The Mechanism of Protonation of Carbyne Complexes; *X*-Ray Crystal Structures of $[HMo(CCH_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$ and $[Mo(CF_3CO_2)(CF_3CO_2H)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$

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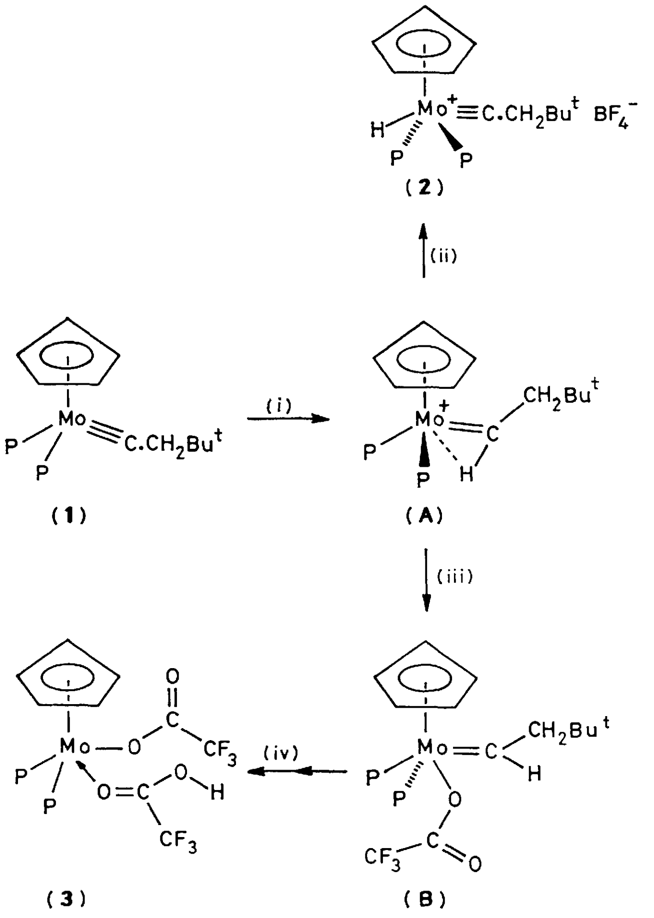
The carbyne hydride complex $[HMo(CCH_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$, structurally identified by *X*-ray crystallography, is formed on protonation of $[Mo(CCH_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ with HBF_4, whereas with CF_3CO_2H loss of the carbyne fragment occurs to give $[Mo(OCOCF_3)(CF_3CO_2H)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$, suggesting kinetic, charge-controlled attack by a proton on carbon.

A recent theoretical study[1] of the carbyne (alkylidyne) complexes $[Mn(CR)(CO)_2(\eta\text{-}C_5H_5)]^+$ indicates that there is a build-up of charge on the carbyne carbon. This study led to the important suggestion that the formation of carbene complexes by nucleophilic attack on carbynes[2] is frontier[3] orbital controlled. We have confirmed that similar charge separation pertains for the isolectronic carbyne complexes $[Mo(CCH_2Bu^t)\{P(OR)_3\}_2(\eta\text{-}C_5H_5)]$ by extended Hückel M.O. calculations[4] (net charges on Mo and carbyne carbon are $+0.93$ and -0.34 e respectively). Recently the protonation of neutral carbynes has raised the fundamental question as to whether these electrophilic reactions are frontier or charge controlled;



Scheme 1. P = $P(OMe)_3$; (i) H^+, (ii) BF_4^-, (iii) $CF_3CO_2^-$, (iv) CF_3CO_2H.

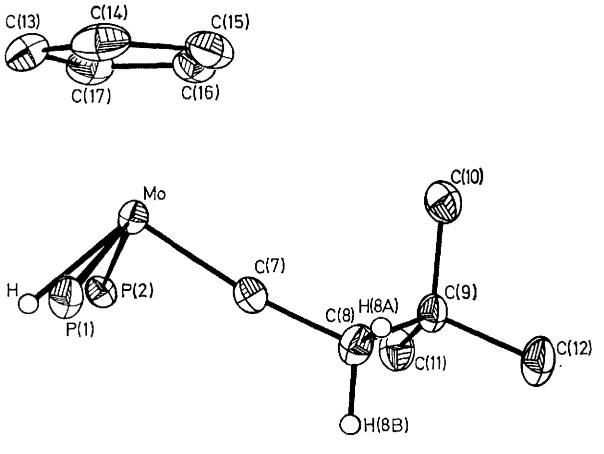


Figure 1. Molecular structure of (2) $[HMo(CCH_2Bu^t)\{P(OMe)_3\}_2(\eta$-$C_5H_5)][BF_4]$ with methoxy groups, methyl and cyclopentadienyl hydrogen atoms omitted for clarity. Important geometrical parameters: Mo–H 1.74(3), Mo≡C 1.798(2), mean Mo–P 2.390 Å (individual e.s.d. 0.001 Å); angles, mean P–Mo–H 62.6, mean P–Mo–C 88.8, (individual e.s.d. <0.07°), H–Mo–C 106.0(8), P–Mo–P 121.9(1)°.

