

Reactions of Three-electron σ, η^2 -Prop-2-ynyl Ligands formed by Deprotonation of Four-electron η^2 -Alkyne Molybdenum Complexes

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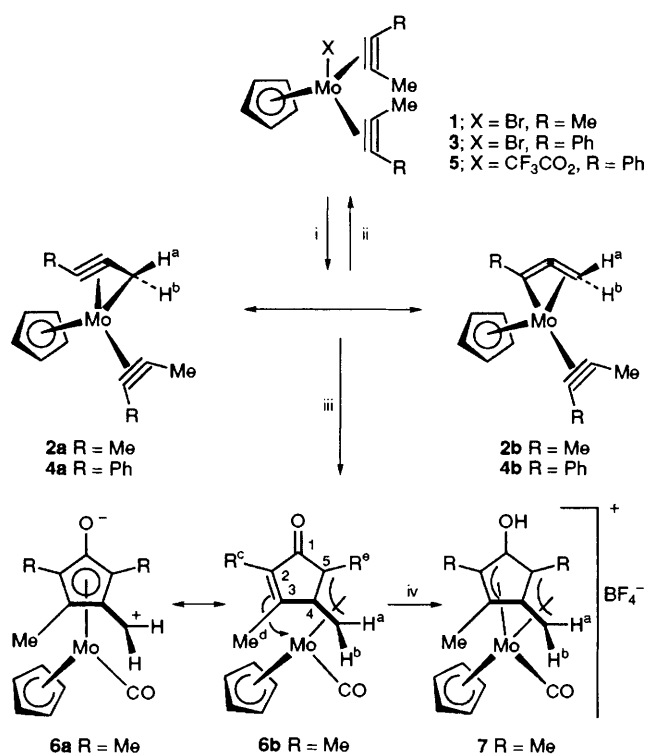
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Reaction of $[\text{MoBr}(\eta^2\text{-MeC}_2\text{R})_2(\eta\text{-C}_5\text{H}_5)]$ ($\text{R} = \text{Me}$, or Ph) with $\text{Li}[\text{N}(\text{SiMe}_3)_2]$ leads to a dehydrohalogenation reaction and the unexpected formation of the three-electron σ, η^2 -prop-2-ynyl complexes $[\text{Mo}(\sigma, \eta^2\text{-CH}_2\text{C}_2\text{R})(\eta^2\text{-MeC}_2\text{R})(\eta\text{-C}_5\text{H}_5)]$; treatment of these reactive molecules with the proton source $\text{CF}_3\text{CO}_2\text{H}$ affords the bis-alkyne complexes $[\text{Mo}(\text{O}_2\text{CCF}_3)(\eta^2\text{-MeC}_2\text{R})_2(\eta\text{-C}_5\text{H}_5)]$, whereas reaction with carbon monoxide leads to a novel carbon-carbon bond forming reaction, and formation of the X-ray crystallographically identified complex $[\text{Mo}\{\eta^2, \eta^3\text{-C}(\text{Me})\text{C}(\text{O})\text{C}(\text{Me})\text{C}(\text{Me})\text{C}-\text{CH}_2\}(\text{CO})(\eta\text{-C}_5\text{H}_5)]$.

Recently,¹ we have shown that treatment of the four-electron donor η^2 -alkyne complexes $[\text{Mo}(\eta^2\text{-PhC}_2\text{CHR}^1\text{R}^2)\text{-}\{\text{P}(\text{OMe})_3\}_2(\eta\text{-C}_5\text{H}_5)][\text{BF}_4^-]$ ($\text{R}^1 = \text{H}$, Ph ; $\text{R}^2 = \text{H}$, Ph) with $\text{KH-Bu}^t\text{OH}$ leads to a deprotonation reaction and formation of the neutral three-electron η^2 -allenyl complexes $[\text{Mo}\{\text{C}(\text{Ph})\text{C}=\text{CR}^1\text{R}^2\}\{\text{P}(\text{OMe})_3\}_2(\eta\text{-C}_5\text{H}_5)]$. In a related study² it has been shown by Templeton and coworkers that deprotonation of the cationic alkyne complexes $[\text{W}(\text{dtc})(\eta^2\text{-MeOC}_2\text{CH}_2\text{Ph})(\text{CO})(\text{dppe})][\text{X}]$ [$\text{dtc} = \text{R}_2\text{NCS}_2$; $\text{dppe} = (\text{Ph}_2\text{PCH}_2)_2$; $\text{X} = \text{CF}_3\text{SO}_3$, BF_4^-] affords the analogous species $[(\text{dtc})\text{W}\{\text{C}(\text{OMe})\text{C}=\text{CHPh}\}(\text{CO})(\text{dppe})]$. In the light of these observations it was thought that reaction of $[\text{MoBr}(\eta^2\text{-MeC}_2\text{Me})_2(\eta\text{-C}_5\text{H}_5)]$ ³ **1** with a suitable base might lead to a dehydrohalogenation reaction and formation of the potentially interesting three-electron η^2 -allenyl-four-electron η^2 -alkyne complex $[\text{Mo}\{\text{C}(\text{Me})\text{C}=\text{CH}_2\}(\eta^2\text{-MeC}_2\text{Me})(\eta\text{-C}_5\text{H}_5)]$. However, this did not occur, and instead a new reaction was observed, which results in the transformation of one of the coordinated but-2-yne molecules into a type of ligand which is currently attracting attention, the three-electron σ, η^2 -prop-2-ynyl ligand.

