Regioselectivity in the Reactions of Dimolybdenum and Ditungsten σ,η^2(4e)-Allenylidene Complexes with Nucleophilic and Electrophilic Reagents; Crystal Structure and Dynamic Behaviour of the Cationic Complex $[W_2(\eta\text{-}HC_2CMe_2)(CO)_4(\eta\text{-}C_5H_5)_2][BF_4]$

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Reaction of the σ,η^2(4e)-allenylidene complexes $[M_2(\sigma,\eta^2\text{-}C{=}C{=}CMe_2)(CO)_4(\eta\text{-}C_5H_5)_2]$ (M = Mo or W) with $K[BHBu^s{}_3]$ or $HBF_4{\cdot}Et_2O$ results in attack on the γ- or the α-carbon atom forming $[M_2(\sigma,\eta^2\text{-}C{\equiv}CPr^i)(CO)_4(\eta\text{-}C_5H_5)_2]^-$ and $[M_2(\mu\text{-}HC_2CMe_2)(CO)_4(\eta\text{-}C_5H_5)_2]^+$, respectively; the *X*-ray crystal structure and solution dynamic behaviour of the cations are discussed in relation to the species $[Co_3(CCH_2)(CO)_9]^+$, and it is shown that the Mo_2 cation undergoes an unusual fragmentation reaction on treatment with Bu^tLi.

Carbon-rich species containing vinylidene and cumulene groups bonded to two or more metal centres can be regarded as models of reactive intermediates formed from surface carbides in catalytic heterogeneous carbon monoxide reduction and alkyne conversion reactions.[1—5] Recently[6] we discovered a synthetic route to an unusual group of molecules containing side-on, σ,η^2(4e)-bonded allenylidene groups, and in exploring their chemistry we have observed interesting site-selectivity on reaction with nucleophilic and electrophilic reagents.

The hydride anion donor $K[BHBu^s{}_3]$ reacts (−78 °C, THF) with a solution of $[Mo_2(\sigma,\eta^2\text{-}C{=}C{=}CMe_2)(CO)_4(\eta\text{-}C_5H_5)_2]$ (**1**), to form an anionic species identical (i.r. and n.m.r.[†]) with the adduct[7] $Li[Mo_2(\sigma,\eta^2\text{-}C{\equiv}CPr^i)(CO)_4(\eta\text{-}C_5H_5)_2]$ (**2**) formed on treatment of $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ with $LiC{\equiv}CPr^i$. Careful examination of the reaction mixture provided no evidence for intermediates, suggesting that kinetically controlled regioselective attack by the nucleophilic reagent occurs on the γ-carbon atom of the allenylidene ligand (Scheme 1).

In contrast, the complex (**1**) and the ditungsten analogue (**3**) react (−78 °C, CH_2Cl_2) with the electrophilic reagent $HBF_4{\cdot}Et_2O$ to form the red, crystalline cations (**4**) and (**5**) respectively. The same cations are formed on protonation ($HBF_4{\cdot}Et_2O$, −78 °C, CH_2Cl_2) of the transversely bonded 3-methylbut-3-en-1-yne complexes $[M_2\{\mu\text{-}HC_2C(Me){=}CH_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$ (**6**) and (**7**). The ^1H and $^{13}C\text{-}\{^1H\}$ n.m.r. spectra[†] of (**4**) and (**5**) revealed that in solution a dynamic process averages the environments of the $\eta\text{-}C_5H_5$ and methyl resonances. For example, (**5**) showed proton signals at δ 5.65 (C_5H_5) and 2.04 (Me) collapsing into two pairs of singlets on cooling [$\Delta G^\ddagger{}_{223}$(Me) – 43.6(±0.5) kJ mol^{-1}; $\Delta G^\ddagger{}_{203}(C_5H_5)$ 42.9 (±0.5) kJ mol^{-1}]. In order to begin to understand this behaviour and the details of the structure and

