THE ROAD FROM ALKYNES TO MOLYBDENUM CARBON MULTIPLE BONDS

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It is well known [1] that alkenes may be activated towards nucleophilic attack by coordination to a transition metal centre, and the synthetic consequences of this effect have attracted considerable interest both from an academic and an industrial viewpoint. In contrast, relatively little is known about the related chemistry of coordinated alkynes. At the start of our work in this area the only previous studies [2] had been concerned with the cations *trans*-$[Pt(Me)L_2(\eta^2\text{-alkyne})][PF_6]$ (L = tertiary phosphine or arsine) where it was observed that reaction with methanol could lead to either formation of a β-methoxyvinyl or a methoxycarbene complex. More recently [3,4], the synthesis of eighteen-electron σ-(E)-vinyl complexes by reaction of a range of nucleophiles with $[Fe(CO)(PPh_3)(\eta^2\text{-MeC}_2Me)(\eta\text{-C}_5H_5)][BF_4]$ had been described.

In the fall of 1976 we discovered that the addition of silver tetrafluoroborate to a methylene chloride solution of the metal–metal bonded species $[Mo_2(CO)_6(\eta^5\text{-}C_9H_7)_2]$ in the presence of an excess of an alkyne resulted in a redox reaction with the formation of a silver mirror and excellent yields of the cationic bis-alkyne complexes $[Mo(CO)(\eta^2\text{-RC}_2R')_2(\eta^5\text{-C}_9H_7)][BF_4]$ (R = R′ = Me; R = R′ = Ph; R = Bu^t, R′ = H; R = Pr^i, R′ = H) [5,6]. These cations proved to be highly reactive towards trimethylphosphite giving access to the unusual blue to purple crystalline mono-alkyne cations $[Mo\{P(OMe)_3\}_2(\eta^2\text{-RC}_2R')(\eta^5\text{-C}_9H_7)][BF_4]$. We were able to extend this methodology to the related η-cyclopentadienyl complexes, and more importantly to avoid the use of expensive silver salts when we found that the carbonylbis(alkyne) cations could be readily obtained by the reaction of the corresponding alkyne with the labile *cis*-bis-acetonitrile cations $[Mo(NCMe)_2(CO)_2(\eta\text{-}C_5H_5$ or $\eta^5\text{-C}_9H_7)][BF_4]$ (Scheme 1) [7]. We recognised [5] that the reactions of these bis(trimethylphosphite) substituted cations with nucleophilic reagents might be particularly interesting, because in these systems the alkyne functions as a four-electron donor [8,9] to the molybdenum centre, and if the alkyne were transformed into a σ-vinyl fragment then the metal centre would be coordinatively unsaturated and unusual molecular rearrangements and bonding modes might be observed.

First the structures of these cations both in solution and in the solid state were established [7], and then the reactions of $[Mo\{P(OMe)_3\}_2(\eta^2\text{-MeC}_2Me)(\eta\text{-}$
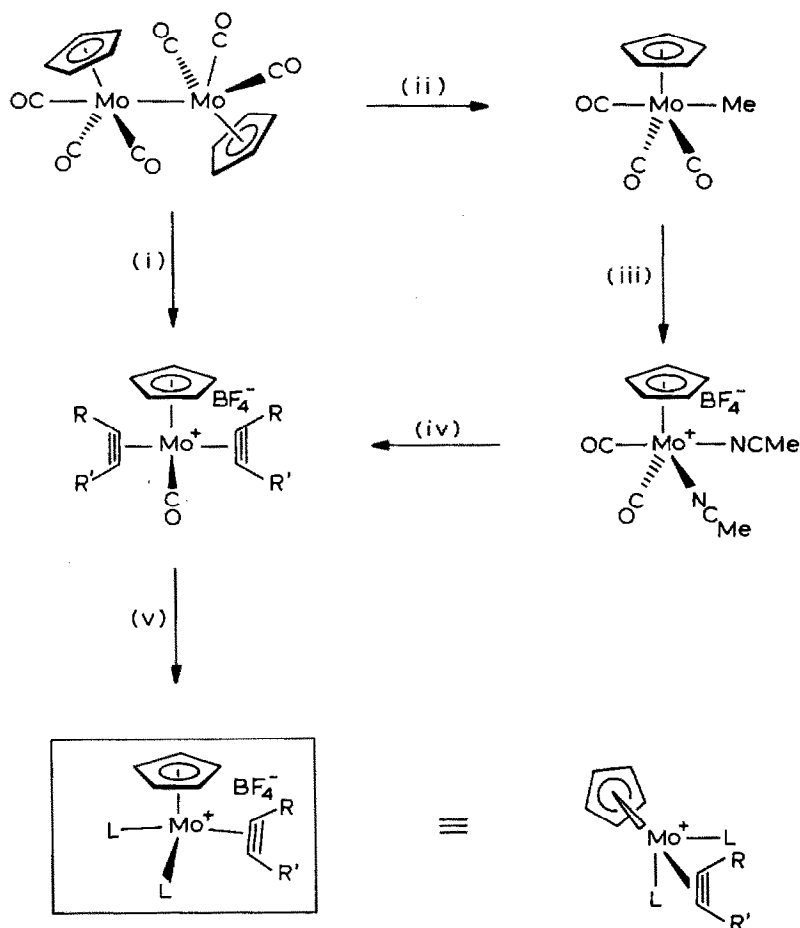
SCHEME 1. (i) AgBF$_4$, RC$_2$R', CH$_2$Cl$_2$; (ii) Na/Hg in thf, +MeI; (iii) HBF$_4$·Et$_2$O, CH$_2$Cl$_2$, $-78°$C, MeCN reflux; (iv) +RC$_2$R', −MeCN, −CO; (v) +P(OMe)$_3$. L = P(OMe)$_3$. A similar chemistry exists for η^5-C$_9$H$_7$ systems.