Treatment [tetrahydrofuran (thf) -78°C] of **1** with one molar equivalent of $\text{Li}[\text{N}(\text{SiMe}_3)_2]$ afforded (75% yield) a red,



Scheme 1 Reagents and conditions: i, $+\text{Li}[\text{N}(\text{SiMe}_3)_2]$, thf; ii, $\text{CF}_3\text{CO}_2\text{H}$, CH_2Cl_2 ; iii, $+\text{CO}$, thf; iv, $\text{HBF}_4 \cdot \text{OEt}_2$, CH_2Cl_2

crystalline, hydrocarbon-soluble, air-sensitive complex **2**. Although elemental analysis and a mass spectrum confirmed the molecular formula $[\text{Mo}(\text{MeC}_2\text{H}_2)(\eta^2\text{-MeC}_2\text{Me})(\eta\text{-C}_5\text{H}_5)]$ for **2**, the absence in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of a low-field resonance (δ ca. 250)^{1,4} attributable to the alkylidene α -carbon of a three-electron η^2 -allenyl fragment showed that the sought for reaction had not occurred. Examination of the ^1H , $^{13}\text{C}\{^1\text{H}\}$ and coupled ^{13}C NMR spectra[†] revealed, however, resonances and coupling constants fully consistent with the illustrated structure for **2** (Scheme 1), where a $\text{Mo}(\eta\text{-C}_5\text{H}_5)$ fragment is coordinated to a four-electron η^2 -bonded but-2-yne and a three-electron σ, η^2 -prop-2-ynyl fragment. Thus, the room temperature ^1H spectrum exhibited a $\eta^5\text{-C}_5\text{H}_5$ resonance at δ 4.95, a methyl propynyl triplet resonance at δ 2.47, and two doublets of quartets centred at δ 4.77 and 3.85 attributable to the inequivalent propynyl hydrogens, which are coupled [gem. $J(\text{H}^a\text{H}^b)$ 9.5 Hz] to each other and the methyl group, the magnitude of $J(\text{H}^a\text{H}^b)$ indicating an important contribution from the canonical form **2a**. The spectrum also showed a singlet at δ 2.5 due to the equivalent methyl groups of a rotating four-electron η^2 -bonded but-2-yne ligand, collapsing at low temperature to singlets at δ 2.27 and 2.15 [$\Delta G^\ddagger(T_c)$ $34(\pm 2)$ kJ mol⁻¹, T_c 198 K]. In the ^1H coupled ^{13}C spectrum, singlets at δ 133.6 and 112.4 were assigned to the quaternary propynyl carbons and a doublet of doublets at δ 38.57 [$J(\text{CH}^a)$ 156.4 Hz, $J(\text{CH}^b)$ 163.0 Hz] to the propynyl CH_2 group, the magnitude of $J(\text{CH})$ being consistent with, though not conclusive evidence for, the importance of the canonical form **2a**. The room temperature $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum demonstrated the presence of a rotating four-

