

Mechanism of Protonation of Side-on Bonded Vinylidene Complexes; Structural Evidence for the Formation of a Cationic Di-molybdenum Complex containing an Asymmetrically Bridged Allyl Ligand

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α -Protonation of side-on bonded vinylidenes is indicated by the observations that reaction of $\text{CF}_3\text{CO}_2\text{D}$ with $[\text{Mo}_2\{\mu\text{-}\sigma,\eta^2(4e)\text{C}=\text{CH}_2\}(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ affords $[\text{Mo}_2\{\sigma\text{-OC(O)CF}_3\}(\eta\text{-CD}=\text{CH}_2)(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$, whereas, $\text{CF}_3\text{CO}_2\text{H}$ and $[\text{Mo}_2\{\mu\text{-}\sigma,\eta^2(4e)\text{C}=\text{CD}_2\}(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ gives $[\text{Mo}_2\{\sigma\text{-OC(O)CF}_3\}(\mu\text{-CH}=\text{CD}_2)(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$; in contrast, reaction of $\text{HBF}_4\cdot\text{Et}_2\text{O}$ with $[\text{Mo}_2\{\mu\text{-}\sigma,\eta^2(4e)\text{C}=\text{CMe}_2\}(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ leads to loss of CO and formation of the Mo_2 triple bonded cation $[\text{Mo}_2(\mu\text{-}\eta^3\text{-2-MeC}_3\text{H}_4)(\text{CO})_3(\eta\text{-C}_5\text{H}_5)_2][\text{BF}_4]$, an asymmetrically bridged allyl complex which is also formed on protonation of $[\text{Mo}_2\{\mu\text{-}\sigma:\eta^3\text{-CHC(Me)CH}_2\}(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$.

It has been suggested¹⁻³ that surface bound vinylidenes might have a role in the Fischer-Tropsch reaction, and this has focused attention on the development of the chemistry of vinylidene ligands⁴ co-ordinated onto mono-, di-, and trinuclear centres. Recently,^{5,6} the side-on bonding mode, *i.e.*, $\mu\text{-}\sigma,\eta^2(4e)$, has been recognised for dinuclear vinylidene complexes and clearly it is important to understand and compare the reactivity of such species with that of conventional upright $[\mu\text{-}\sigma,\sigma(2e)]$ bonded vinylidenes.⁷ In establishing the regioselectivity of protonation reactions we have obtained structural evidence for the formation of an unusually bonded bridged allyl system.