C$_5$H$_5$)][BF$_4$] with the potential hydride anion donors Na[BH$_4$] and K[BHBu$^s_3$] in tetrahydrofuran (thf) were examined [5,10]. As is shown in Scheme 2 a smooth reaction occurred to afford a yellow crystalline η^3-anti-1-methylallyl complex, and when the reaction was repeated with Na[BD$_4$] in thf this lead to the selective formation of the complex [Mo{P(OMe)$_3$}$_2$(η^3-anti-CH$_2$═CH═CDMe)(η-C$_5$H$_5$)]. This proved to be a general reaction, the cations [Mo{P(OMe)$_3$}$_2$(η^2-MeC$_2$R)(η-C$_5$H$_5$)]][BF$_4$] (R = Et, Pr^i) and [Mo(Ph$_2$PCH=CHPPh$_2$)(η^2-MeC$_2$Me)(η-C$_5$H$_5$)][BF$_4$] reacting to give the corresponding η^3-anti-1-substituted allyl complexes. Possible pathways (Scheme 2) to the η^3-allyl systems involve either reaction of 'H$^-$' with the molybdenum centre, a process which is assisted by a switch [4e(η^2) → 2e(η^2)] in the bonding mode of the butyne, or direct attack at an alkyne carbon, thus gaining access via the illustrated equilibrium to the 16-electron σ-vinyl species (A). The intermediate (A) carries a methyl substituent on the α-carbon and a β-hydrogen atom of the methyl group is positioned such that a β-hydrogen elimination reaction
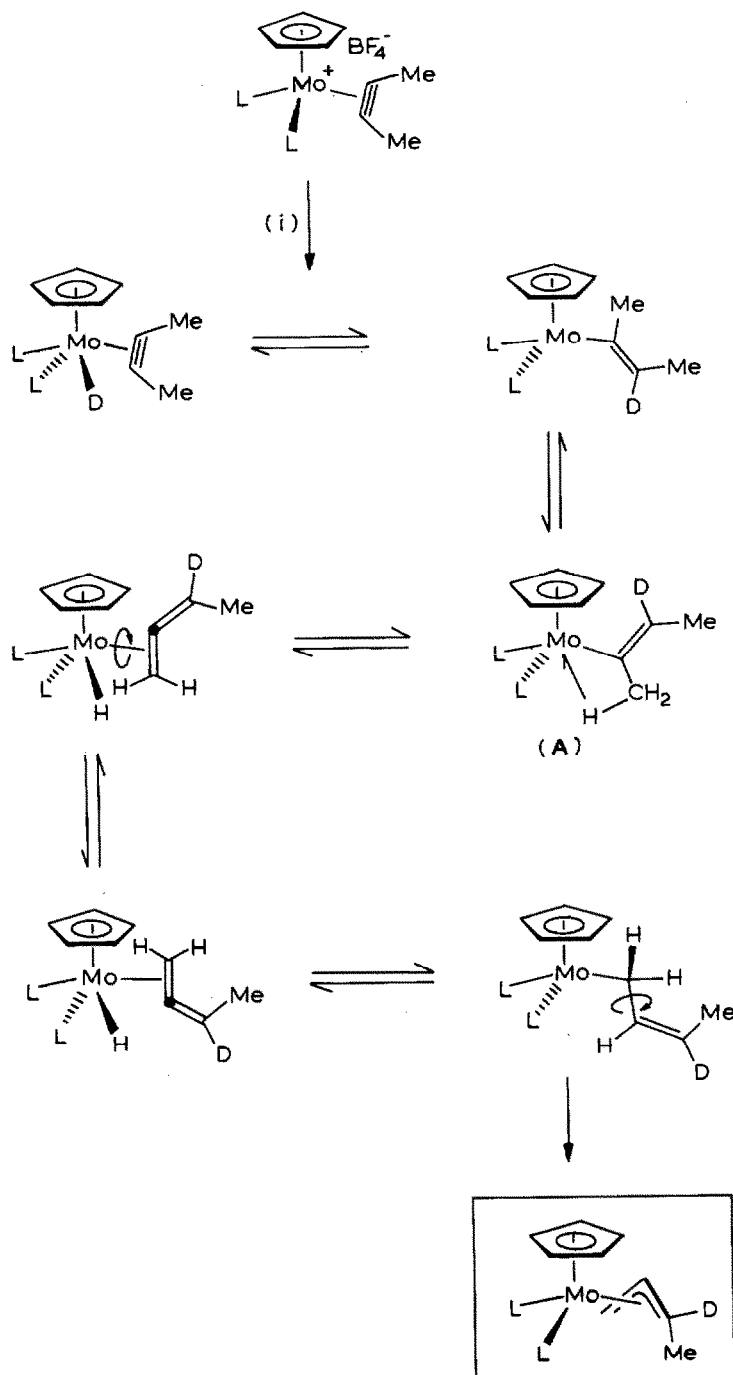
SCHEME 2. L = P(OMe)$_3$. (i) Na[BD$_4$], thf.

can occur via a *cis*-coplanar transition state to give a hydrido(allene) complex. Rotation of the resultant η^2-bonded allene followed by migration of the molybdenum-bonded hydrogen onto the central atoms of the coordinated allene
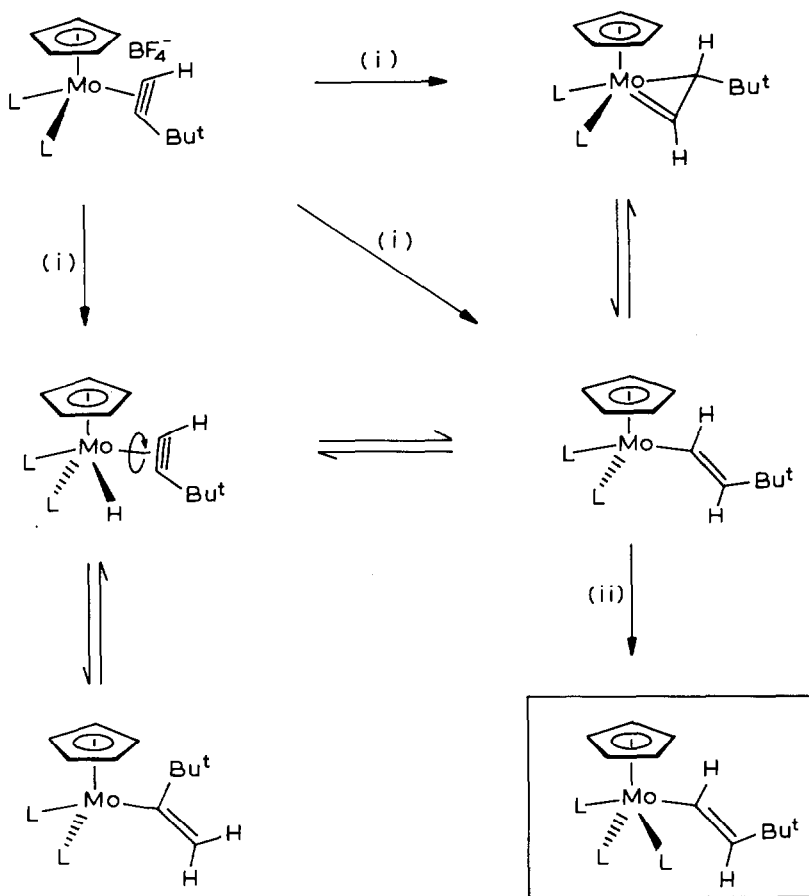
SCHEME 3. L = P(OMe)$_3$. (i) Na[BH$_4$], thf; (ii) P(OMe)$_3$.

affords a 16-electron σ-bonded allyl species, which would be expected to collapse to the η^3-anti-1-methylallyl complex.

In this reaction scheme it is assumed that a 16-electron σ-vinyl complex is accessed either directly or indirectly, and we recognised that if such a species were to be intercepted then it would be necessary to explore the related reactions of alkyne cations where the contact carbons of the coordinated alkyne did not carry methyl groups, i.e. potential β-hydrogen atoms. We, therefore, next examined the reaction of Na[BH$_4$] with the 3,3-dimethylbut-1-yne cation [Mo{P(OMe)$_3$}$_2$(η^2-HC$_2$Bu^t)(η-C$_5$H$_5$)][BF$_4$] in the presence of an excess of trimethylphosphite [10]. This resulted in the formation of the tris(phosphite)vinyl species [Mo{P(OMe)$_3$}$_3${σ-(E)-CH= CHBu^t}(η-C$_5$H$_5$)] (Scheme 3), the corresponding reaction with Na[BD]$_4$ affording [Mo{P(OMe)$_3$}$_3${σ-(E)-CH=CDBu^t}(η-C$_5$H$_5$)], the structure of this σ-vinyl complex being confirmed by X-ray crystallography. Although these observation supported the idea that 16-electron σ-vinyl species are involved in these reactions, they did not establish whether the reactions were kinetically or thermodynamically controlled, moreover, if hydride attack actually occurred on carbon then the 16-electron η1(σ)-vinyl species could in principle be formed either directly as shown
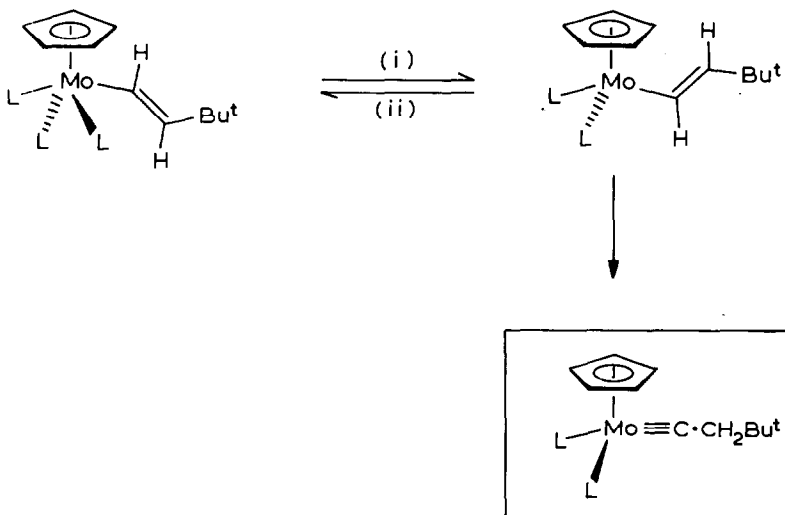
SCHEME 4. L = P(OMe)$_3$. (i) − P(OMe)$_3$; (ii) + P(OMe)$_3$.