[†] Selected spectroscopic data for compound **2**: NMR ^1H (C_6D_6) δ 4.95 (s, 5H, C_5H_5), 4.77 [dq, 1H, H^a , $J(\text{H}^a\text{H}^b)$ 9.5, $J(\text{HMe})$ 2.2 Hz], 3.85 [dq, 1H, H^b , $J(\text{H}^a\text{H}^b)$ 9.5, $J(\text{HMe})$ 2.2 Hz], 2.50 (s, 6H, MeC_2Me), 2.47 [t, 3H, $\text{CH}_2\text{C}(\text{Me})$, $J(\text{HMe})$ 2.2 Hz]; $^{13}\text{C}\{^1\text{H}\}$ (C_6D_6), δ 199.7 (MeC_2Me), 133.6 (=C=), 112.4 (CMe), 93.28 (C_5H_5), 38.57 (CH_2) [^1H coupled ^{13}C , dd, CH^aH^b , $J(\text{CH})$ 156.4 Hz, $J(\text{CH}^b)$ 163.0 Hz], 20.39 (CMe), 18.98 (MeC_2Me). Compound **4**: NMR ^1H (C_6D_6), δ 8.03–6.99 (m, 10H, Ph), 5.01 [d, 1H, H^a , $J(\text{H}^a\text{H}^b)$ 10.8 Hz], 4.88 (s, 5H, C_5H_5), 3.90 [d, 1H, H^b , $J(\text{H}^a\text{H}^b)$ 10.81 Hz], 2.42 (s, 3H, MeC_2Ph); $^{13}\text{C}\{^1\text{H}\}$ (C_6D_6), δ 207.38 (MeC_2Ph), 197.04 (MeC_2Ph), 142.3 (=C=), 140.82–126.78 (Ph), 124.86 (CPh), 93.62 (C_5H_5), 41.62 (CH_2) [^1H coupled ^{13}C , dd, CH^aH^b , $J(\text{CH}^a)$ 158.6 Hz, $J(\text{CH}^b)$ 165.3 Hz], 18.95 (MeC_2Ph). Compound **5**: NMR ^1H (CD_2Cl_2), δ 7.75–7.00 (m, 10H, Ph), 5.26 (s, 5H, C_5H_5), 2.57 (s, 6H, MeC_2Ph). Compound **6**: $\nu_{\text{CO}}/\text{cm}^{-1}$ (CH_2Cl_2) 1916s, 1595m; NMR ^1H (CD_2Cl_2), δ 4.96 (s, 5H, C_5H_5), 3.27 [d, 1H, H^a , $J(\text{H}^a\text{H}^b)$ 2.2 Hz], 2.94 [d, 1H, H^b , $J(\text{H}^a\text{H}^b)$ 2.2 Hz], 1.88 (s, 3H, Me^c), 1.74 (s, 3H, Me^d), 1.64 (s, 3H, Me^e); $^{13}\text{C}\{^1\text{H}\}$ (CD_2Cl_2), δ 241.2 (CO), 170.4 (C=O), 107.67 (C^3), 100.4 (C^2), 99.9 (C^4), 96.57 (C^5), 89.2 (C_5H_5), 49.96 (CH_2) [^1H coupled ^{13}C , dd, CH^aH^b , $J(\text{CH}^a)$ 156.4 Hz, $J(\text{CH}^b)$ 163.0 Hz], 12.99 (Me^e), 10.5 (Me^d), 9.15 (Me^c). Compound **7**: $\nu_{\text{CO}}/\text{cm}^{-1}$ (CH_2Cl_2) 1980s; NMR ^1H (CD_2Cl_2), δ 5.28 (s, 5H, C_5H_5), 3.62 [d, 1H, $J(\text{H}^a\text{H}^b)$ 2.57 Hz], 3.32 [d, 1H, H^b , $J(\text{H}^a\text{H}^b)$ 2.57 Hz], 2.25 (s, 3H, Me), 2.02 (s, 3H, Me), 1.71 (s, 3H, Me), 1.27 (s, 1H, OH); $^{13}\text{C}\{^1\text{H}\}$ (CD_3NO_2), δ 233.4 (CO), 141.8 (C^1OH), 108.2 (C^3 or C^2), 106.3 (C^2 or C^3), 103.9 (C^4), 100.3 (C^5), 93.5 (C_5H_5), 52.8 (CH_2), 12.2 (Me), 10.3 (Me), 10.2 (Me).

electron η^2 -bonded but-2-yne ligand exhibiting one contact carbon resonance at δ 199.7, and one MeC_2Me signal.