frontier control might be expected to lead to attack on the metal (since the HOMO is localised largely on the metal[1]) and charge control to reaction at carbon.

Protonation of the carbyne complex (**1**) $[Mo(CCH_2Bu^t)\{P(OMe)_3\}_2(\eta$-$C_5H_5)]$ with HBF_4 affords[5] an apparent hydrido-carbyne complex (**2**) $[HMo(CCH_2Bu^t)\{P(OMe)_3\}_2(\eta$-$C_5H_5)][BF_4]$. In contrast $[W(CH)L_4Cl]$ reacts with CF_3SO_3H to give $[W(CH_2)L_4Cl][CF_3SO_3]$ when L = PMe_3, but $[HW(CH)L_4Cl][CF_3SO_3]$ when L_2 = $Me_2PCH_2CH_2PMe_2$.[6] In group 8 $[Os(CPh)(CO)(PPh_3)_2Cl]$ reacts with HCl to give $[Os(CHPh)(CO)(PPh_3)_2Cl_2]$.[7] Thus, protonation seems to be able to occur at either carbon or the metal. In this paper we report a detailed study of the protonation of (**1**), which suggests that it occurs initially at the carbon.

The structure originally suggested[5] for the protonation product of (**1**) was based on n.m.r. parameters; however, the data did not exclude an alternative structure in which the proton was attached to the carbyne carbon but was interacting with a 16 e molybdenum centre. Since there were no structurally authenticated hydrido-carbyne complexes a single-crystal *X*-ray diffraction study of (**2**) was undertaken.[†] The structure shown in Figure 1 confirms the presence of a metal-bound hydride ligand and was solved by heavy atom (Patterson and Fourier) methods and refined using blocked cascade full-matrix least-squares.[‡] For 4609 unique, absorption-corrected, observed data $[I > 2\sigma(I)]$, measured at 200 K on a Nicolet P3m diffractometer in the range $3° < 2\theta < 50°$, the current residual *R* is 0.022.[§] All non-hydrogen atoms were refined anisotropically, and all hydrogens were located in difference maps and refined isotropically, those in methyl and cyclopentadienyl groups being constrained to idealised geometries.

The geometry about the molybdenum atom in (**2**) is that of a four-legged piano-stool where P–Mo–P = 121.9(1), P–Mo–C_α = 88.8 (average), and H–Mo–C_α = 106.0(8)°. The Mo–H distance of 1.74(3) Å is close to the neutron diffraction-determined value of 1.685(3) Å for the terminal Mo–H bond length in $[MoH_2(\eta$-$C_5H_5)_2]$.[8] The mean Mo–P distance of 2.390 Å is longer than that observed[9] in the parent carbyne complex (**1**) (2.329 Å), reflecting the formal incease in Mo oxidation state; however, it is interesting to note that the Mo≡C_α bond distance in (**2**) of 1.798(2) Å is identical to that in (**1**).[9]

In contrast the reaction of (**1**) with CF_3CO_2H at −20 °C leads to protolytic cleavage of the carbyne fragment from the metal, a type of reaction not previously observed. The product of this reaction, red crystalline (**3**) $[Mo(OCOCF_3)(CF_3CO_2H)\{P(OMe)_3\}_2(\eta$-$C_5H_5)]$, was structurally formulated on the basis of an *X*-ray diffraction study[¶] (Figure 2). Data collection, structure solution, and refinement procedures were as for (**2**), excepting that the minor (32%) component of the disordered CF_3CO_2 moiety was refined isotropically and the acidic hydrogen {^{1}H n.m.r. ($C_6D_5CD_3$), δ 7.66 [t, 1 H, *J*(PH) 78 Hz]} was not directly located. Current residual *R* is 0.075. The co-ordination around molybdenum is again of the four-legged piano-stool type although with phosphite ligands

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[†] *Crystal Data:* (**2**), $C_{17}H_{35}BF_4MoO_6P_2$, *M* = 579.9, monoclinic, space group $P2_1/n$, *a* = 9.440(2), *b* = 15.012(5), *c* = 18.135(6) Å, β = 103.97(2)°, *U* = 2494(1) Å^3, *Z* = 4, D_c = 1.54 g cm^{-3}, *F*(000) = 1192 electrons, μ(Mo-K_α) = 6.96 cm^{-1}, Mo-K_α *X*-radiation, λ = 0.710 69 Å.