(Scheme 3) or, alternatively, there was the interesting idea that a metallacyclopropene was produced initially and this then opened to give a $\eta^1(\sigma)$-vinyl.

At this point in our studies a serendipitous observation was made [5,11]. When the complex [Mo{P(OMe)$_3$}$_3${σ-(E)-CH=CHBu^t}(η-C$_5$H$_5$)] was heated (80°C) in hexane solution one equivalent of trimethylphosphite was liberated and a yellow crystalline complex was formed, which was identified by NMR and X-ray crystallography as the neopentyl-substituted carbyne(alkylidene) complex [Mo(≡CCH$_2$Bu^t)-{P(OMe)$_3$}$_2$(η-C$_5$H$_5$)] (Scheme 4). This was an exciting observation which suggested that if a 16-electron-$\eta^1(\sigma)$-vinyl species could indeed be generated where the α-carbon atom carries a hydrogen substituent, then a hydrogen shift process (α to the β carbon) could intervene resulting in the formation of a molybdenum to carbon triple bond. Although carbonyl substituted carbynes had been synthesised by Fischer and co-workers, and their chemistry explored [12], attempts to replace the carbonyl ligands by phosphorus ligands led to the formation of η^2-ketenyl complexes [13]. Our reaction represented a new synthetic approach to carbyne complexes. In addition the mechanism of the σ-vinyl to carbyne rearrangement reaction was especially interesting. Did the migrating hydrogen first move onto the metal or was a direct 1,2-H shift possible?

Further insight into the factors controlling these reactions was obtained when the corresponding chemistry of the 3-methylbut-1-yne cation was studied [10,14]. Treatment of a suspension of [Mo{P(OMe)$_3$}$_2$(η^2-HC$_2$Pr^i)(η-C$_5$H$_5$)][BF$_4$] in thf with Na[BH$_4$] in the presence of P(OMe)$_3$ at room temperature gave a good yield of the carbyne complex [Mo(≡CCH$_2$Pr^i){P(OMe)$_3$}$_2$(η-C$_5$H$_5$)]. In contrast, reaction of the same cation with K[BHBu$^s_3$] at −78°C in the absence of P(OMe)$_3$ led to a rapid reaction and the formation of the allyl complex [Mo{P(OMe)$_3$}$_2$(η^3-CH$_2$ ⋯ CH ⋯ CMe$_2$)(η-C$_5$H$_5$)], and when Li[BDEt$_3$] was used as a source of 'D$^-$', the deuterium-substituted analogue of the η^3-allyl complex was obtained where the deuterium exclusively occupied the *syn*-position on the allyl fragment.

Although these observations are at first sight rather surprising they can in fact be

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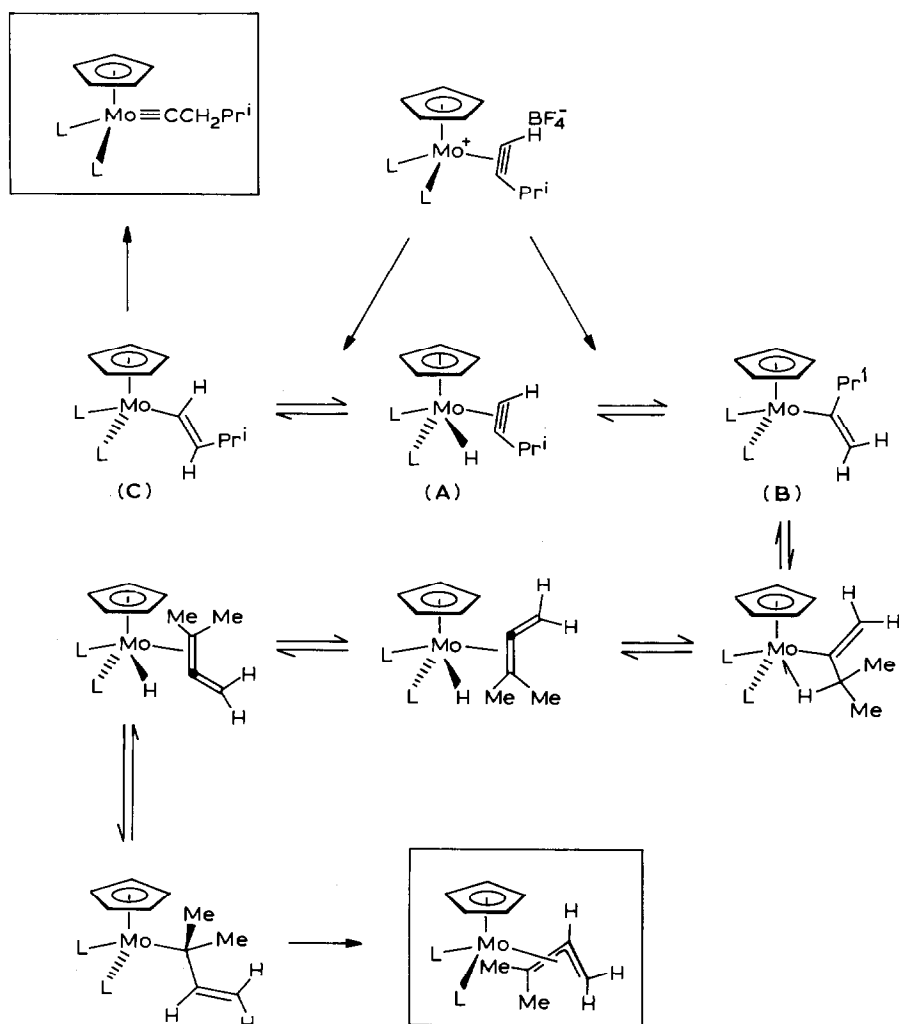
SCHEME 5. L = P(OMe)$_3$.

understood in terms of the previously suggested reaction paths. Access is gained either directly or indirectly to an 18-electron hydrido (alkyne) intermediate (A) (Scheme 5). At low temperature the reversible formation of the 16-electron $\eta^1(\sigma)$-vinyl intermediate (B) is favoured, which as is shown can provide a pathway to the η^3-allylic complex. Alternatively, at higher temperatures (i.e. room temperature) the $\eta^1(\sigma)$-vinyl species (C) can be accessed where the α-carbon of the vinyl fragment now carries a hydrogen substituent, and can transform into the carbyne complex. Of course this still does not provide insight into how this last step occurs.

