The Formation of η^2(3e)-Bonded Allenyl Complexes by Deprotonation of Four-electron Donor Alkyne Metal Complexes

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Addition of Et_3N to a solution of $[Mo(\eta^2\text{-}PhC_2CH_2Ph)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$ in $(CD_3)_2CO$ results in a selective deuteriation of the methylene hydrogens, whereas treatment with KH–Bu^tOH–Et_2O results in H_2 loss and formation of the air- and moisture-sensitive η^2(3e)-allenyl complexes $[\overline{Mo\{=C(Ph)C}=CHPh\}\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$; this reaction can be generalised and electrophiles react with these new molecules to form four-electron donor alkyne cations.

In the reactions of nucleophiles with the four-electron donor alkyne complexes $[Mo(\eta^2\text{-}RC_2R')\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$ (R, R′ = alkyl, aryl, $SiMe_3$, H), two competing reaction paths have been identified. Direct reaction at the molybdenum centre results[1,2] in loss of $P(OMe)_3$ and formation of the neutral species $[MoR''(\eta^2\text{-}RC_2R')\{P(OMe)_3\}(\eta\text{-}C_5H_5)]$ (R″ = alkyl, aryl), whereas attack on a co-ordinated alkyne carbon atom leads[2] to η^2-vinyl complexes. There is a third type of reaction which has so far not been observed, involving deprotonation of cations like $[Mo(\eta^2\text{-}PhC_2CH_2Ph)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$ (**1**). Such a reaction might be expected to lead to the formation of a potentially interesting group of molecules, η^2-allenyl or metallamethylenecyclopropene complexes. To gain synthetic access to molecules of this type a proton-specific nucleophile is required.

In order to assess whether a deprotonation reaction could actually be effected, a solution of (**1**) in deuterioacetone was treated with Et_3N (12 h, 25 °C). This led to a facile hydrogen to deuterium exchange reaction and the formation in high yield of purple, crystalline $[Mo(\eta^2\text{-}PhC_2CD_2Ph)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5][BF_4]$. This observation can be compared to the report[3] that the cation $[Mo(CO)(\eta^2\text{-}MeC_2Me)_2(\eta\text{-}C_5H_5][PF_6]$ catalyses deuterium–hydrogen exchange between free but-2-yne and deuterioacetone on addition of a strong base. However, this exchange process was interpreted in terms of the intermediacy of the σ-allenyl species $[Mo\{\sigma\text{-}C(Me)=C=CH_2\}$-

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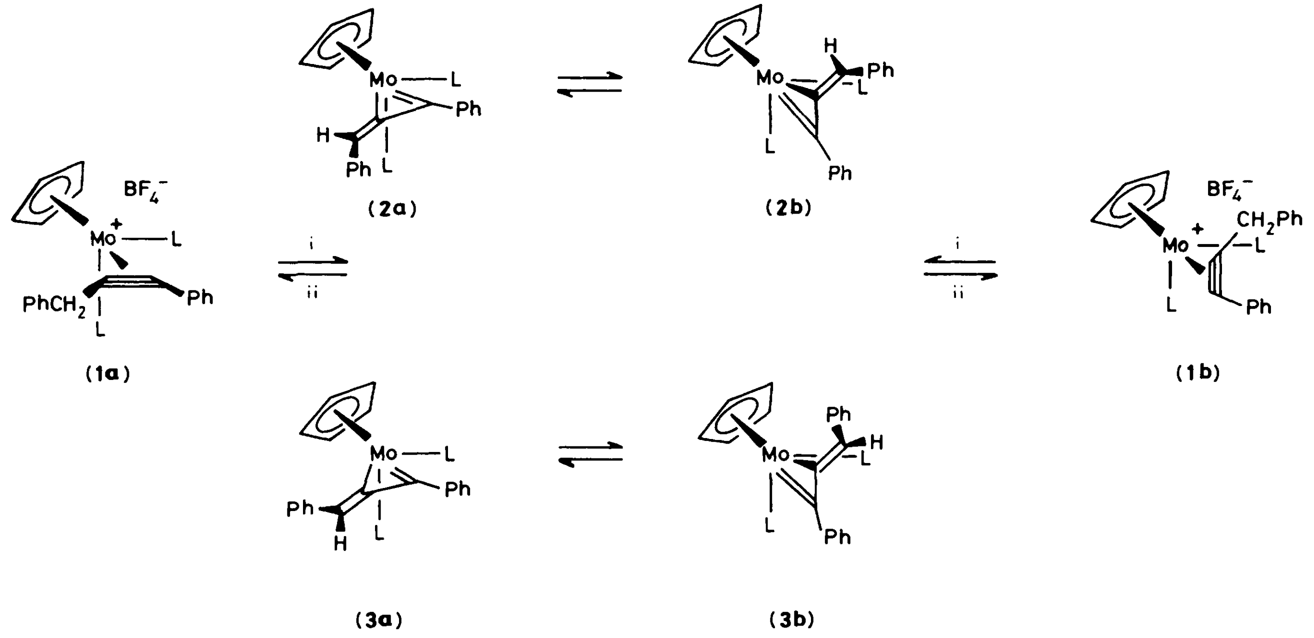
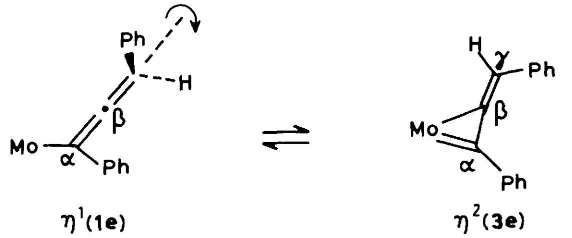


Scheme 1. L = P(OMe)_3; i, KH, Et_2O, Bu^{t}OH, $-\text{H}_2$; ii, $\text{HBF}_4\cdot\text{Et}_2\text{O}$.