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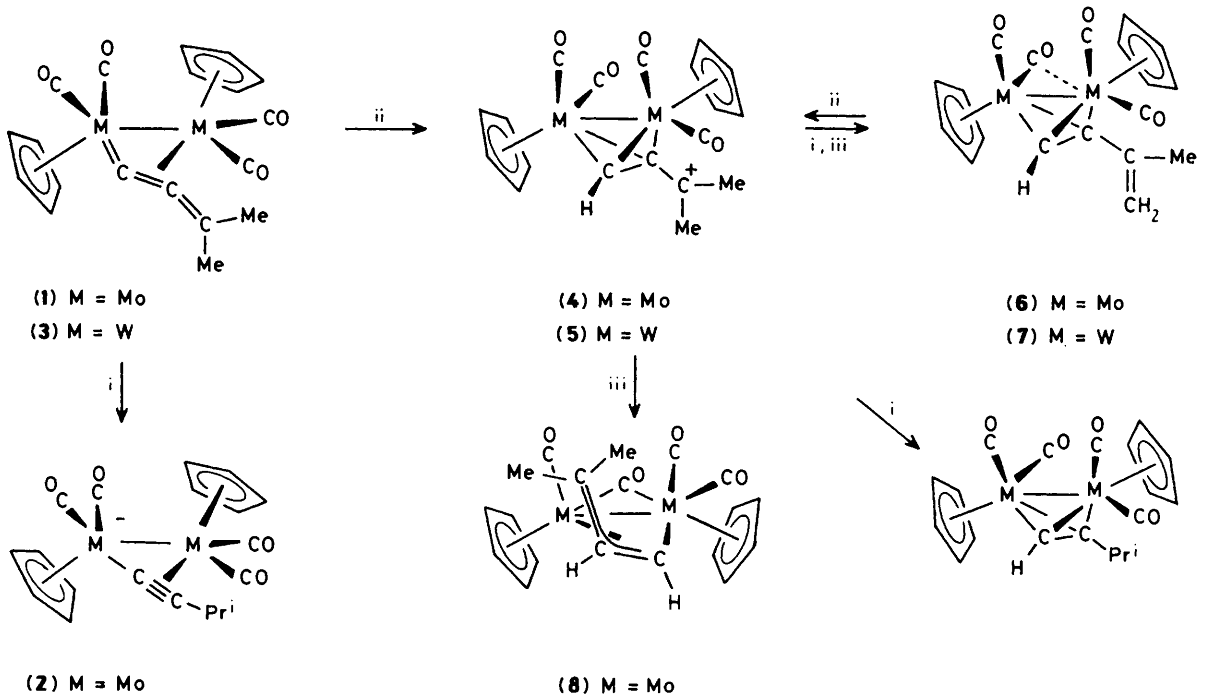
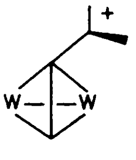
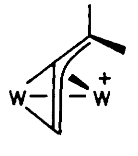
[†] *Selected spectroscopic data* for compound (**2**) [characterised as $(Ph_3P)_2N^+$ salt]: δ_H (CD_2Cl_2) 7.7—7.4 (m, 30H, Ph), 4.98 (s, 10H, C_5H_5), 3.16 (ah, 1H, $CHMe_2$, $J_{H,H}$ 6.8 Hz), 1.34 (d, 3H, CH*Me*, $J_{H,H}$ 6.8 Hz), and 1.19 (d, 3H, CH*Me*, $J_{H,H}$ 6.8 Hz). Compound (**4**): ν_{CO} (CH_2Cl_2) 2053w, 2031w, and 1999m cm^{-1}; δ_H (CD_2Cl_2; room temp.) 6.29 (s, 1H, *H*C), 5.64 (s, 10H, C_5H_5), and 2.07 (s, 6H, Me); $^{13}C\text{-}\{^1H\}$ (CD_2Cl_2; room temp.) δ 223.1, 222.8 (CO), 147.7 (CMe_2), 104.7 ($HCCCMe_2$), 94.3 (C_5H_5), 75.7 ($HCCCMe_2$), and 32.7 (Me). Compound (**5**): ν_{CO} (Nujol) 2044w, 1970m, and 1866w cm^{-1}; δ_H (CD_2Cl_2; room temp.) 5.65 (s, 10H, C_5H_5), 5.21 (s, 1H, *H*C), and 2.04 (s, 6H, Me); δ_H (CD_2Cl_2; 173 K) 5.72 (s, 5H, C_5H_5), 5.65 (s, 5H, C_5H_5), 5.1 (s, 1H, HC), 2.33 (s, 3H, Me), and 1.87 (s, 3H, Me); $^{13}C\text{-}\{^1H\}$ (CD_2Cl_2; room temp.) δ 209.2, 205.7 (CO), 151.9 (CMe_2), 93.2 ($HCCCMe_2$), 90.7 (C_5H_5), 52.2 ($HCCCMe_2$), and 33.1 (Me). Compound (**6**): ν_{CO} (hexane) 1993m, 1937sh, 1929s, and 1849m cm^{-1}; δ_H ($CDCl_3$) 5.61 (s, 1H, HC), 5.30 (s, 10H, C_5H_5), 4.96 (dq, 1H, $J_{H,H}$ 2.2, $J_{Me,H}$ 1.3 Hz), 4.75 (dq, 1H, $J_{H,H}$ 2.2, $J_{Me,H}$ 0.65 Hz), and 1.8 (dd, 3H, Me, $J_{Me,H}$ 1.3, $J_{Me,H}$ 0.65 Hz).