In trying to provide an answer to this question we decided to adopt two strategies. The first was to examine more carefully the rearrangement of [Mo{P(OMe)$_3$}$_3$ {σ-(E)-CH=CHBu^t}(η-C$_5$H$_5$)] into [Mo($\equiv$CCH$_2$Bu^t){P(OMe)$_3$}$_2$(η-C$_5$H$_5$)]. Our plan was to attempt a cross-over experiment in order to decide whether the hydrogen migration reaction was intra- or inter-molecular. The deuterium substituted vinyl

complex $[Mo\{P(OMe)_3\}_3\{\sigma\text{-}(E)\text{-}CD{=}CDBu^t\}(\eta\text{-}C_5H_5)]$ was prepared straightfor-wardly by treating $[Mo\{P(OMe)_3\}_2(\eta^2\text{-}DC_2Bu^t)(\eta\text{-}C_5H_5)][BF_4]$ with $P(OMe)_3$ and $Li[BDEt_3]$. Thermolysis of the dideuterio trisphosphite complex smoothly occurred to give $[Mo({\equiv}CCD_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$. However, when mixtures of $[Mo\{P(OMe)_3\}_3\{\sigma\text{-}(E)\text{-}CD{=}CDBu^t\}(\eta\text{-}C_5H_5)]$ and $[Mo\{P(OMe)_3\}_3\{\sigma\text{-}(E)CH{=}CHBu^t\}(\eta\text{-}C_5H_5)]$ were heated in hexane solution widely varying proportions of the carbynes $Mo{\equiv}CCH_2Bu^t$, $Mo{\equiv}CCHDBu^t$ and $Mo{\equiv}CCD_2Bu^t$ were obtained depend-ing on reaction times and concentrations. This led us to consider that perhaps the cross-over experiment was invalidated by the intervention of a base (trimethylphos-phite)-catalysed exchange process. Specifically, was it possible to deprotonate the carbyne $[Mo({\equiv}CCH_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ to form a vinylidene anion $[Mo({=}C{=}CHBu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]^-$, and if so would this reprotonate on the β carbon?

The validity of this idea was confirmed [15,16] when it was found that addition of Bu^nLi in tetrahydrofuran or Et_2O solution to $[Mo({\equiv}CCH_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ gave a deep-red solution, which on quenching with D_2O afforded a mixture of $[Mo({\equiv}CCHDBu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ and $[Mo({\equiv}CCD_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$. This implied an interesting parallel with the base-promoted reversible isomerisation of alkynes into 1,2-dienes. Addition of the base Bu^nLi to the carbyne leads to a facile deprotonation reaction and the formation of an ambident mono-an-ion, which is regio-selectively protonated on carbon, the di-deuterio complex result-ing from a primary kinetic isotope effect (Scheme 6). This reaction has obvious
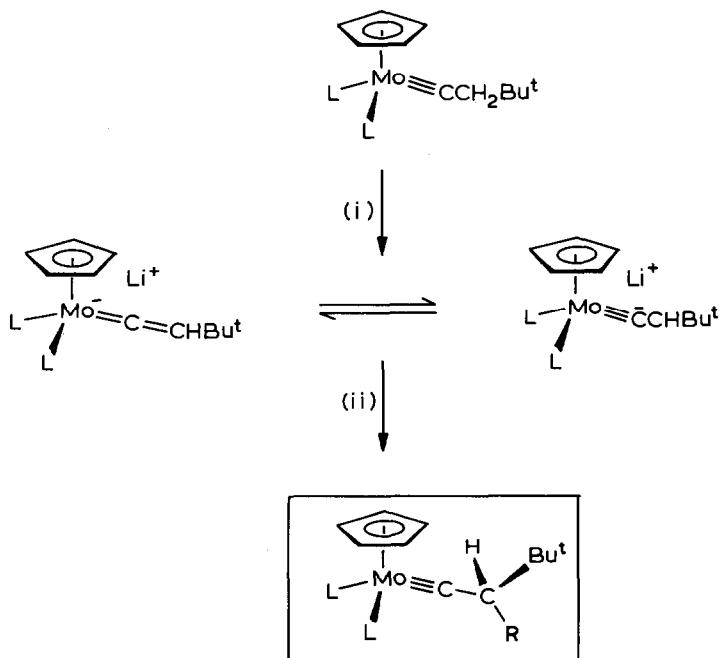
SCHEME 6. $L = P(OMe)_3$. (i) Bu^nLi, thf; (ii) D_2O, MeI, Me_3SiCl, Me_2S_2, Bu^tCOCl.
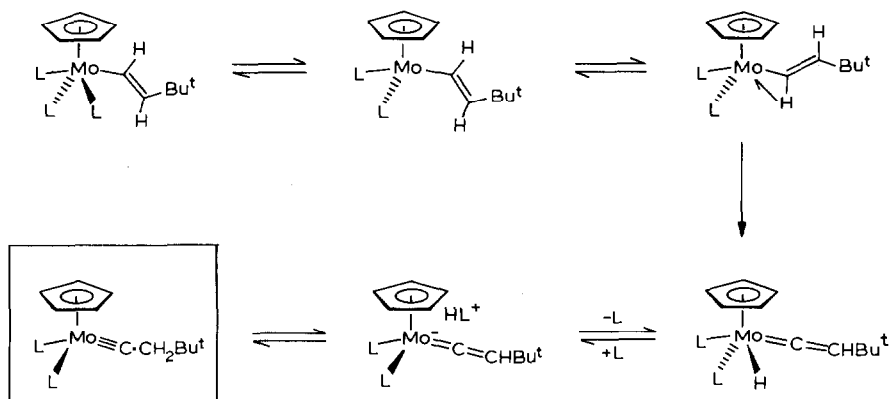
SCHEME 7. L = P(OMe)$_3$.

synthetic consequences and when the anion is quenched with MeI, Me$_3$SiCl, Me$_2$S$_2$ or Bu^{t}COCl the corresponding carbon substituted carbynes are formed in good yield.

Thus, returning to the question of the mechanism of the carbyne forming reaction one way in which [Mo{P(OMe)$_3$}$_3${σ-(E)-CH=CHBu^t}(η-C$_5$H$_5$)] could arrange into [Mo($\equiv$CCH$_2$Bu^t){P(OMe)$_3$}$_2$(η-C$_5$H$_5$)] would be initial dissociative loss of P(OMe)$_3$, followed by an α-hydrogen abstraction of the vinylic hydrogen to form a hydrido(vinylidene) complex, deprotonation by P(OMe)$_3$, and reprotonation on the end β carbon leading to the formation of the carbyne (Scheme 7). Although such α-hydrogen abstraction reactions had not been previously observed it is interesting to note that formyl complexes [17] readily rearrange into hydrido(carbonyl) complexes, and a parallel can be seen with a σ-vinyl to hydrido(vinylidene) rearrangement.

A second strategy for understanding this chemistry was to continue to investigate the reactions of the cations [Mo{P(OMe)$_3$}$_2$(η^2-alkyne)(η-C$_5$H$_5$)][BF$_4$] with nucleophiles, and it was clear that if the alkyne did not carry hydrogen or methyl groups on the alkyne contact carbons then η^3-allyl or carbyne forming reactions would be blocked. Would such reactions lead to metallacyclopropenes? The reaction of [Mo{P(OMe)$_3$}$_2$(η^2-PhC$_2$Ph)(η-C$_5$H$_5$)][BF$_4$] with K[BHBu$^s_3$] was therefore examined [18,19]. This led to the formation ($-78°$C) of a green crystalline complex with molecular formula [Mo{C(Ph)CHPh}{P(OMe)$_3$}$_2$(η-C$_5$H$_5$)]. The structurally related compounds [Mo{C(Bu^t)CHPh}{P(OMe)$_3$}$_2$(η-C$_5$H$_5$)] and [Mo{C(Me)-CPh$_2$}{P(OMe)$_3$}$_2$(η-C$_5$H$_5$)] were obtained as red crystalline materials by reaction ($-78°$C, thf) of lithium diphenylcuprate with [Mo{P(OMe)$_3$}$_2$(η^2-HC$_2$Bu^t)(η-C$_5$H$_5$)][BF$_4$] and [Mo{P(OMe)$_3$}$_2$(η^2-MeC$_2$Ph)(η-C$_5$H$_5$)][BF$_4$]. Examination of the ^{13}C NMR spectra of these complexes revealed low field chemical shifts in the range 286–237 ppm characteristic of a carbenoid carbon. An additional interesting NMR feature was that whereas the ^{31}P spectra of the first two complexes showed two resonances, the spectrum of the complex [Mo{C(Me)CPh$_2$}{P(OMe)$_3$}$_2$(η-C$_5$H$_5$)] showed only one resonance down to a temperature of $-90°$C. Whilst it was possible that the two phosphorus nuclei are accidentally equivalent the appearance of the MoC(Me) signal in the ^{13}C-{^{1}H} NMR spectrum as a triplet (J(PC) 28 Hz)

indicates equal J(PC) couplings, and hence, it is more likely that the molecule is fluxional with a time averaging of the ^{31}P environments.