$(\text{CO})(\eta^2\text{-MeC}_2\text{Me})(\eta\text{-C}_5\text{H}_5)]$, whereas it is suggested that deuteriation of the bis(trimethyl phosphite) complex (**1**) involves the reversible deprotonation of (**1**) to form the η^2(3e)-bonded allenyl complexes $[\overline{\text{Mo}\{=\text{C(Ph)}\text{C}}\text{=CHPh}\}\text{-}\{\text{P(OMe)}_3\}_2(\eta\text{-C}_5\text{H}_5)]$. This is supported by the observation that when a suspension of (**1**) in diethyl ether is treated (0.5 h, room temp.) with KH in the presence of a catalytic amount (5 µl in 10 ml Et_2O) of Bu^{t}OH, gas evolution occurs and a thermally and hydrolytically sensitive, neutral, purple complex is formed, which can be recrystallised (195 K) from pentane. This material was identified‡ as a mixture (7 : 3) of the two isomeric η^2(3e)-allenyl complexes (**2**) and (**3**) (Scheme 1), which differ with respect to the relative dispositions of the phenyl and hydrogen substituents on the γ-carbon. The presence of a molybdenum to carbon double bond is supported by the $^{13}\text{C-}\{^1\text{H}\}$ n.m.r. spectra. Thus, the spectrum of the major isomer shows triplet signals at δ 253.5 [J(CP) 11.0 Hz], 151.6 [J(CP) 17.6 Hz], and 109.0 [J(CP) 4.4 Hz], which are assigned to the C_α (alkylidene), C_β, and C_γ carbon atoms, respectively. The $^{31}\text{P-}\{^1\text{H}\}$ n.m.r. spectrum measured at 190 K shows the expected two (ratio 7 : 3) AB quartets; however, on warming to 199 K these coalesce, and at room temperature two sharp singlets (ratio 7 : 3) are observed [$\Delta G^\ddagger_{199}$ 40.0 ($\pm$0.5) kJ mol^{-1}]. These observations are consistent with the picture illustrated in Scheme 1. In solution the alkyne cation§ exists as a mixture of the two enantiomers (**1a**) and (**1b**), which can interconvert *via* a windscreen wiper motion. Deprotonation of a benzylic carbon–hydrogen bond can then afford either of the two isomers (**2**) and (**3**), the relative proportion depending on the direction of approach by the base and the barrier to rotation of the benzyl group. Each of the two isomers can then interconvert by a windscreen wiper motion into its mirror image, *i.e.* (**2a**) $\rightleftharpoons$ (**2b**) and (**3a**) $\rightleftharpoons$ (**3b**).



Scheme 2

As shown in Scheme 2, the η^2-allenyl fragment would be expected[2,4] to adopt an essentially planar geometry, since in

