Synthesis and Reactivity of η^3-Butadienyl Molybdenum Complexes formed by Deprotonation or Desilylation of 1,3-Diene Cations; Structure of $[Mo(CO)_2(\eta^3\text{-}CH_2 \overset{\cdots}{-} CH \overset{\cdots}{-} C{=}CH_2)(\eta\text{-}C_5Me_5)]$

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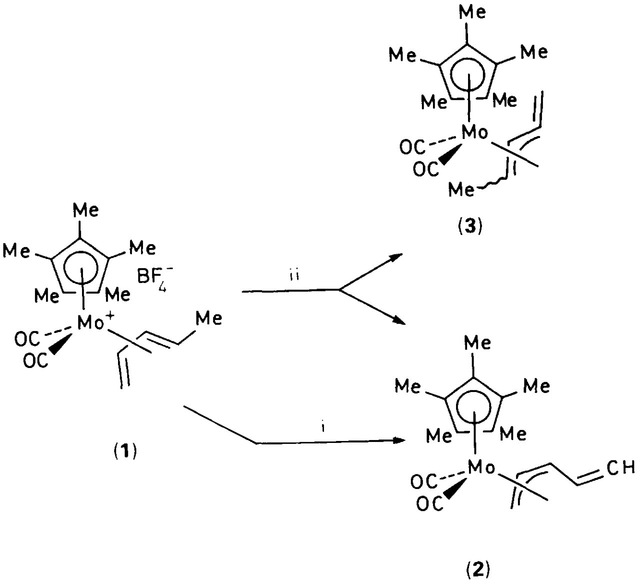
Reaction of $[Mo(CO)_2(\eta^4\text{-}CH_2{=}CH{-}CH{=}CH_2)(\eta\text{-}C_5Me_5)][BF_4]$ (**4**) with $Li[N(SiMe_3)_2]$ in tetrahydrofuran (THF) at −78 °C results in an unusual deprotonation reaction affording, in low yield, the novel η^3-butadienyl complex $[Mo(CO)_2(\eta^3\text{-}CH_2 \overset{\cdots}{-} CH \overset{\cdots}{-} C{=}CH_2)(\eta\text{-}C_5Me_5)]$ (**5**), which has been characterised by *X*-ray crystallography; the fluoride anion-induced desilylation of $[Mo(CO)_2(\eta^4\text{-}CH_2{=}CH{-}C{-}\{SiEt_3\}{=}CH_2)(\eta\text{-}C_5Me_5)][BF_4]$ (**6**), using Bu_4NF affords (**5**) in quantitative yield, facilitating a rational strategy for the synthesis of these complexes, which on protonation access cationic species containing η^3-vinylcarbene ligands.

As part of an ongoing investigation into the chemistry of functionalised π-allyl complexes, we have recently described the conversion of η^3-pentadienyl complexes into cationic η^4-diene species upon treatment with strong acids.[1] Thus addition of CF_3SO_3H to *exo-anti*-$[Mo(CO)_2(\eta^3\text{-}CH_2 \overset{\cdots}{-} CH \overset{\cdots}{-} CHCH{=}CH_2)(\eta\text{-}C_5Me_5)]$ (**2**) generates $[Mo(CO)_2(\eta^4\text{-}trans\text{-}CH_2{=}CH{-}CH{=}CHMe)(\eta\text{-}C_5Me_5)][CF_3SO_3]$ (**1**) in quantitative yield. We now report details of the reverse reaction, in which an unexpected deprotonation reaction was observed upon treatment with strong base.

Addition of Et_3N to a CH_2Cl_2 solution of (**1**) resulted in the slow regeneration of (**2**) as the sole product. Substitution of the more powerful reagent $Li[N(SiMe_3)_2]$, however, gave after chromatographic work up a bright yellow solid shown by ^1H and ^{13}C NMR to be a 1 : 1 mixture of (**2**) and a second species (**3**). A tentative characterisation of (**3**) as a η^3-butadienyl derivative[2] (Scheme 1) led us to investigate the deprotonation of the corresponding butadiene complex $[Mo(CO)_2(\eta^4\text{-}CH_2{=}CH{-}CH{=}CH_2)(\eta\text{-}C_5Me_5)][BF_4]$ (**4**) under these conditions. This gave a mixture of products from which a slightly air-sensitive yellow crystalline solid (**5**) (Scheme 2) could be isolated in *ca.* 25% yield. The ^1H NMR spectrum of (**5**) (CD_2Cl_2)† showed signals at δ 2.60, 2.37, and 1.46 with a characteristic $CH_2{=}CH$ connectivity pattern. A pair of low-field doublets at δ 6.09 and 5.20 confirmed the presence of a separate vinylic CH_2 centre, similarly visible in the ^{13}C spectrum (δ = 102.6). The observation in the latter of a quarternary carbon resonance at δ 174.8 provided additional evidence for the proposed structure, and a single-crystal *X*-ray diffraction study was undertaken. The solid-state structure of (**5**)‡ shows clearly the presence of a transoid η^3-butadienyl ligand in an *exo* orientation with respect to the C_5Me_5 ring. The interatomic distances for C(6)–C(7), C(7)–C(8), and C(8)–C(9) of 1.35, 1.39, and 1.35 Å, respectively, demonstrate a delocalisation of electron density throughout the ligand, as anticipated. Both these, and the Mo–C distances for the butadienyl ligand compare closely with values obtained for other substituted complexes containing this type of ligand.[2] It should be noted that by analogy with the relationship between allyl halides and π-allyl complexes, (**5**) is formally derived from the allenyl halide $CH_2{=}C{=}CHCH_2X$, and as such may be viewed as an η^3-π-allenyl complex. The corresponding reaction with the indenyl analogue of (**4**) did not yield an η^3-butadienyl species, and it was thought that a mechanism for the formation of (**5**) might involve the initial abstraction of a