An understanding of the bonding and molecular geometries of these molecules was obtained from single crystal X-ray diffraction studies, and as expected the molecules showed close similarities, each containing a $Mo\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$ fragment (Scheme 8). In all cases a vinyl moiety was coordinated via one short and one long Mo–C bond (ca. 1.95 and 2.3 Å) prompting description of these species as molybdenacyclopropenes. Alternatively, these molecules can be described as η^2-vinyl complexes where the vinyl group adopts an η^2 (3e) bonding mode in order to achieve an 18 electron molybdenum configuration. An interesting consequence of this change from the more familiar η^1 (1e) bonding to the η^2 (3e) mode is that a formal double bond is generated between the molybdenum and a carbon atom, suggesting that these molecules can also be thought of as carbene(alkylidene) complexes, an aspect which is reflected in the low field ^{13}C chemical shifts of the C_α carbons. As is illustrated in Scheme 8 in each complex the C_α–C_β vector is orientated so that there is one L–Mo–C_α–C_β torsion angle of ca. $-90°$. In the first two complexes, the other torsion angle is ca. $0°$, whereas, in $[Mo\{C(Me)CPh_2\}\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ the second L–Mo–C_α–C_β angle is ca. $180°$. A consequence of this is that the C_α (carbene)carbon is remote from the plane of the η^5-cyclopentadienyl ligand in the
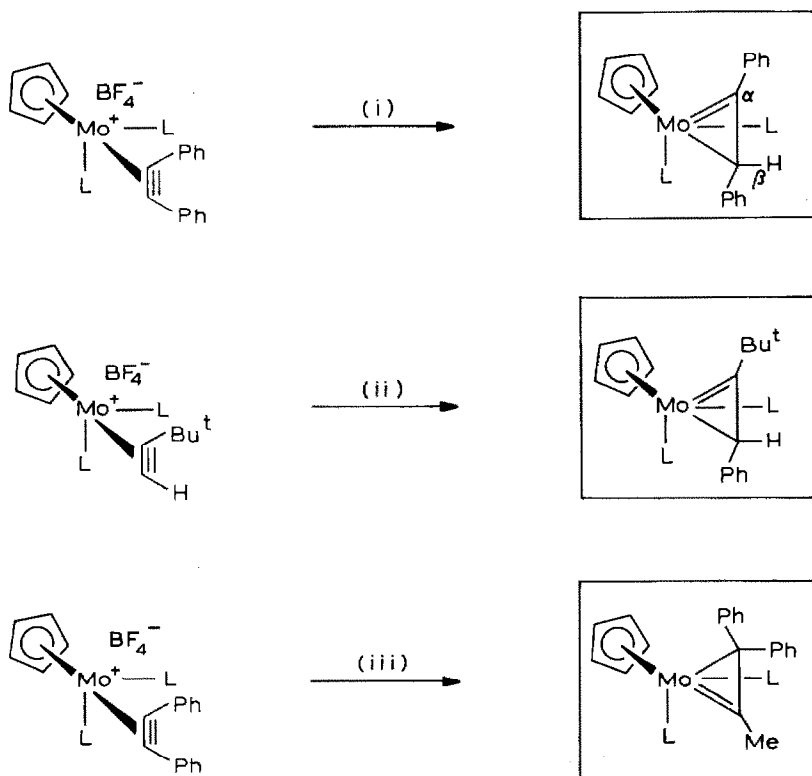

SCHEME 8. L = $P(OMe)_3$. (i) $K[BHBu^s{}_3]$; (ii) $LiCuPh_2$.

diphenyl substituted species. An additional interesting structural feature is that in the first two molecules the bulky phenyl group on C_β occupies a pseudo-equatorial position, suggesting the possible importance of thermodynamic control in these reactions.