[‡] All crystallographic calculations were carried out with the SHELXTL program package on a Nicolet R3m structure determination system.

[§] Atomic co-ordinates are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[¶] *Crystal Data:* (**3**), $C_{15}H_{24}F_6MoO_{10}P_2$, *M* = 636.2, monoclinic, space group $P2_1/c$, *a* = 8.496(5), *b* = 13.911(9), *c* = 19.527(13) Å, β = 90.13(5)°, *U* = 2308(3) Å^3, *Z* = 4, D_c = 1.51 g cm^{-3}, *F*(000) = 1280 electrons, μ(Mo-K_α) = 7.78 cm^{-1}, Mo-K_α *X*-radiation, λ = 0.710 69 Å.

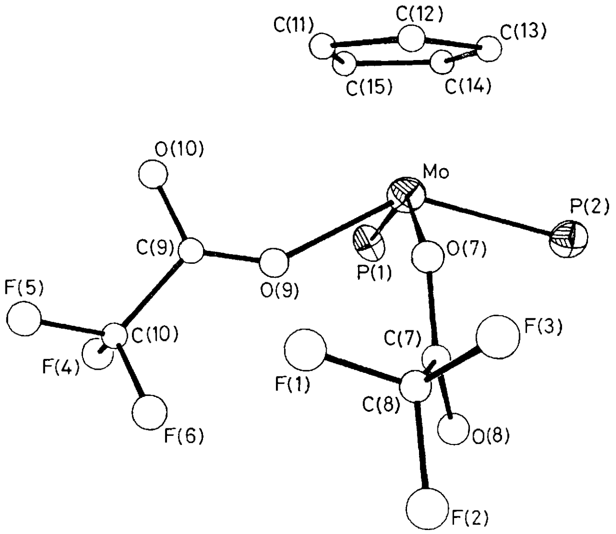

Figure 2. Molecular structure of (3) [Mo(OCOCF$_3$)(CF$_3$CO$_2$H)-{P(OMe)$_3$}$_2$(η-C$_5$H$_5$)] with methoxy groups and hydrogens omitted, showing the major (68%) orientation of atoms O(9), O(10), C(9), F(5), and F(6). Important geometrical parameters: Mo–P(1) 2.403(3), Mo–P(2) 2.413(3), Mo–O(7) 2.157(8), Mo–O(9) 2.109(12), C(7)–O(7) 1.280(15), C(7)–O(8) 1.175(18), C(9)–O(9) 1.13(2), C(9)–O(10) 1.22(3) Å.

cisoid here, P–Mo–P 89.0(1), P–Mo–O(*cisoid*) 83.5 (average), P–Mo–O(*transoid*) 140.0 (average), and O–Mo–O 78.2° (average). The geometry of the disordered CF$_3$CO$_2$ group suggests that the acidic hydrogen is associated with its unco-ordinated oxygen atom in the solid state. This indicates that protolysis has occurred at the carbyne carbon since treatment of (2) with CF$_3$CO$_2^-$/CF$_3$CO$_2$H does not result in the formation of (3).

These observations are consistent with protonation of (**1**) by HBF$_4$ and CF$_3$CO$_2$H both proceeding *via* initial kinetic attack on the carbyne resulting in an intermediate 16 e carbene complex (A) (Scheme 1). In the absence of a co-ordinating anion intermediate (A) undergoes an α-elimination reaction[6] leading to the thermodynamically controlled product, the hydridocarbyne complex (**2**). In the case of the CF$_3$CO$_2$H reaction, the trifluoroacetate anion attacks the molybdenum forming the neutral molybdenum oxygen bound species (**B**), which can give (**3**) *via* further protolysis of the carbene (alkylidene) carbon atom followed by elimination of the six-carbon fragment (the nature of the hydrocarbon eliminated, presumably either 3,3-dimethylbut-1-ene or 2,2-dimethylbutane, is under investigation). Thus, it is suggested that the reaction of the carbyne (**1**) with a proton is a *charge controlled* reaction with initial attack on the carbyne carbon.

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