C}\mathrm{Bu^t}$), 87·0 (s, $\mathit{C}_5\mathrm{H}_5$), 50·2 (s, $\mathrm{PO}\mathit{C}\mathrm{H_3}$), 33·1 [s, $\mathit{C}\mathrm{(CH_3)_3}$], and 27·2 [s, $\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$]. Comparison with the corresponding n.m.r. parameters for $[\mathrm{Mo(CCH_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)}]$[5] {$\delta$ 299·9 [t, $\mathrm{Mo}\mathit{C}\mathrm{CH_2Bu^t}$, $^2J(\mathrm{CP})$ 27·0 Hz] and 62·5 p.p.m. (s, $\mathrm{MoC}\mathit{C}\mathrm{H_2Bu^t}$)} and $[\mathrm{IMo{=}C{=}CHBu^t\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)}]$[6] {$\delta$ 326·4 [t, $\mathrm{Mo}\mathit{C}\mathrm{CH_2Bu^t}$, $^2J(\mathrm{CP})$ 51 Hz] and 132·7 p.p.m. [t, $\mathrm{MoC}\mathit{C}\mathrm{HBu^t}$, $^3J(\mathrm{CP})$ 12 Hz]}

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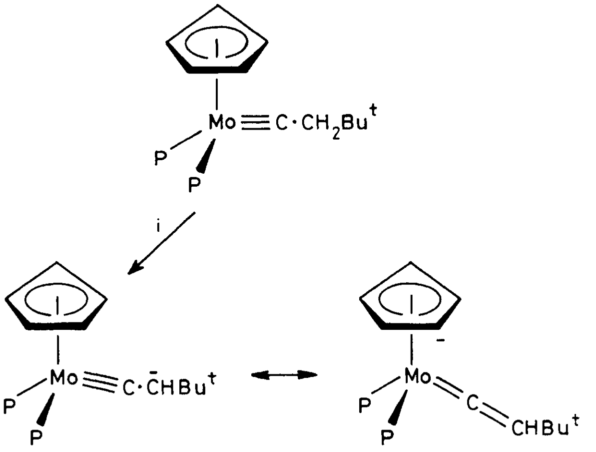
† Recent calculations (ref. 3) suggest that in this anionic vinylalkylidene complex the plane of the $\mathrm{CHBu^t}$ fragment should lie parallel to the plane of the $\mathrm{C_5H_5}$ ligand, although the barrier to rotation is calculated to be low.

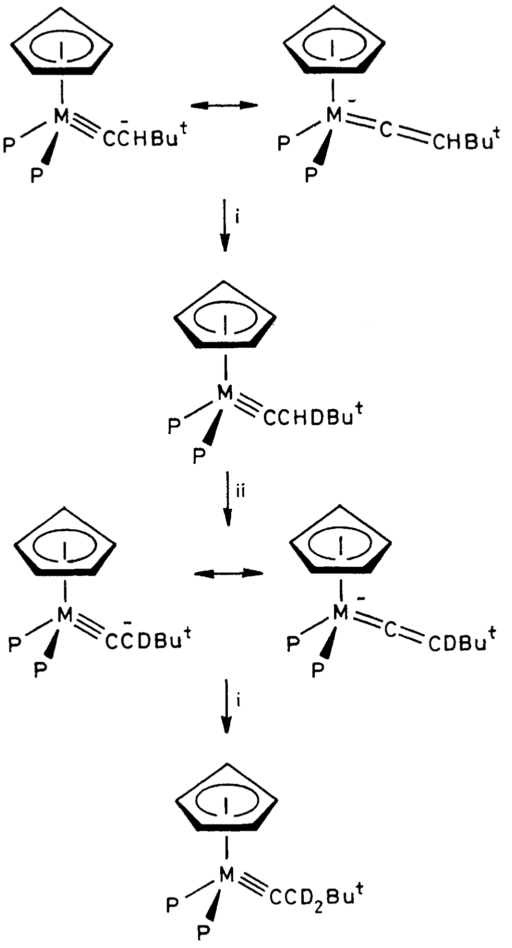
suggests that addition of Bu^nLi to the alkylidyne complex results in proton loss from the carbon attached to the alkylidyne carbon, forming an anionic vinylalkylidene complex in which the charge largely resides on the molybdenum (see Scheme 1). This conclusion was reinforced[6] by the presence of a band at 1 602 mbr cm^{-1} (THF) in the i.r. spectrum of the red solution.



Scheme 1. P = $P(OMe)_3$; i, Bu^nLi/THF.

Addition of D_2O to a diethyl ether solution of the anionic complex led to the regioselective formation of the alkylidyne complex with deuterium bonded to the carbon atom β to the metal (see Scheme 2). The ^1H n.m.r. spectrum (C_6D_6) showed resonances at δ (p.p.m.) 5·26 [t, 5 H, C_5H_5, ^3J(HP) 0·9 ($\pm$0·2) Hz], 3·51 [m, 18 H, POMe, ^2J(PP) 70 ($\pm$20) Hz], 2·17 (m, 0·5 H, *C*H*D*), and 1·10 (s, 9 H, Bu^t), indicating the presence of equal amounts of $[Mo(CCHDBu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ and $[Mo(CCD_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ where the signal at δ 2·17 is complex owing to coupling to two equivalent ^{31}P nuclei and to a ^2H nucleus (spin 1). In agreement, the ^2H spectrum (CH_2Cl_2, rel. to $CHDCl_2$) showed a broad signal at 1·98 p.p.m. The $^{13}C\{^1H\}$ n.m.r. spectrum [C_6D_6, $Cr(acac)_3$] confirmed these conclusions showing resonances at δ (p.p.m.) 299·9 [t, Mo(*C*CHDBu^t) and Mo(*C*CD$_2$Bu^t), ^2J(CP) 27·0 Hz], 89·27 (s, C_5H_5), 62·68 [t, Mo(C*C*HDBu^t), J(CD) 19·5 ($\pm$0·2) Hz], 61·64 [pentuplet, Mo(C*C*D$_2$Bu^t), J(CD) 19·5 ($\pm$0·2) Hz], 51·03 (s, PO*Me*), 32·72 (s, *C*Me$_3$), and 29·79 (C*Me*$_3$).

A similar reaction of $[W(CCH_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ with Bu^nLi in Et_2O followed by quenching of the resultant red solution with D_2O gave a mixture (1 : 1) of $[W(CCHDBu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ and $[W(CCD_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$.



Scheme 2. M = Mo, W; i, D_2O; ii, $+[M(CCHBu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]^-$.

The deuterium oxide quenching reactions provide strong support for the suggestion that addition of the base Bu^nLi to the alkylidyne complexes leads to a facile deprotonation reaction (see Scheme 2). The di-deuterio-complexes are formed because of the operation of a primary kinetic isotope effect, in which the anion $[M(CCHBu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]^-$ (M = Mo, W) selectively abstracts a proton from $[M(CCHDBu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ before the quenching reaction is complete.

These observations have interesting synthetic conquences.

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