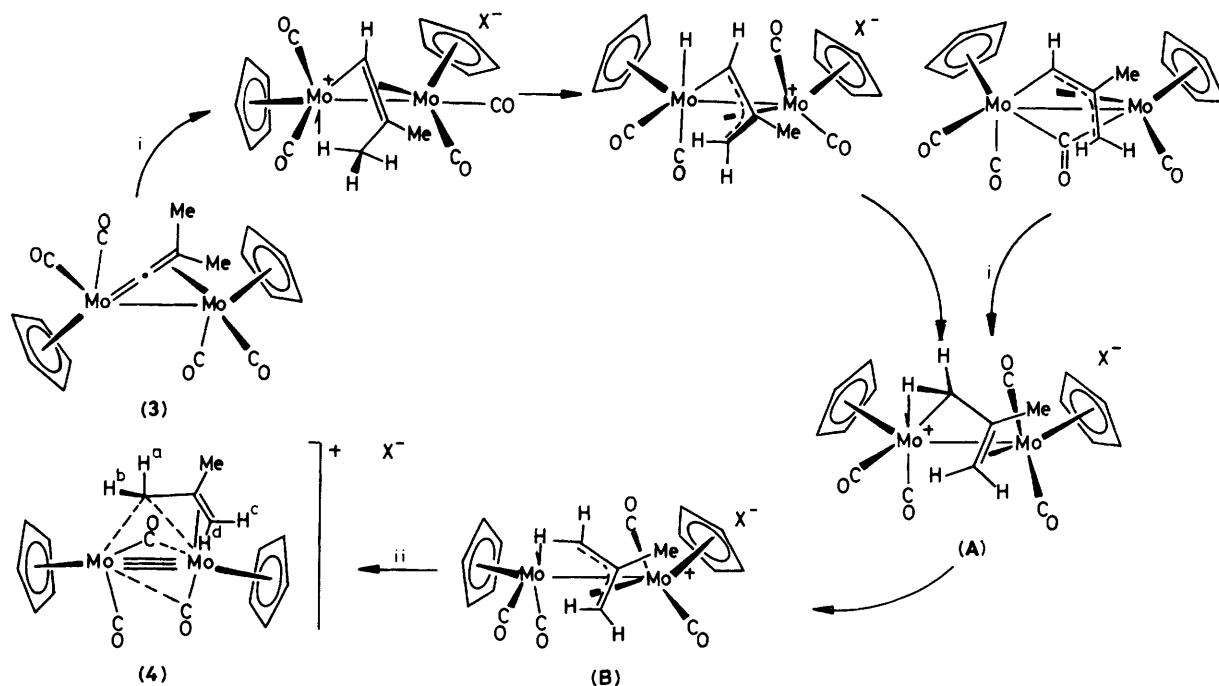
Protonation (-78°C , toluene) of $[\text{Mo}_2\{\mu\text{-}\sigma,\eta^2(4e)\text{C}=\text{CH}_2\}(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ ⁶ (**1**) with trifluoroacetic acid afforded† bright red crystals of the bridged vinyl complex $[\text{Mo}_2\{\sigma\text{-OC(O)CF}_3\}(\mu\text{-CH}=\text{CH}_2)(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ (**2**). This reaction can be explained if a proton is delivered either directly or indirectly‡ to the α or carbenoid carbon of (**1**) followed by capture of the resulting unsaturated μ -vinyl cation with trifluoroacetate anion. There is, however, an alternative pathway from (**1**) to (**2**), which is suggested by recent studies with μ -carbyne Fe_2 ⁸ and Os_3 ⁹ complexes. This involves delivery of a proton to the β -carbon of the $\mu\text{-}\sigma,\eta^2(4e)\text{-C}=\text{CH}_2$ fragment of (**1**) resulting in the formation of a cationic bridged μ -carbyne complex $[\text{Mo}_2(\mu\text{-CCH}_3)(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2][\text{CF}_3\text{CO}_2]$, which then undergoes a 1,2-hydrogen shift from

the methyl carbon to the electron deficient carbyne carbon thus generating the μ -vinyl ligand. We have distinguished between these two pathways by deuterium labelling experiments. Protonation (-78°C , toluene) of (**1**) with $\text{CF}_3\text{CO}_2\text{D}$ afforded $[\text{Mo}_2\{\sigma\text{-OC(O)CF}_3\}(\mu\text{-CD}=\text{CH}_2)(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$.§ Secondly, reaction of $\text{CF}_3\text{CO}_2\text{H}$ with $[\text{Mo}_2\{\mu\text{-}\sigma,\eta^2(4e)\text{C}=\text{CD}_2\}(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$, which was synthesised by deprotonation⁶ [-78°C , Bu^nLi , tetrahydrofuran (thf)] of $[\text{Mo}_2(\mu\text{-DC}_2\text{D})(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ followed by quenching (-78°C) with $\text{CF}_3\text{CO}_2\text{D}$, gave $[\text{Mo}_2\{\sigma\text{-OC(O)CF}_3\}$ -