Scheme 1. *Reagents and conditions*: i, Et_3N, CH_2Cl_2; ii, $Li[N(SiMe_3)_2]$, THF, −78 °C.

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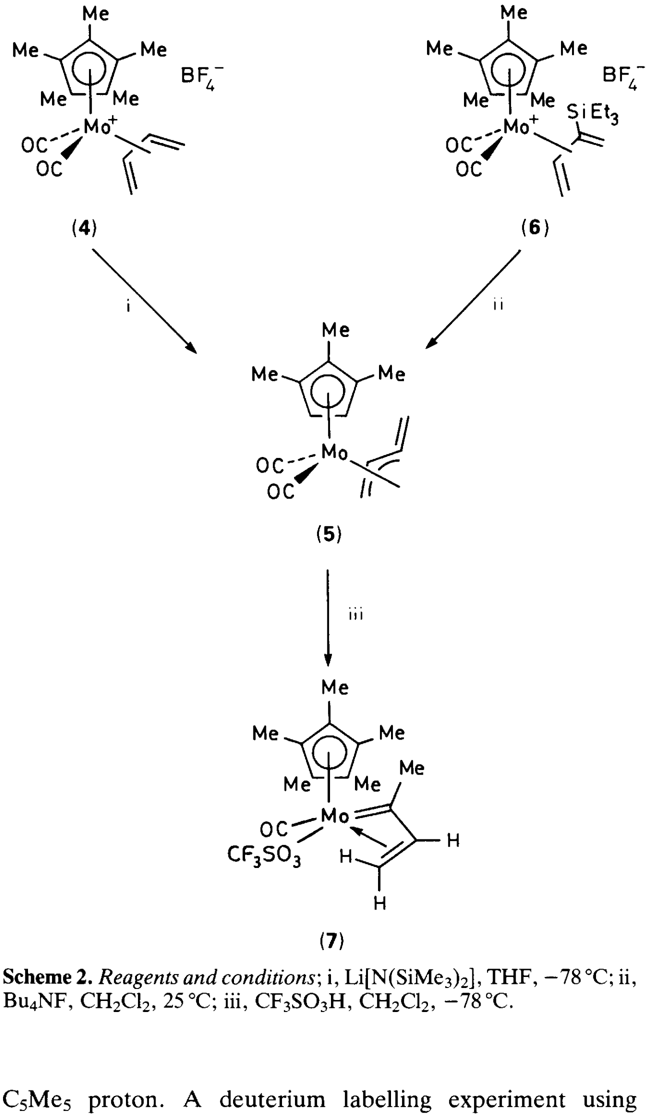
† *Selected spectroscopic data* (coupling constants are in Hz): (**3**) IR (CH_2Cl_2) ν_{CO} 1934, 1854 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 6.07 (d, 1H, *J* 2.2, $=CH_2$), 5.16 (d, 1H, *J* 2.2, $=CH_2$), 2.76 [dt, 1H, *J* 2.3 (t), 9.7, CH], 2.22 [dq, 1H, *J* 6.2 (q), 9.7, C*H*Me], 1.88 (s, 15H, C_5Me_5), and 1.73 (d, 3H, J 6.1, Me); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 241.8 and 235.0 (CO), 174.2 (quarternary), 104.8 (*C*$_5$Me$_5$), 103.7 ($=CH_2$), 65.9 (CH), 57.9 (CH), 17.3 (Me), and 10.8 (C$_5$*Me*$_5$). (**5**) IR (CH_2Cl_2) ν_{CO} 1941, 1862 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 6.09 (d, 1H, *J* 2.3, $=CH_2$), 5.20 (d, 1H, *J* 1.7 $=CH_2$), 2.60 (dd, 1H, *J* 10.1, 7.8, CH), 2.37 (d, 1H, *J* 7.7, CHC*H*$_2$), 1.86 (s, 15H, C$_5$*Me*$_5$), and 1.46 (d, 1H, *J* 10.3, CHC*H*$_2$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 238.1 and 235.1 (CO), 174.8 (quaternary), 104.8 (*C*$_5$Me$_5$), 102.6 ($=CH_2$), 53.0 (CH), 44.6 (CH_2), and 10.4 (C$_5$*Me*$_5$). (**7**) IR (CH_2Cl_2) ν_{CO} 2006 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 6.48 (t, 1H, *J* 8.8, CH) 2.99 (dd, 1H, *J* 1.3, 8.3, CH_2) 2.41 (s, 3H, Me), 1.98 (dd, 1H, *J* 1.8, 9.3, CH_2), and 1.88 (s, 15H, C$_5$*Me*$_5$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 255.6 (quarternary), 224.0 (CO), 135.0 (CH), 119.1 (q, CF_3SO_3), 106.4 (*C*$_5$Me$_5$), 63.6 (CH_2), 15.3 (Me), and 9.9 (C$_5$*Me*$_5$).

