

Evidence for a Facile Switch in the Bonding Mode of μ -Vinylidene Ligands from σ, η^2 to σ, σ ; Synthesis and Structure of a Dinuclear μ - σ, η^2 -Allenylidene Complex

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Methylation ($\text{MeOSO}_2\text{CF}_3$) of the adducts formed between MeC_2Li and $[\text{M}_2(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ ($\text{M} = \text{Mo}, \text{W}$) forms $[\text{M}_2(\mu\text{-MeC}_2\text{Me})(\eta\text{-C}_5\text{H}_5)_2]$ and $[\text{M}_2(\mu\text{-}\sigma, \eta^2\text{-C=CMe}_2)(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$, variable temperature ^1H n.m.r. studies with the latter showing that these species can undergo a facile $\mu\text{-}\sigma, \eta^2(4e)$ to $\mu\text{-}\sigma, \sigma(2e)$ switch; protonation of the corresponding adduct from $\text{CH}_2=\text{C}(\text{Me})\text{C}\equiv\text{CLi}$ and $[\text{M}_2(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ provides access to the first $\mu\text{-}\sigma, \eta^2(4e)$ allenylidene complexes which show dynamic behaviour in solution and which have been structurally identified by X-ray crystallography.

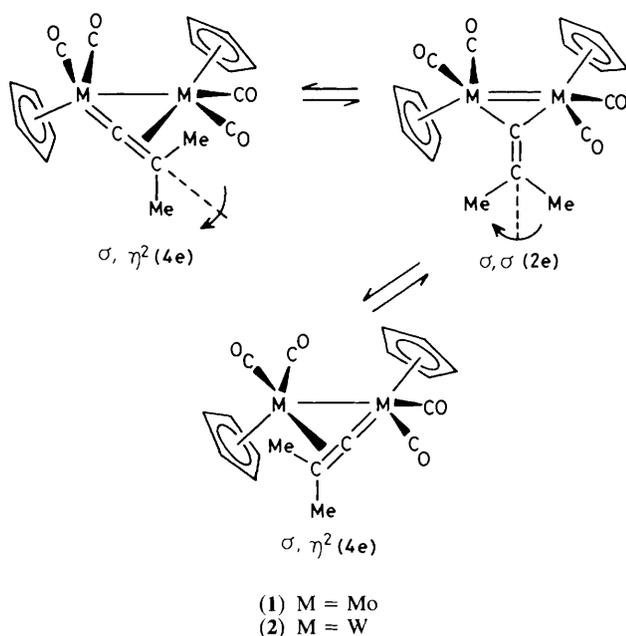
By comparison with the rapid developments in the chemistry of transition metal complexes of alkylidene and alkylidyne ligands less is known¹ about complexes containing vinylidene and allenylidene fragments, although the presence of unsaturation in such molecules might be expected to confer high reactivity. Recently² we showed that it is possible to synthesise dinuclear vinylidene complexes in which an unsymmetrical σ, η^2 bonding mode is adopted, and where the vinylidene functions as a four-electron donor. It was clearly important to understand the relationship between this bonding mode and the usual $\sigma, \sigma(2e)$ arrangement,¹ and to discover whether $\sigma, \eta^2(4e)$ bonding is also possible for μ -allenylidene ligands.³⁻⁵ This paper addresses these two problems.

One way of detecting a $\sigma, \eta^2(4e)$ to $\sigma, \sigma(2e)$ interconversion of μ -vinylidene complexes is to examine the variable temperature n.m.r. spectra of a $\sigma, \eta^2(4e)$ -vinylidene complex in which the β -carbon atom carries identical substituents. Access to such molecules was gained by reacting $[-78^\circ\text{C}$, tetrahydrofuran (thf)] $\text{MeC}\equiv\text{CLi}$ with the dinuclear complexes $[\text{M}_2(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ ($\text{M} = \text{Mo}, \text{W}$). This led to a rapid colour change and the formation of 1 : 1 adducts. Removal of the thf *in vacuo* and replacement with CH_2Cl_2 as solvent followed by addition (-78°C , CH_2Cl_2) of $\text{MeOSO}_2\text{CF}_3$ afforded a mixture of the red transversely bonded alkyne complexes $[\text{M}_2(\mu\text{-}$