§ Selected spectroscopic data for compound (**1**): n.m.r. ^1H (CDCl_3), δ 5.44 (s, 5H, C_5H_5), 5.30 (s, 5H, C_5H_5), 3.44 [d, 1H, =CHH, J (HH) 14.2 Hz], 2.83 [d, 1H, =CHH, 14.2 Hz]; ^{13}C - $\{^1\text{H}\}$ (CDCl_3), δ 329.5 (Mo=C), 241.8, 231.6, 231.0, 230.3 (CO), 94.6 (C_5H_5), 93.0 (C_5H_5), 40.0 (Mo=C=CH₂); ν_{CO} (hexane) 1976w, 1928s, 1905m, 1868w cm^{-1} . Compound (**2-D**): n.m.r. ^1H (CDCl_3), δ 9.05 (dd, $\text{CH}=\text{CH}_2$, J (H,H) 12, J (H,H) 8 Hz, 10%), 5.32 (s, 5H, C_5H_5), 5.16 (s, 5H, C_5H_5), 4.00 (bs, 1H, $\text{CD}=\text{CH}_2$), 3.30 (bs, 1H, $\text{CD}=\text{CH}_2$); ^2D (CH_2Cl_2), δ 9.05 p.p.m. (bs, 1D, $\text{CD}=\text{CH}_2$). Compound (**2-D**): n.m.r. ^1H (CDCl_3), δ 9.05 (bs, 1H, $\text{CH}=\text{CD}_2$), 5.32 (s, 5H, C_5H_5), 5.16 (s, 5H, C_5H_5), 4.00 [d, $\text{CH}=\text{CH}_2$, residual proton <5%, J (HH) 12 Hz], 3.30 [d, $\text{CH}=\text{CH}_2$, residual proton <5%, J (HH) 8 Hz]. Compound (**4**): n.m.r. ^1H (CD_2Cl_2 , room temperature), δ 5.66 (s, 5H, C_5H_5), 5.41 (s, 5H, C_5H_5), 3.05 (br. s, 2H), 2.56 (s, 3H, Me), 1.95 (br. s, 2H); ^1H (CD_2Cl_2 , -60°C), δ 5.72 (s, 5H, C_5H_5), 5.47 (s, 5H, C_5H_5), 3.59 [d, 1H, H^a, J (H^aH^c) 3.3 Hz] 2.56 (s, 3H, Me), 2.43 [dd, 1H, H^c, J (H^aH^c) 3.3, J (H^bH^d) 1.9 Hz], 2.36 [d, 1H, H^d, J (H^aH^c) 1.9 Hz], 1.53 (s, 1H, H^b); ^{13}C - $\{^1\text{H}\}$ (CD_2Cl_2 , -60°C), δ 233.4 (CO), 228.8 (CO), 228.1 (CO), 111.5 [$\text{CH}_2\text{C}(\text{Me})\text{CH}$], 98.5 (C_5H_5), 95.3 (C_5H_5), 43.1 [at, CH_2 , J (CH) 160 Hz], 25.0 [at, CH_2 , J (CH) 150 Hz], 29.6 [Me, J (CH) 130 Hz]; ν_{CO} (CH_2Cl_2) 1999w, 1938m, 1920 sh cm^{-1} . Compound (**5**): n.m.r. ^1H (CDCl_2 , -40°C), δ 7.61–7.40 (m, 5H, Ph), 5.78 (s, 5H, C_5H_5), 5.07 (s, 5H, C_5H_5), 4.12 [d, 1H, H^a, J (H^aH^c) 3.9 Hz], 2.85 [dd, 1H, H^c, J (H^cH^a) 3.9, J (H^cH^d) 2.8 Hz], 2.37 [d, 1H, H^d, J (H^aH^c) 2.8 Hz], 1.83 (s, 1H, H^b).

† A similar reaction has been reported (ref. 5) between $[\text{Mo}_2\{\mu\text{-}\sigma,\eta^2(4e)\text{C}=\text{CH}_2\}(\text{CO})_4(\eta\text{-C}_5\text{Me}_5)_2]$ and $\text{CF}_3\text{CO}_2\text{H}$.

‡ Protonation of the molybdenum atom which carries the μ -vinylidene, *i.e.* $\text{Mo}=\text{C}=\text{CH}_2$, followed by migratory insertion of the hydrogen onto the α -carbon would also lead to the same regioselectivity. It is planned to carry out calculations which should help to distinguish between these two paths.



Scheme 1. X = BF₄⁻ or CF₃SO₃⁻; i, HBF₄·Et₂O, or CF₃SO₃H; ii, -CO.