An additional interesting structural aspect of this complex, which is highlighted by canonical form **2a**, is that the molecule can be viewed as containing two coordinated alkynes, one adopting a normal U configuration, *i.e.* the but-2-yne, and the second, which is part of the propynyl ligand, an unusual Z configuration. In principle either could function as a four-electron donor to the molybdenum; however, the NMR data[†] show that it is the U alkyne which is the four-electron donor, whereas the formal Z alkyne functions as a two-electron donor. Importantly, the NMR data also show that the plane in which the three-electron σ, η^2 -propynyl ligand lies is not perpendicular to that of the η^5 - C_5H_5 . It would be expected that in the static state, *i.e.* at low temperature, the four-electron η^2 -but-2-yne would lie parallel to the Mo-CH₂ vector so as to maximise backbonding.

Although three-electron σ, η^2 -propynyl complexes of Fe,⁵ Ru,⁶ Os⁷ and W⁸ carrying a =CHR group attached to the propynyl terminus, *i.e.* σ, η^2 -RC₂C=CHR, have been reported and shown to be formed in alkynyl-vinylidene coupling reactions, unsubstituted systems are rare. Thus, the unsubstituted three-electron σ, η^2 -propynyl complex [Mo(σ, η^2 -CH₂C₂H)(CO)₂(η^6 -C₆Me₆)] [BF₄] was prepared⁹ by photolysis of [Mo(CO)₃(η^6 -C₆Me₆)] and prop-2-ynyl alcohol in the presence of HBF₄, and recently¹⁰ hydride abstraction by [Ph₃C][PF₆] from the two-electron butyne complex [Re(η^2 -MeC₂Me)(CO)₂(η -C₅Me₅)] has been shown to give the three-electron butynyl complex [Re{ σ, η^2 -CH₂C₂Me}(CO)₂(η -C₅Me₅)] [PF₆]. The preparation of **2** constitutes the first synthesis of a three-electron σ, η^2 -propynyl complex by deprotonation of a three- or four-electron η^2 -alkyne ligand, and preliminary experiments show that the reaction can be generalised, the three-electron alkynyl complex [Mo(σ, η^2 -

CH₂C₂Ph)(η^2 -MeC₂Ph)(η -C₅H₅)] **4** being formed in good yield by reaction of Li[N(SiMe₃)₂] with the corresponding bis-alkyne halo complex [MoBr(η^2 -MeC₂Ph)₂(η -C₅H₅)]³.

These neutral four-electron η^2 -alkyne-three-electron σ, η^2 -propynyl complexes are obviously also of interest from the standpoint of reactivity.¹¹ Treatment (0 °C, CH₂Cl₂) of **4** with trifluoroacetic acid results in protolytic cleavage of the propynyl molybdenum to carbon σ -bond, *i.e.* structure **4a**, and formation of the bis-phenylmethylacetylene trifluoroacetate complex **5**[†] (Scheme 1). This reaction is interesting because protolysis might have been expected to give the complex [Mo(O₂CCF₃)(η^2 -MeC₂Ph)₂(η -C₅H₅)] containing a U-bonded and a Z-bonded phenylmethylacetylene. It is suggested that the initially formed U-Z isomer readily switches its bonding mode to give the isolated U-U complex **5**. Of course it should be noted that, in the reverse reaction, *i.e.* deprotonation, a switch (U to Z) in the geometry of one of the alkynes also occurs, and possible reasons for this will be discussed in a full paper.

Though **2** and **4** can be viewed as 18-electron systems the ability of the η^2 -alkyne (4e \rightarrow 2e) and η^3 -propynyl (3e \rightarrow 1e) ligands to switch their bonding modes implies that these unusual molecules should also be reactive towards donor ligands. This was confirmed when it was observed that bubbling (20 min, room temp., thf) carbon monoxide through a solution of **2** resulted in a change in colour from red to yellow and the formation in good yield of the orange-yellow crystalline complex **6**. Although examination of the spectroscopic data[†] revealed that two molecules of carbon monoxide had been incorporated, one as a terminal carbonyl (ν_{CO} 1916 cm⁻¹; ¹³C resonance δ 241.2) and the second as an acyl system (ν_{CO} 1595 cm⁻¹; ¹³C resonance δ 170.4), the data did not fully establish the structural identity of the complex; in fact it is suggested that an unusual reaction had occurred. This was confirmed by a single crystal X-ray diffraction study,[‡] which showed (Fig. 1) that a new type of cyclisation reaction had occurred leading to the formation of a novel alicyclic C₅ ligand with exocyclic oxygen and CH₂ groups. The carbon-carbon bond lengths within the new ligand suggest contributions from both of the canonical forms **6a** and **6b**, however, the C-O bond length [C(7)-O(2) 1.268(9) Å], the long Mo(1)-C(7) distance [2.637(7) Å], the NMR inequivalence of the exocyclic methylene hydrogens, and the acyl IR C-O stretch at 1595 cm⁻¹ imply that structure **6b** is more important. It is also interesting to note that C(13) lies 0.92 Å above the plane defined by C(8), C(9), C(10) and C(11). In a sense **6** can be viewed as being related to the electron-rich molecule [Mo(CO)(η -C₅H₅)₂], and therefore might be expected to react with electrophilic reagents. This was confirmed by a preliminary study in which it was found that treatment of **6** with HBF₄·OEt₂ leads to regioselective protonation of the acyl oxygen and formation of the unusual bis- η^3 -allylic substituted cation **7**.[†]