Additional insight into the nature of these interesting molecules was obtained from a fragment molecular orbital analysis. The frontier orbitals of the $[MoL_2(\eta\text{-}C_5H_5)]^+$, HC_2H, and $CHCH_2^-$ moieties are shown in Scheme 9. In a theoretical analysis of the bonding of alkynes to d_4 ML_5 species including $[MoL_2(\eta\text{-}C_5H_5)]^+$, Templeton et al. [20] concluded that the role of the $\pi_\perp^\star$ orbital was minimal, the principal interaction being via the $\pi_\parallel^\star$, σ and $\pi_\perp$ orbitals of the alkyne. These find
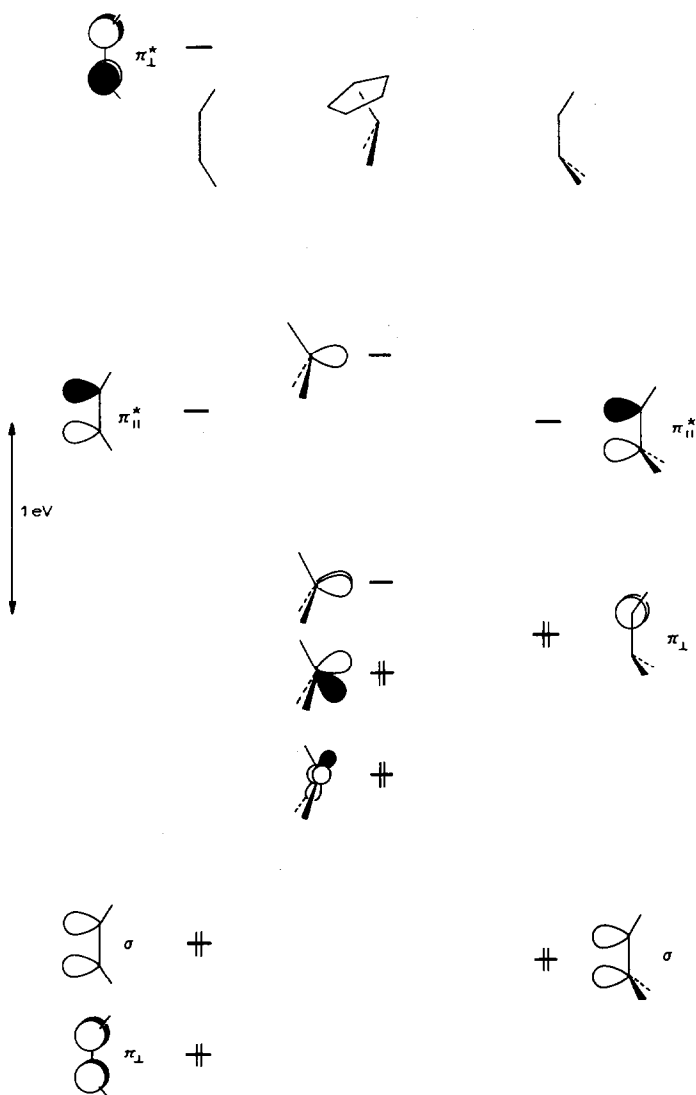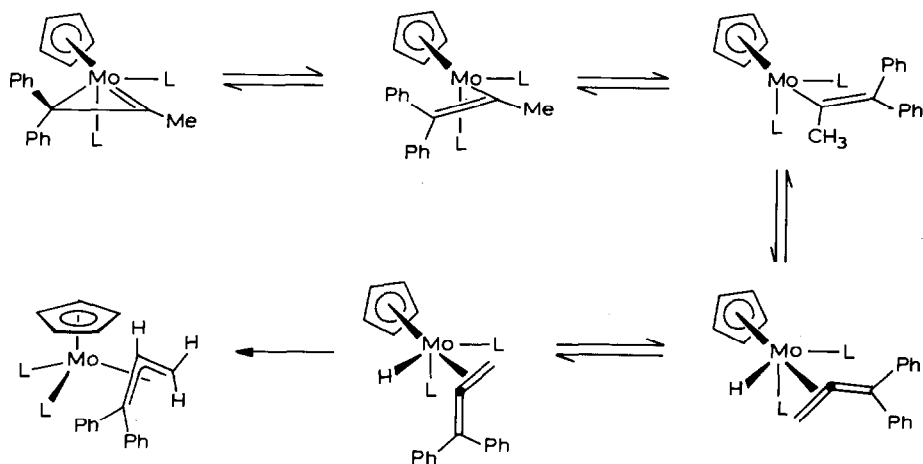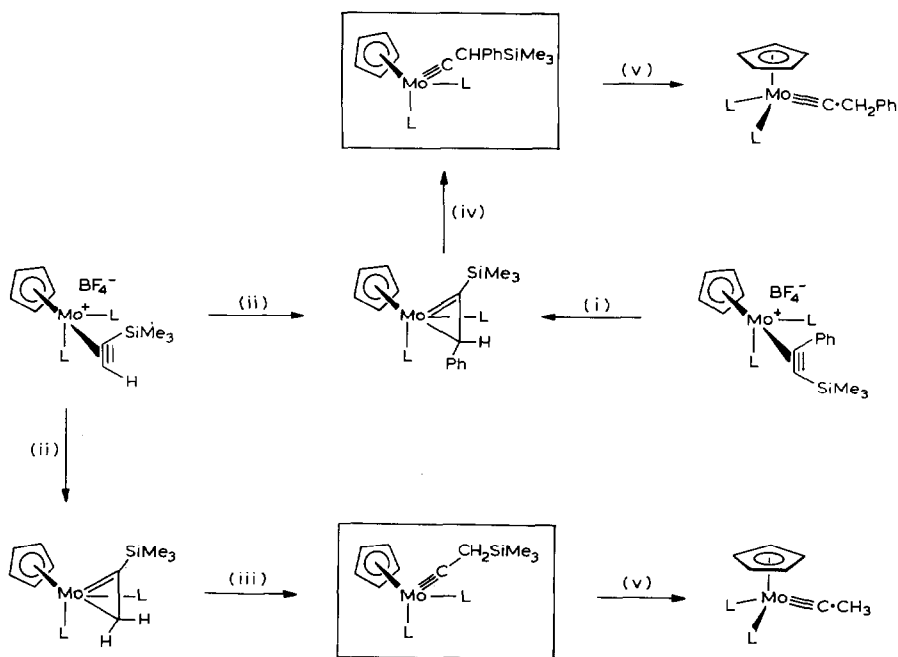

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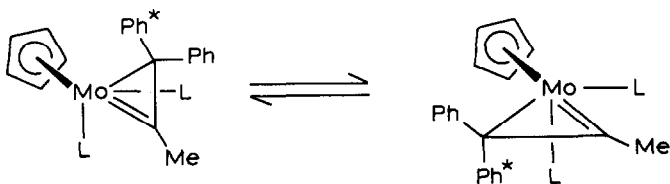
SCHEME 10. L = P(OMe)$_3$.

suitable matches from the σ and π orbitals on the metal fragment leading to electron donation from the alkyne σ and $\pi_\perp$ orbitals, and back donatión into the $\pi_\parallel^*$ orbital. Precisely the same interactions are available to the η^2-vinyl ligand. Both these interactions cause a reduction of the C_α–C_β bond order towards unity, as they lead to occupancy of the σ and $\pi_\parallel^*$ orbitals being reduced and increased, respectively. The major difference between the alkyne and η^2-$C_2H_3^-$ frontier orbitals lie in the energy and spatial nature of the $\pi_\perp$ orbital. In the vinyl ligand this orbital is essentially pure $C_\alpha(p)$ in character, and therefore is both asymmetric with respect to the two contact carbons and at higher energy than the $\pi_\perp$ orbital of the alkyne. Therefore, this orbital leads to better donor ability, on energetic grounds, of η^2-$C_2H_3^-$ than C_2H_2, and to a localised Mo–C_α double bond in accord with the metallacyclopropene analogy. The orientation adopted by the η^2-vinyl ligands and the fluxionality of the related cationic alkyne species is paralleled by that of the η^2-vinyl ligands in the case where it can be observed, i.e. in [Mo{C(Me)CPh$_2$}-{P(OMe)$_3$}$_2$(η-C$_5$H$_5$)]. This exchange process can be described as a 'wind-screen-wiper' motion and as shown in Scheme 10 exchanges the R_β and $R_{\beta'}$ sites and phosphorus environments by alteration of the torsion angle by 90°, simple calculations suggesting a barrier of ca. 20 kJ mol^{-1} for this process.

In addition to the rotational process there is evidence [19] that η^2-vinyl complexes can in fact transform into η^1 (σ)-vinyls as we previously speculated. At room temperature (3 days) a toluene solution of [Mo{C(Me)CPh$_2$}{P(OMe)$_3$}$_2$(η-C$_5$H$_5$)]

SCHEME 11. L = P(OMe)$_3$.

rearranges into an isomeric η^3-allylic complex (Scheme 11). This isomerisation reaction involves a hydrogen shift process and can be understood in terms of an initial $\eta^2 \to \sigma$ change in the bonding mode of the vinyl ligand followed by β-hydrogen transfer to the metal, rotation of the resultant 1,1-diphenylallene ligand, and migration of hydrogen from the molybdenum to the central carbon of the coordinated allene.

Returning to the mechanism of the carbyne forming reactions, an interesting relationship between η^2-vinyl species and carbyne complexes was revealed when the reactions of nucleophiles with trimethylsilyl substituted alkyne cations were examined (Scheme 12) [21,22]. Treatment of $[\text{Mo}\{\text{P(OMe)}_3\}_2(\eta^2\text{-HC}_2\text{SiMe}_3)(\eta\text{-}C_5\text{H}_5)][\text{BF}_4]$ with $\text{K}[\text{BHBu}^s_3]$ gave on low temperature work-up a deep-blue air-sensitive material, which was shown to be an η^2-vinyl complex carrying a Me_3Si substituent on C_α by a single crystal X-ray diffraction study on the analogous η^5-indenyl complex and by comparison of NMR data. As expected the ^{31}P NMR spectrum of the blue complex showed only a single resonance at -70°C consistent with the occurence of a facile 'windscreen-wiper' process. Both the η-cyclopentadienyl and η^5-indenyl η^2-vinyl complexes rearranged quantitatively at room temperature in toluene solution to form yellow carbyne complexes. Similarly, reaction of $[\text{Mo}\{\text{P(OMe)}_3\}_2(\eta^2\text{-HC}_2\text{SiMe}_3)(\eta\text{-C}_5\text{H}_5)][\text{BF}_4]$ with LiCuPh_2 gave an analogous phenyl substituted η^2-vinyl complex, which could alternatively be synthesised by reaction of $\text{K}[\text{BHBu}^s_3]$ with the cation $[\text{Mo}\{\text{P(OMe)}_3\}_2(\eta^2\text{-PhC}_2\text{SiMe}_3)(\eta\text{-}C_5\text{H}_5)][\text{BF}_4]$. A similar facile rearrangement reaction occurred at 60°C in toluene to


SCHEME 12. $\text{L} = \text{P(OMe)}_3$. (i) $\text{K}[\text{BHBu}^s_3]$, thf; (ii) LiCuPh_2, thf; (iii) room temp.; (iv) 60°C; (v) NaF, aqueous MeCN, room temp.

form a phenyltrimethylsilyl-substituted carbyne. Both of these trimethylsilyl carbyne complexes could be readily desilylated with NaF/aqueous MeCN to form methyl and benzyl substituted carbynes.