‡ *Crystal data* for (**5**): $C_{16}H_{20}O_2Mo$, $M = 340.23$, monoclinic, space group $P2_1/c$, $a = 14.686(3)$, $b = 8.961(1)$, $c = 12.172(2)$ Å, $\beta = 100.63(2)°$, $U = 1574.36$ Å^3, $F(000) = 680$, $\mu(Mo\text{-}K_\alpha) = 28.31$ cm^{-1}, $Z = 4$, $D_c = 1.44$ g cm^{-3}. A yellow crystal of size 0.32 × 0.18 × 0.16 mm, obtained from ether solution, was used in data collection. Data collected in θ-range 3—25° with a scan width of 0.90°; $R = 0.0560$ for 1443 reflections with $I/\sigma(I) > 3.0$. 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.



Scheme 2. *Reagents and conditions*; i, Li[N(SiMe$_3$)$_2$], THF, −78 °C; ii, Bu$_4$NF, CH$_2$Cl$_2$, 25 °C; iii, CF$_3$SO$_3$H, CH$_2$Cl$_2$, −78 °C.

C$_5$Me$_5$ proton. A deuterium labelling experiment using [1,1,4,4-^{2}H$_4$](**4**) gave only [1,1,4,4-^{2}H$_4$](**5**) with no incorporation of deuterium into the C$_5$Me$_5$ ring. Complex (**5**) could not be isolated from the equivalent reaction using [2,3-^{2}H$_2$](**4**), this being attributable to a deceleration in the rate of formation of (**5**) relative to competing reactions, owing to the kinetic isotope effect.

In an effort to develop a rational strategy for the synthesis of (**5**), the 2-triethylsilylbutadiene complex (**6**) was prepared. Treatment with Bu$_4$NF in CH$_2$Cl$_2$ resulted in an immediate desilylation, furnishing after work up, (**5**) in 90% yield. Preliminary studies suggest the scope of this synthetic approach to be fairly wide ranging, thus facilitating a useful opportunity to increase our understanding of these unusual species.[2,3,4]

In an initial study the protonation of (**5**) (CF$_3$SO$_3$H, CH$_2$Cl$_2$, −78 °C) was examined. This leads to the formation of a cationic η^3-vinylcarbene complex (**7**) (Scheme 2), which was characterised by IR and NMR spectroscopy.†

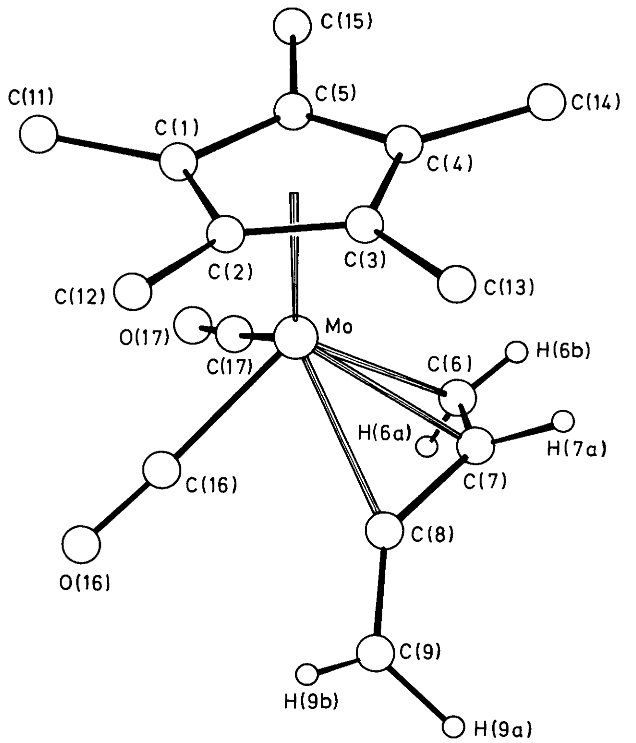


Figure 1. Structure of (5): hydrogen atoms on the C$_5$Me$_5$ ring omitted for clarity. Selected distances (Å) and angles (°): Mo–C(6) 2.328(13), Mo–C(7) 2.208(14), Mo–C(8) 2.198(15), C(6)–C(7) 1.348(22), C(7)–C(8) 1.391(20), C(8)–C(9) 1.353(24), C(6)–C(7)–C(8) 120(1), C(7)–C(8)–C(9) 139(1).

In summary, novel deprotonation and desilylation reactions are described which provide synthetic access to a potentially interesting group of molecules carrying η^3-butadienyl ligands.

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