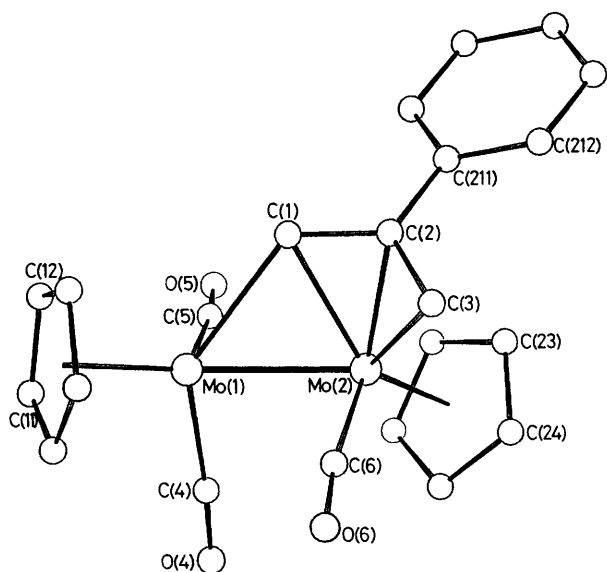


Figure 1. The structure of the novel asymmetrically bridging allyl complex [Mo₂{μ-σ:η³-CH₂C(Ph)CH₂}(CO)₃(η⁵-C₅H₅)₂][CF₃SO₃]⁺ (5). Principal bond lengths (Å) and angles (°): Mo(1)-Mo(2) 2.561(2), Mo(1)-C(1) 2.462(18), Mo(1)-C(4) 1.975(19), Mo(1)-C(5) 2.016(18), Mo(1)-C(6) 2.692(20), Mo(2)-C(1) 2.364(18), Mo(2)-C(2) 2.197(17), Mo(2)-C(3) 2.317(16), Mo(2)-C(6) 1.937(20), C(1)-C(2) 1.450(23), C(2)-C(3) 1.455(25), C(2)-C(211) 1.478(20); C(1)-Mo(1)-Mo(2) 56.1(4), C(1)-Mo(2)-Mo(1) 59.8(4), C(2)-Mo(2)-Mo(1) 96.1(4), C(2)-Mo(2)-C(1) 36.8(6), C(3)-Mo(2)-Mo(1) 107.8(4), C(3)-Mo(2)-C(1) 63.5(6), C(3)-Mo(2)-C(2) 37.5(6), C(3)-Mo(2)-C(1) 63.5(6), C(3)-Mo(2)-C(2) 37.5(6), Mo(2)-C(1)-Mo(1) 64.1(5), C(2)-C(1)-Mo(1) 128(1), C(2)-C(1)-Mo(2) 65.3(9), C(1)-C(2)-Mo(2) 78(1), C(3)-C(2)-Mo(2) 76(1), C(3)-C(2)-C(1) 116(1), C(2)-C(3)-Mo(2) 66.8(9).

(μ-CH=CD₂)(CO)₄(η-C₅H₅)₂] there being no evidence for deuterium leakage onto the α-carbon of the vinyl ligand. Thus, these observations strongly support the former mechanism, *i.e.*, α-protonation.

Additional insight into the reaction paths available in the protonation reaction came from a study of the related reactions of β,β'-disubstituted vinylidenes such as [Mo₂{μ-σ,η²(4e)C=CMe₂}(CO)₄(η-C₅H₅)₂]¹⁰ (3), which when protonated with CF₃CO₂H undergoes an analogous reaction leading to the formation of [Mo₂{σ-OC(O)CF₃}(μ-CH=CMe₂)(CO)₄(η-C₅H₅)₂]. However, protonation of (3) with HBF₄·Et₂O did not afford a stable μ-vinyl complex. Instead the ¹H and ¹³C-{¹H} n.m.r. spectra[†] of the cationic product (4) showed the presence of only one methyl group and three terminal carbonyl ligands. Interestingly, the same cation was obtained on protonation[‡] (HBF₄·Et₂O or CF₃SO₃H) of the μ-allylidene complex [Mo₂{μ-σ:η³-CH·C(Me)CH₂}(CO)₄(η-C₅H₅)₂] formed on thermolysis⁶ (70 °C, hexane, 4 h) of [Mo₂{μ-σ,η²(4e)C=CMe₂}(CO)₄(η-C₅H₅)₂]. An insight into the structural identity of (4) was gained from an X-ray diffraction study^{||} of the related cation (5), which was prepared by reaction (-78 °C, CH₂Cl₂) of CF₃SO₃H with [Mo₂{μ-σ:η³-CHC(Ph)CH₂}(CO)₄(η-C₅H₅)₂].⁶

[†] Addition (-78 °C) of K[BHBU₃] to a tetrahydrofuran (thf) suspension of (4) results in a deprotonation/disproportionation reaction and formation (30%) of [Mo₂{μ-σ:η³-CH·C(Me)CH₂}(CO)₄(η-C₅H₅)₂].