These molecular rearrangement reactions are particularly interesting and involve an apparent 1,2-trimethylsilyl shift. It is possible that a concerted process is involved in which the Me_3Si group migrates from the α to the β carbon atom with concomitant formation of a metal to carbon triple bond. Detailed mechanistic studies are at present in hand involving chiral complexes, which should show whether the η^2-vinyl complex rearranges directly to the carbyne or first opens to a $\eta^1(\sigma)$-vinyl. It is, of course, possible that in the rearrangement of $[Mo\{P(OMe)_3\}_3-\{\sigma-(E)-CH=CHBu^t(\eta-C_5H_5)\}]$ into $[Mo(\equiv CCH_2Bu^t)\{P(OMe)_3\}_2(\eta-C_5H_5)]$ a related mechanism is involved where a 16-electron $\eta^1(\sigma)$-vinyl complex formed by dissociative loss of $P(OMe)_3$ collapses to a η^2-vinyl intermediate carrying a hydrogen substitutent on the α carbon atom, which then undergoes a 1,2-shift to form the carbyne. The understanding of these molecular rearrangements presents a real mechanistic challenge.

When the reaction of $[Mo\{P(OMe)_3\}_2(\eta^2-PhC_2Ph)(\eta-C_5H_5)][BF_4]$ with lithium dimethylcuprate was examined it was observed [19] that two products were formed, one being identified as the expected η^2-vinyl complex and the other as $[MoCH_3\{P(OMe)_3\}(\eta^2-PhC_2Ph)(\eta-C_5H_5)]$. Recently [2,3] we found that the corresponding reactions with Grignard reagents CH_3MgX (X = Br, I) led to selective attack on the molybdenum thus providing a simple synthetic entry to an interesting group of molecules which contain a σ-bonded alkyl group and a four-electron alkyne (Scheme 13).

Attempts [19] to convert this molecule into the η^2-vinyl complex by treatment with trimethylphospite under a variety of conditions were unsuccessful, suggesting that in the reaction of dimethyl cuprates with cationic molybdenum alkyne complexes competitive reactions are involved where a methyl group is delivered either directly to the molybdenum centre with loss of $P(OMe)_3$ or to an alkyne carbon leading to formation of an η^2-vinyl species.
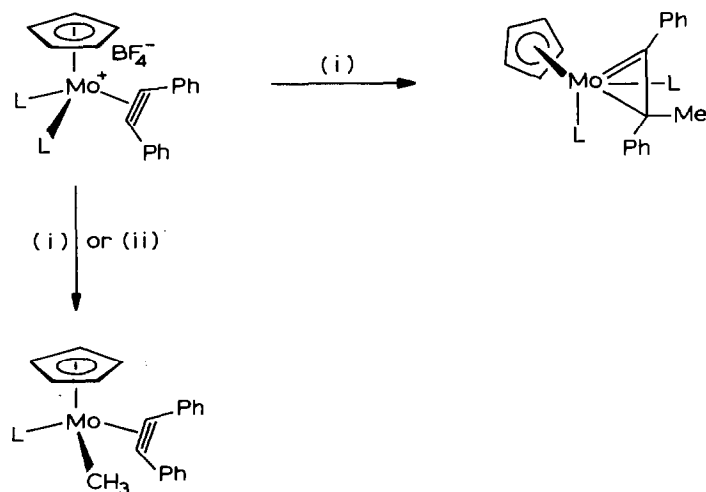
SCHEME 13. L = P(OMe)$_3$. (i) LiCuMe$_2$, thf; (ii) CH$_3$MgI, thf.
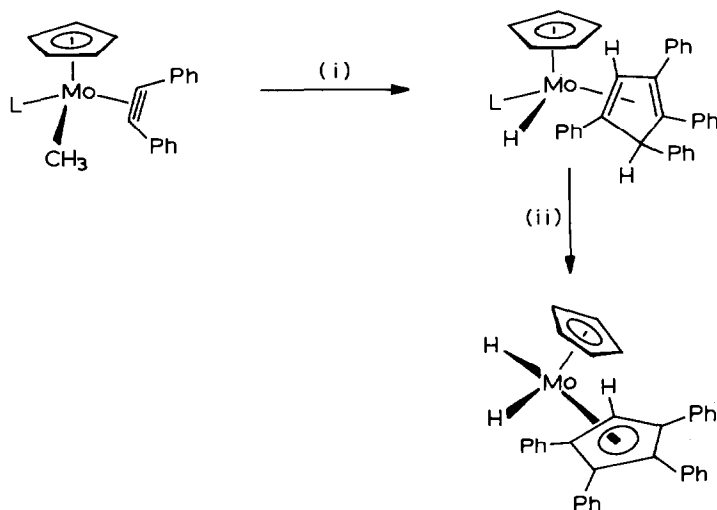
SCHEME 14. L = P(OMe)$_3$. (i) PhC$_2$Ph, C$_6$H$_6$, 78°C; (ii) C$_6$H$_6$, 100°C.

Whereas, the migration of a methyl group onto coordinated PhC$_2$Ph is apparently a high energy process, an excess of diphenylacetylene reacted smoothly in benzene (78°C) with [MoCH$_3$\{P(OMe)$_3$\}(η^2-PhC$_2$Ph)(η-C$_5$H$_5$)] to give the illustrated hydrido(1,3-diene) complex (Scheme 14), which was characterised structurally by both NMR and X-ray crystallography [23]. At 100°C in benzene as solvent this molecule loses trimethylphosphite and undergoes a hydrogen transfer reaction from the C$_5$ ring to the molybdenum forming a dihydridomolybdenum complex (Scheme 14).

This unexpected sequence of reactions can be explained by assuming that the coordinated diphenylacetylene switches its bonding mode from four to two electrons, thus providing a coordination site for the σ-bonded methyl group to undergo a α-hydrogen abstraction reaction. This results in the formation of a methylene-molybdenum complex, which is captured by the η^2 (2e) bonded PhC$_2$Ph to give a 16 electron hydridomolybdenacyclobutene. Further reaction with a second molecule of PhC$_2$Ph rather than a reductive elimination reaction then leads to the formation of the C$_5$ ring, which undergoes a hydrogen shift to form the hydrido(1,3-diene) complex (Scheme 15).

Thus a key concept in this reaction sequence is the apparent ability of the methyl-substituted system to undergo an α-hydrogen abstraction reaction. Since one of the pathways by which σ-vinyl complexes could rearrange into carbynes also involves an initial α-hydrogen abstraction reaction, it was therefore of considerable interest to treat [Mo\{P(OMe)$_3$\}$_2$(η^2-PhC$_2$Ph)(η-C$_5$H$_5$)][BF$_4$] with CH$_2$=CHMgBr in thf as solvent. This led to a clean reaction and the formation in good yield of a η^3-cyclopropenyl complex (Scheme 16) [23].