$\text{MeC}_2\text{Me})(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ ($\text{M} = \text{Mo}, \text{W}$) and the $\mu\text{-}\sigma, \eta^2(4e)$ -vinylidene complexes $[\text{M}_2(\mu\text{-}\sigma, \eta^2\text{-C=CMe}_2)(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$, (**1**, $\text{M} = \text{Mo}$, blue black) and (**2**, $\text{M} = \text{W}$, deep blue) separable by column chromatography. This is in contrast with the corresponding reaction of $\text{MeOSO}_2\text{CF}_3$ with $\text{Li}[\text{Mo}_2(\mu\text{-C}_2\text{Ph})(\text{CO})_4(\eta\text{-C}_5\text{H}_5)]^2$ where there was no evidence for the formation of $[\text{Mo}_2(\mu\text{-PhC}_2\text{Me})(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$.

Examination of the ^1H and $^{13}\text{C}\{-^1\text{H}\}$ spectra[†] of (**1**) at ambient temperature revealed signals corresponding to only one methyl and one cyclopentadienyl environment rather than the expected two environments. The tungsten complex (**2**) did, however, show four resonances, but with considerable broadening of the ^1H signals, implying that in both cases a site averaging process was occurring in solution. This was confirmed by variable temperature ^1H n.m.r. measurements. At 213 K (CD_2Cl_2) the ^1H spectrum of (**1**) showed two Me and two C_5H_5 signals which coalesced reversibly on warming with $\Delta G_{\text{Tc}}^\ddagger$ values of $61(\pm 2)$ and $59(\pm 2)$ kJ mol^{-1} respectively, the corresponding value for (**2**) being $\Delta G_{\text{Tc}}^\ddagger$ (Me) $68(\pm 2)$ and $\Delta G_{\text{Tc}}^\ddagger$ (C_5H_5) $66(\pm 2)$ kJ mol^{-1} . A simple and interesting explanation for these observations is that site exchange occurs *via* a higher energy, but accessible $\sigma, \sigma(2e)$ -bonded vinylidene. As is shown in Scheme 1 such a process involves a rotational movement of the C_2 vinylidene fragment without substantial movement of the carbonyl or cyclopentadienyl ligands. In the exchange process there is also a synchronous change in the metal-to- α -carbon and metal-to-metal bond order.

This ability to switch bonding modes is clearly important and could relate to reactivity. It was therefore relevant to discover whether μ -allenylidene ligands would show similar behaviour. The only previously described μ -allenylidene complexes adopt a symmetrical $\mu\text{-}\sigma, \sigma$ -bonding mode,³⁻⁵ however, an adaptation of our synthetic approach² to $\mu\text{-}\sigma, \eta^2$ -