^{||} Recently a complex has been reported in which an η³-allyl group bonded to Mo is involved in an agostic interaction to a Mn atom. C. M. Hay, A. D. Horton, M. J. Mays, and P. R. Raithby, *Polyhedron*, 1988, 7, 897.

The structure** of the protonated product (5) is shown in Figure 1. The metal-metal bond length of 2.561(2) Å is comparable to that found for other formally triply bonded dimolybdenum structures.¹¹ This compound is the first structurally characterised cationic species with a μ -allyl ligand, which adopts a markedly different bridging role to that usually observed where the central C-atom bonds symmetrically to both metal atoms.¹² In (5), the unusual bonding may be envisaged as η^2 -co-ordination to Mo(2) only [Mo(2)-C(2) 2.197(17) and Mo(2)-C(3) 2.317(16) Å], and a 3c-2e interaction between the α -carbon and both metal atoms [Mo(1)-C(1) 2.462(18) and Mo(2)-C(1) 2.364(18) Å]. This type of three centred bonding is rare for alkyl ligands,^{13,14} and has not been previously observed for an allyl group. Variable temperature n.m.r. studies§ show that in solution there is a dynamic process which on the n.m.r. time scale equilibrates the two ends of the allyl ligand, *i.e.*, $H^a \rightleftharpoons H^c$, $H^b \rightleftharpoons H^d$.

It is reasonable to suggest that the formation of (4) involves α -protonation of the μ - $\sigma, \eta^2(4e)$ bonded vinylidene to form a co-ordinatively unsaturated vinyl species. Unlike the reaction with CF_3CO_2H , an agostic Mo(μ -H)C interaction with one of the β -methyl groups intervenes when the counteranion is BF_4^- . This sets things up for transfer, *via* the metal, of a hydrogen from one end of the C_3 chain to the other (see Scheme 1), thus allowing formation of the cation (A). This same cation is apparently accessed by α -protonation of the μ -allylidene complex $[Mo_2\{\mu-\sigma:\eta^3-CHC(Me)CH_2\}(CO)_4(\eta-C_5H_5)_2]$. This latter reaction relates to the formation¹⁵ of $[Mo_2(\mu-C_8Me_8)(\mu_{Mo,C}-H)(\eta-C_5H_5)_2][BF_4]$ from the bis- μ -allylidene complex $[Mo_2(\mu-C_8Me_8)(\eta-C_5H_5)_2]$. However, in the carbonyl substituted system the reaction does not stop at either (A) or (B)|| (Scheme 1), instead carbon monoxide is lost and stability is achieved by formation of a metal-metal multiple bond. Examination of the i.r., ¹H and ¹³C n.m.r. spectra§ of (4) and (5) showed that there was no evidence for

an agostic Mo(μ -H)C interaction.¹⁶ This leads to the important conclusion that although in mononuclear systems unsaturation at a metal centre frequently leads to stabilisation by an agostic M(μ -H)C interaction, in dinuclear and perhaps in polynuclear systems alternative modes of achieving stability may over-ride M(μ -H)C interactions.

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** Crystal data for (5): $C_{23}H_{19}Mo_2O_6S$, $M = 672.25$, orthorhombic, space group $Pbca$, $a = 20.665(4)$, $b = 20.274(4)$, $c = 11.446(2)$ Å, $U = 4795.44$ Å³, $Z = 8$, $D_c = 1.86$ g cm⁻³, $F(000) = 2656$, $\mu(Mo-K\alpha) = 10.70$ cm⁻¹. Data were collected on a Philips PW 1100 diffractometer in the θ -range 3–25°, with a scan width of 0.70°. Equivalent reflections were merged to give 1757 absorption corrected data with $I/\sigma(I) > 3.0$. $R = 0.0619$ and $R_w = 0.0582$ with weights of $w = 1/\sigma^2 F_o$ assigned to the individual reflections.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.