In summary, a novel pathway to the three-electron σ, η^2 -propynyl ligand has been established and unusual chemical reactivity demonstrated.

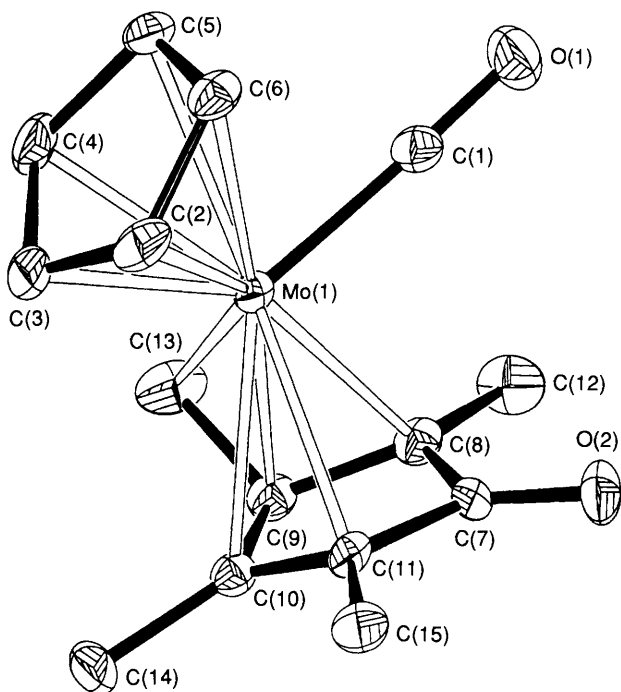


Fig. 1 Molecular structure of one enantiomer of **6** showing labelling scheme. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Mo(1)-C(8) 2.332(7), Mo(1)-C(9) 2.150(7), Mo(1)-C(10) 2.251(7), Mo(1)-C(11) 2.390(7), Mo(1)-C(13) 2.335(7), C(7)-O(2) 1.268(9), C(7)-C(8) 1.466(10), C(8)-C(9) 1.454(10), C(9)-C(10) 1.444(9), C(10)-C(11) 1.406(10), C(7)-C(11) 1.434(9), C(9)-C(13) 1.435(11); C(12)-C(8)-C(9) 125.7(6), C(13)-C(9)-C(8) 117.4(6), C(11)-C(10)-C(9) 108.1(6), C(14)-C(10)-C(11) 126.3(6), C(15)-C(11)-C(7) 122.2(6), C(10)-C(9)-C(8) 106.8(6), C(13)-C(9)-C(10) 121.1(6).

[‡] Crystal data: C₁₅H₁₆O₂Mo, *M* = 324.2, monoclinic, *a* = 7.826(1), *b* = 15.098(3), *c* = 21.635(4) Å, β = 95.14(2)°, *U* = 2546.0 Å³, space group *P*2₁/*n*, *Z* = 8, *D*_c = 1.69 g cm⁻³, μ (Mo-K α) = 9.09 cm⁻¹, *F*(000) = 1312. Data were measured at room temperature on a CAD4 automatic four-circle diffractometer in the range 2 \leq θ \leq 24°. 4480 reflections were collected of which 2686 were unique with *I* \geq 3 σ (*I*). Data were corrected for Lorentz and polarization effects but not for absorption. The structure was solved by Patterson methods, to yield final *R* = *R*_w = 0.0351 for unit weights. Atomic coordinates, bond lengths and angles, and thermal parameters of both enantiomers have been deposited at the Cambridge Crystallographic Centre. See Notice to Authors, Issue No. 1.

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