Scheme 1. *Reagents:* i, K[BHBu$^s_3$]; ii, $HBF_4 \cdot Et_2O$; iii, Bu^{t}Li.



(5a)



(5b)

bonding, a single crystal *X*-ray study‡ of (**5**) was undertaken, establishing the solid state molecular geometry for the cation which is displayed in Figure 1.

The cation is dinuclear with each metal atom co-ordinated by a η-C_5H_5 ring and two carbonyl ligands. The metal-to-metal bond length is typical of a W–W single bond [W(1)–W(2) 2.943(1) Å]. One of the carbonyl ligands, C(9)O(9), is bonded in a semi-bridging mode (see caption to Figure 1). In addition, the W–W bond is bridged by a propargylic carbocation, stabilisation by partial delocalisation of the positive charge being reflected in a C(1)–C(2) bond distance of 1.356(19) Å, longer than the corresponding bonds in neutral μ-alkyne complexes.[8] In contrast to neutral transversely bridged alkyne complexes, in (**5**) C(1) and C(2) are asymmetrically bonded, and the C(1)–C(2)–C(3) plane is not normal to the W · · · W vector, the C(2)–C(3) bond being rotated from this plane by approximately 35°. This rotation brings C(3) into the proximity of W(2) [W(2)–C(3) 2.837 Å], but does not cause 'bend-back' of C(4) and C(5), a planar geometry being maintained around C(3). However, the C(2)–C(3) bond length of 1.415(21) Å is approximately midway between lengths of a typical single and double bond, reflecting the partial delocalisation in the system. This is also seen in the near planarity of the propargylic ligand as a whole. Thus, the solid state structure of the core could be described as intermediate between forms (**5a**) and (**5b**).

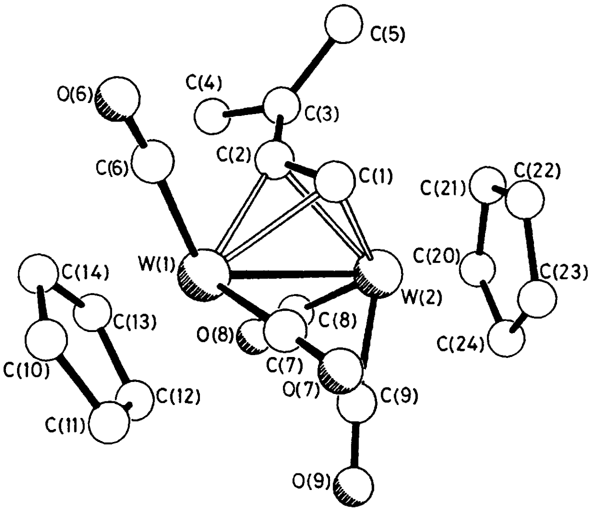


Figure 1. Molecular structure of (**5**); selected bond lengths (Å) and bond angles (°): W(1)–W(2) 2.943(1), W(1)–C(1) 2.151(14), W(1)–C(2) 2.103(14), W(2)–C(1) 2.215(14), W(2)–C(2) 2.268(12), C(1)–C(2) 1.536(19), C(2)–C(3) 1.415(21), C(9)–O(9) 1.162(18), C(9)–W(1) 2.881; C(1)C(2)C(3), 136.1(14), C(2)C(3)C(4) 120.7(16), C(2)C(3)C(5) 119.6(14), C(4)C(3)C(5) 117.9(15), W(2)C(9)O(9) 171.4(12).