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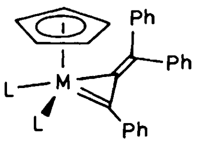
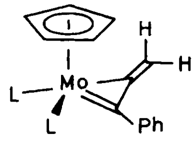
‡ *Selected spectroscopic data* for compound (**2**): n.m.r. $^1\text{H}(\text{C}_6\text{D}_6)$, δ 7.43—7.32, 7.20—7.02 (m, 10H, Ph), 6.55 (m, 1H, =C*H*Ph), 5.11 [t, 5H, C_5H_5, J(HP) 0.88 Hz], 3.38 [at, 18H, POMe, $|J(\text{HP}) + J(\text{HP}')|$ 11.38 Hz]; $^{13}\text{C-}\{^1\text{H}\}$ (C_6D_6), δ 253.5 [t, C_α, J(CP) 11.0 Hz], 151.6 [t, C_β, J(CP) 17.6 Hz], 148.3 (*ipso*-Ph), 143.4 (*ipso*-Ph), 128.5, 127.7, 126.5, 125.2 (Ph), 109.0 [t, C_γ, J(CP) 4.4 Hz], 92.4 (C_5H_5), 51.8 [P(O*Me*)$_3$]; $^{31}\text{P-}\{^1\text{H}\}(\text{C}_6\text{D}_5\text{CD}_3$, 190 K), δ 202.62 p.p.m. (br. AB system). Compound (**3**): n.m.r. ^1H (C_6D_6), δ 7.53—7.43 (m, 10H, Ph), 5.19 [t, 5H, C_5H_5, J(HP) 1.2 Hz], 5.15 (m, 1H, =C*H*Ph), 3.22 [at, 18H, POMe $|J(\text{HP}) + J(\text{HP}')|$ 11.7 Hz]: $^{31}\text{P-}\{^1\text{H}\}(\text{C}_6\text{D}_5\text{CD}_3$, 190 K), δ_A 198.77, δ_B 198.28 p.p.m. [AB system, J(PP′) 58.0 Hz]. Compound (**4**): n.m.r. $^1\text{H}(\text{CD}_2\text{Cl}_2)$, δ 7.9—7.8, 7.35—6.52 (m, 15H, Ph), 5.12 [t, 5H, C_5H_5, J(HP) 1.1 Hz], 3.47 [at, 18H, POMe, $|J(\text{HP}) + J(\text{HP}')|$ 10.94 Hz]; $^{13}\text{C-}\{^1\text{H}\}$ (C_6D_6), δ 245.02 [t, C_α, J(CP) 20.9 Hz], 147.85 [t, C_β, J(CP) 6.6 Hz], 130.05, 127.71, 127.22, 126.44, 124.38, 123.60, 123.01 (Ph), 91.44 (C_5H_5), 50.65 [P(O*Me*)$_3$]; $^{31}\text{P-}\{^1\text{H}\}(\text{C}_6\text{D}_6)$, δ 195.75 p.p.m. Compound (**5**): n.m.r. ^1H (C_6D_6), δ 8.42—6.56 (m, 35H, Ph), 4.76 [t, 5H, C_5H_5, J(HP) 0.89 Hz], 2.02 (m, 4H, CH_2); $^{31}\text{P-}\{^1\text{H}\}$ (C_6D_6), δ 62.56 p.p.m. Compound (**6**): n.m.r. ^1H (CD_2Cl_2), δ 7.75—7.16 (m, 5H, Ph), 6.06 (m, 1H, =C*H*H′), 5.18 [t, 5H, C_5H_5, J(HP) 0.88 Hz], 4.57 (m, 1H, =CH*H′*), 3.45 [at, 18H, POMe, $|J(\text{HP}) + J(\text{HP}')|$ 11.37 Hz]; $^{31}\text{P-}\{^1\text{H}\}$ (C_6D_6), δ 200.80 p.p.m. Compound (**7**): n.m.r. $^{31}\text{P-}\{^1\text{H}\}$ (C_6D_6), δ 157.19 p.p.m. [J(WP) 566.4 Hz]. ('at' = apparent triplet).

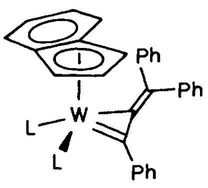
§ *X*-Ray crystallography[2] shows that in the solid state a conformation is adopted in which the C_2 axis of the co-ordinated alkyne lies parallel to an Mo–P vector, whereas, in solution, a windscreen wiper motion makes the two ^{31}P environments equivalent. If complete rotation (2π) of the alkyne could occur then four not two isomeric η^2-allenyl complexes would be observed.



[**4**, M = Mo,
L = $P(OMe)_3$]
(**5**, M = Mo,
L = $Ph_2PCH_2CH_2PPh_2$)



[**6**, L = $P(OMe)_3$]



[**7**, L = $P(OMe)_3$]

transforming an η^1(1e) allenyl group into an η^2(3e) bonding mode, the allenyl fragment must undergo a rotational movement to allow interaction of the C_α–C_β π system with the metal centre.

The ratio of the two isomers (**2**) and (**3**) is invariant in the temperature range 190—353 K indicating that in contrast with methylenecyclopropenes,[5] there is a relatively high barrier to rotation about the exocyclic double bond. It is also interesting that phosphite exchange [with $P(OCD_3)_3$] only occurs at elevated temperatures (4 h, 351 K).

The deprotonation reaction can be generalised; treatment of the appropriate cationic alkyne complexes with KH–Bu^{t}OH in Et_2O affording the η^2-allenyl complexes (**4**) (purple), (**5**) (red-purple), (**6**) (green-yellow), and (**7**) (blue-black). Each of these species, which are air- and moisture-sensitive, showed n.m.r. spectra‡ characteristic of an η^2-allenyl complex.

All these η^2-allenyl complexes react with $HBF_4{\cdot}Et_2O$ in CH_2Cl_2 to reform the parent alkyne cations by selective protonation of the γ-carbon atom. The electrophilic reagent CF_3SO_3Me also reacts with, for example, the isomeric η^2-allenyl complexes (**2**) and (**3**), and (**6**) to form the alkyne cations $[Mo\{\eta^2\text{-}PhC_2CH(Me)Ph\}\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][CF_3SO_3]$ (**8**), and $[Mo(\eta^2\text{-}PhC_2Et)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][CF_3SO_3]$ (**9**), respectively, the former containing a chiral carbon centre. In view of the isolobal relationship[6] $CH \xleftrightarrow[0]{} MoL_2(\eta\text{-}C_5H_5)$, it is interesting to relate these reactions with electrophiles to the observation[5] that protonation of methylenecyclopropenes gives cyclopropenium cations.

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