This is a fascinating reaction and it is likely that the initial step involves replacement of a phosphite ligand by a vinyl group delivered by the Grignard reagent. Then, as is assumed to occur with the methyl system, the coordinated alkyne switches its bonding mode so allowing an α-hydrogen abstraction reaction to occur which leads to a hydrido(vinylidene) complex. Deprotonation by trimethylphosphite and reprotonation on the β-carbon atom generates a methyl-substituted carbyne
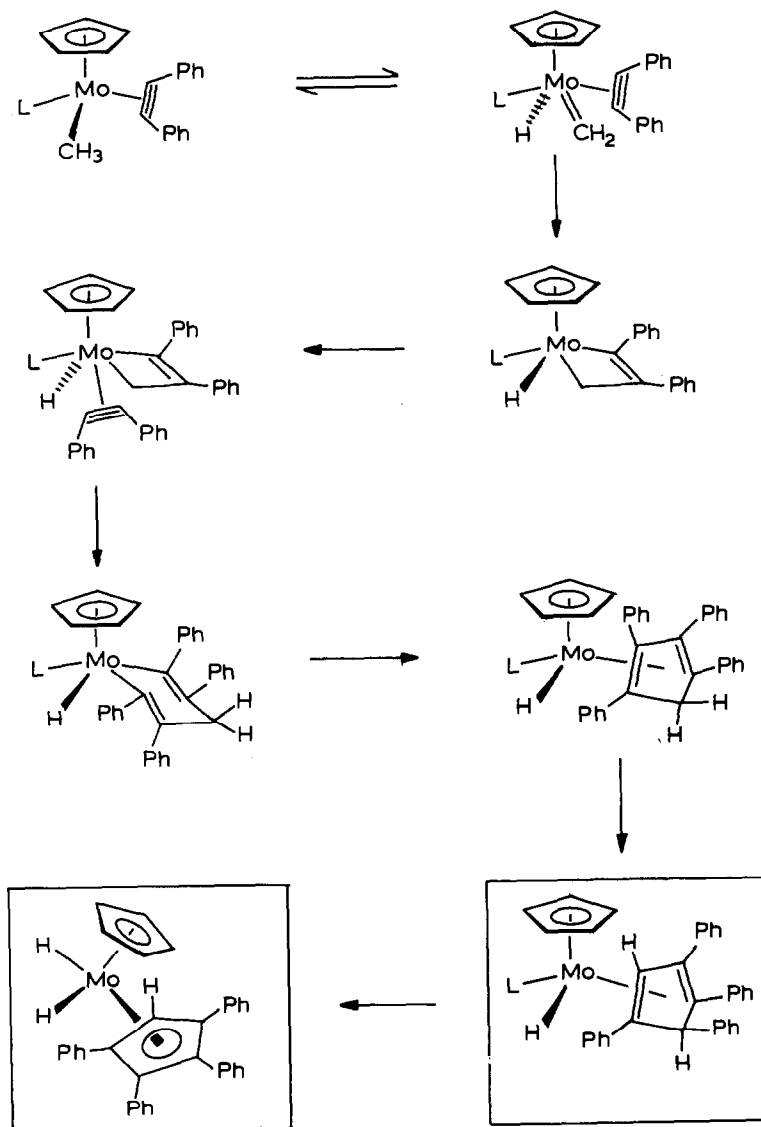
SCHEME 15. L = P(OMe)$_3$.

complex which also has coordinated onto the molybdenum centre, a PhC$_2$Ph ligand functioning as a two-electron system. From the work of Schrock and coworkers [24] this type of intermediate would be expected to transform into a metallacyclo-butadiene, and in high oxidation state tungsten chemistry such species are known to collapse into η^3-cyclopropenyl complexes. It is particularly interesting that such reactions apparently also occur with lower oxidation state η-cyclopentadienylmo-lybdenum complexes, and additional support for this idea is provided by our recent observation [23] that UV irradiation of a solution of [Mo($\equiv$CCH$_2$Bu^t)-{P(OMe)$_3$}$_2$(η-C$_5$H$_5$)] and PhC$_2$Ph in hexane affords the η^3-cyclopropenyl complex [Mo{P(OMe)$_3$}$_2${η^3-C(Ph)C(Ph)C(CH$_2$Bu^t)}(η-C$_5$H$_5$)].
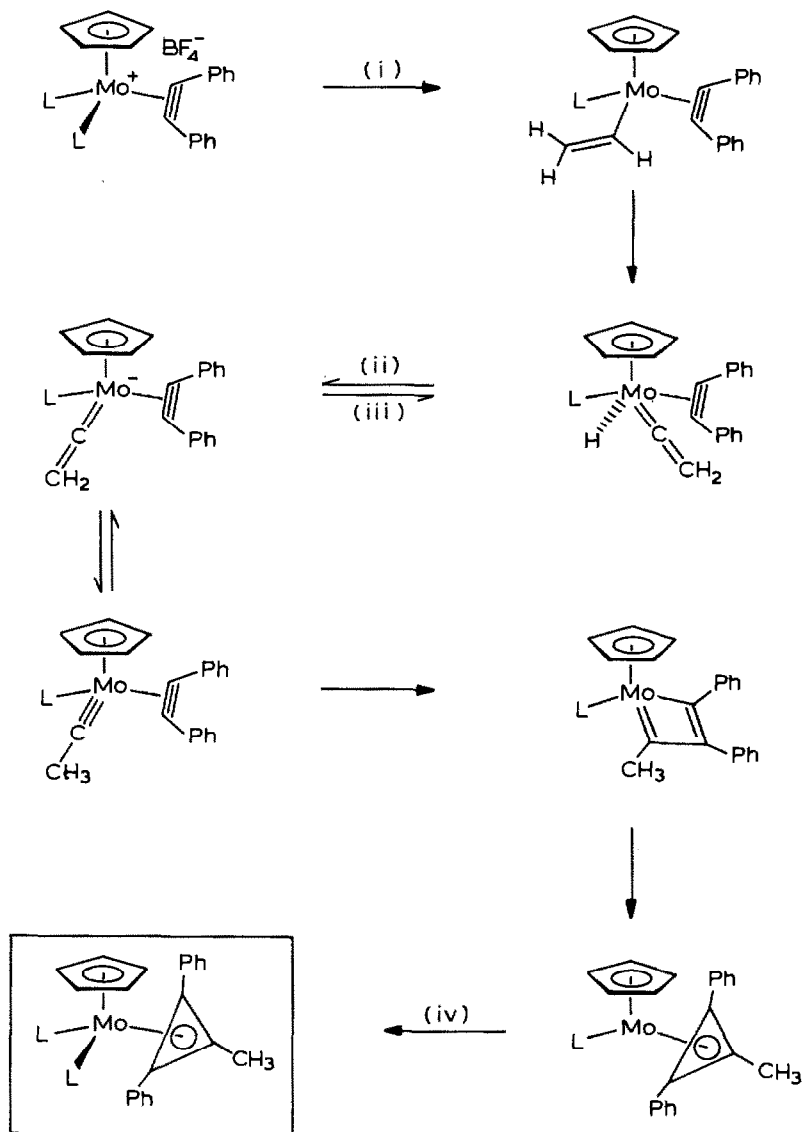
SCHEME 16. $L = P(OMe)_3$. (i) $CH_2=CHMgBr$, thf; (ii) $-HP(OMe)_3^+$; (iii) $+HP(OMe)_3^+$; (iv) $+P(OMe)_3$.

In this article I have tried to show how our understanding of this area of chemistry has slowly unfolded. There have been many surprises, and some red herrings, but as with all good areas of research we have still miles to go before we sleep.

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