The isolobal analogy[9] between the inorganic fragments $MoL_2(\eta\text{-}C_5H_5)$ and $Co(CO)_3$ and the organic unit CH also

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‡ *Crystal data:* (**5**) $C_{19}H_{17}BF_4O_4W_2$, M = 763.9, orthorhombic, a = 9.849(3), b = 12.830(5), c = 16.571(4) Å, U = 2094 Å^3, space group $P2_12_12_1$, Z = 4, D_c = 2.42 g cm^{-3}, $\mu(\text{Cu-}K_\alpha)$ = 208 cm^{-3}. Data were measured with a Nicolet R3m diffractometer, with Cu-K_α radiation (graphite monochromator) using ω-scans. The structure was solved by the heavy-atom method and refined anisotropically using absorption corrected data to give R = 0.043, R_w = 0.044 for 1581 independent observed reflections [$|F_o| > 3\sigma|F_o|$, $\theta \leqslant 58°$]. 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.

suggests an interesting structural relationship between (**4**) and (**5**) and the carbocation $[Co_3(CCH_2)(CO)_9]^+$, the parent molecule of a class widely studied by Seyferth and his co-workers.[10] These tricobalt cations were originally depicted as species in which a CCH_2^+ fragment stands in an upright position relative to a triangle of three cobalt atoms; however, a subsequent theoretical analysis[11] and study[12] of the variable-temperature n.m.r. spectrum of $[Co_3(CCHPr^i)(CO)_9]^+$ suggested that such a structure is at an energy maximum, and that in the energy minimum the CHR group is actually bent towards a cobalt atom with the plane of the CH_2 or CHR fragment orientated approximately parallel to the trinuclear plane. This structural feature has not been confirmed in the solid state by *X*-ray crytallographic studies either for Co_3 cations or for the related $[Co_2(HCCCR_2)(CO)_6]^+$ cations,[13] and it is, therefore, particularly interesting that these ideas are supported by the structure now found for the isoelectronic cation (**5**) where the CMe_2 group is placed over one of the tungsten atoms. As already mentioned, the $[Co_3(CCH_2)(CO)_9]^+$ cations undergo a dynamic process, which has been described[12] as a disrotatory correlated rotation, achieving circumambulation of the Co_3 triangle by a CH_2 or CXY group. At first sight it might be expected that a similar process would occur with (**4**) and (**5**); however, the apparent synchronous averaging on the n.m.r. time scale of both the methyl and the cyclopentadienyl group suggests that a more subtle process is involved; discussion of possible pathways is deferred to a full paper.

Finally, the reactivity of nucleophilic reagents towards the cation (**4**) has been briefly explored. Whereas treatment (−78 °C; THF) with $K[BHBu^s_3]$ results in competitive nucleophilic substitution and elimination reactions leading to $[Mo_2(\mu\text{-}HC_2Pr^i)(CO)_4(\eta\text{-}C_5H_5)_2]$ and (**6**), respectively, reaction (−78 °C; THF) with Bu^tLi, while again affording (**6**), gives two unexpected products, identified as $[Mo_2(\mu\text{-}\sigma:\eta^3\text{-}CHCHCMe_2)(CO)_4(\eta\text{-}C_5H_5)_2]$[14] and $[Mo_2(\mu\text{-}HC_2Pr^i)(CO)_4(\eta\text{-}C_5H_5)_2]$. Although the formation of these latter complexes can be formally understood in terms of the delivery of 'H^-' by Bu^tLi to either the β- or the γ-carbon atom of the propargylic system, it is unlikely that such a process is actually involved. Instead we suggest that Bu^tLi substitutes C(3) of (**4**) to form the sterically very hindered μ-alkyne complex $[Mo_2(\mu\text{-}HC_2CMe_2Bu^t)(CO_4)(\eta\text{-}C_5H_5)_2]$, and that this then undergoes a novel fragmentation reaction with extrusion of isobutene, thus accessing the reaction manifold we have previously discussed[14] for the thermolysis of $[Mo_2(\mu\text{-}\sigma:\eta^3\text{-}CHCHCMe_2)(CO)_4(\eta\text{-}C_5H_5)_2]$.

In summary, σ,η^2(4e)-allenylidene complexes undergo regioselective reactions with nucleophilic and electrophilic reagents on the γ- and the α-carbon atom, respectively, the latter reaction generating dimetal-stabilised propargylic cations.

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