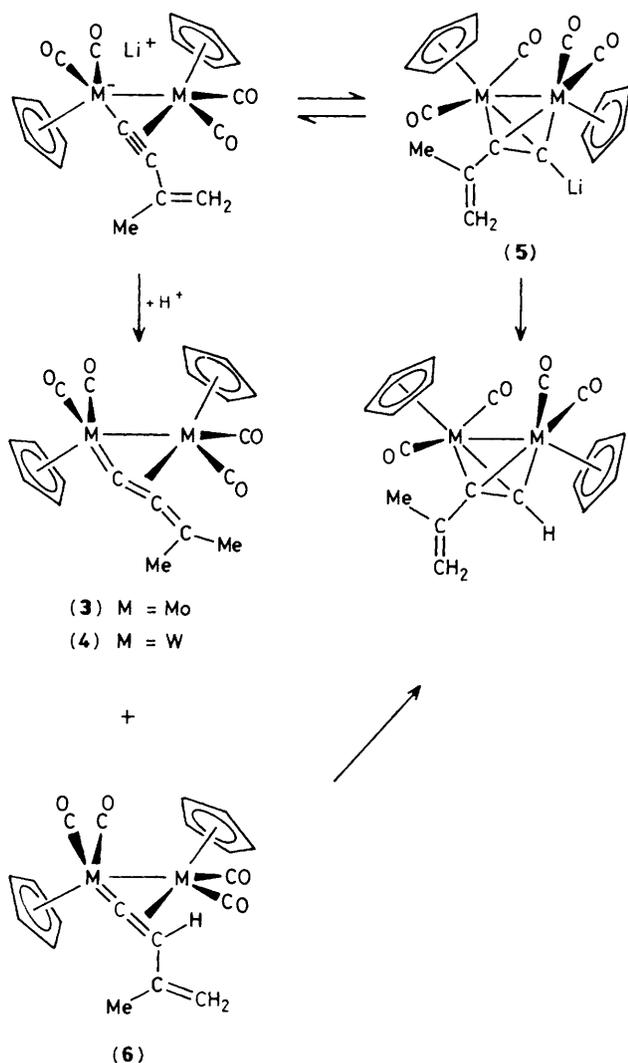
Scheme 1

[†] Selected spectroscopic data for compound (**1**): ν_{CO} (hexane) 1967w, 1924s, 1895m, 1867w cm^{-1} ; n.m.r. ^1H (CD_2Cl_2 , 213 K), δ 5.54 (s, 5H, C_5H_5), 5.39 (s, 5H, C_5H_5), 1.73 (s, 3H, Me), 1.67 (s, 3H, Me); $^{13}\text{C}\{-^1\text{H}\}$ (CD_2Cl_2 , 213 K), δ 342.9 (C_α), 243.6 (CO), 237.0 (CO), 236.5 (CO), 226.1 (CO), 96.1 ($\text{C}_\gamma\text{H}_5$), 92.8 ($\text{C}_\delta\text{H}_5$), 79.8 (C_β), 28.7 (Me), and 27.9 (Me).

Compound (**2**): ν_{CO} (hexane) 1957w, 1913s, 1885m, 1858w cm^{-1} ; n.m.r. ^1H (CDCl_3 , 233 K) δ 5.59 (s, 5H, C_5H_5), 5.50 (s, 5H, C_5H_5), 1.93 (s, 3H, Me), 1.75 (s, 3H, Me); $^{13}\text{C}\{-^1\text{H}\}$ (CDCl_3), δ 315.2 (C_α).

Compound (**3**): ν_{CO} (hexane) 1969w, 1925s, 1905w, 1869w cm^{-1} ; n.m.r. ^1H (CDCl_3), δ 5.47 (s, 5H, C_5H_5), 5.29 (s, 5H, C_5H_5), 2.42 [q, 3H, Me, $J(\text{HH})$ 0.73 Hz], 2.17 [q, 3H, Me, $J(\text{HH})$ 0.73 Hz]; $^{13}\text{C}\{-^1\text{H}\}$ (CD_2Cl_2), δ 287.7 (C_α), 238.2 (CO), 233.0 (CO), 231.5 (CO), 230.8 (CO), 149.4 (C_β), 148.9 (C_γ), 95.03 ($\text{C}_\delta\text{H}_5$), 93.7 ($\text{C}_\delta\text{H}_5$), 33.1 (Me), 25.24 (Me).

Compound (**4**): n.m.r. $^{13}\text{C}\{-^1\text{H}\}$ (CD_2Cl_2), δ 260.2 (C_α), 146.1 (C_β), 145.6 (C_γ).



Scheme 2. M = Mo or W. Only one isomeric form of the μ -acetylide is depicted for the sake of clarity.

vinylidenes provided the first examples of asymmetrically bridged allenylidenes. Addition (-78°C , thf) of $\text{CH}_2=\text{C}(\text{Me})\text{C}\equiv\text{CLi}$ to $[\text{M}_2(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ (M = Mo, W) led to the rapid formation of 1:1 adducts. Addition of the reaction mixture directly to an alumina packed column led to protonation and the formation of a separable mixture of $[\text{M}_2\{\mu\text{-HC}_2\text{C}(\text{Me})=\text{CH}_2\}(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$, and $[\text{M}_2\{\mu\text{-}\sigma,\eta^2\text{-C}=\text{C}=\text{CMe}_2\}(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ [(3) M = Mo, (4) M = W (both dark green crystals obtained in 50% yield)] (Scheme 2). The $\mu\text{-}\sigma,\eta^2$ -allenylidenes arise by δ -protonation of the μ -acetylide anions, however, the μ -alkyne complexes could be formed either by direct protonation of (5) or indirectly by initial β -protonation of the μ -acetylide to form (6) followed by a hydrogen-shift process as previously² observed.

Unlike the dimethyl substituted μ -vinylidenes (1) and (2), the ^1H n.m.r. spectra[†] of the μ -allenylidenes (3) and (4) showed two methyl and two cyclopentadienyl resonances, the signals showing no evidence of line broadening. However, irradiation at one of the methyl signals led to progressive spin saturation transfer (Hoffman-Forsen experiment) and to the partial collapse of the second Me signal showing that at

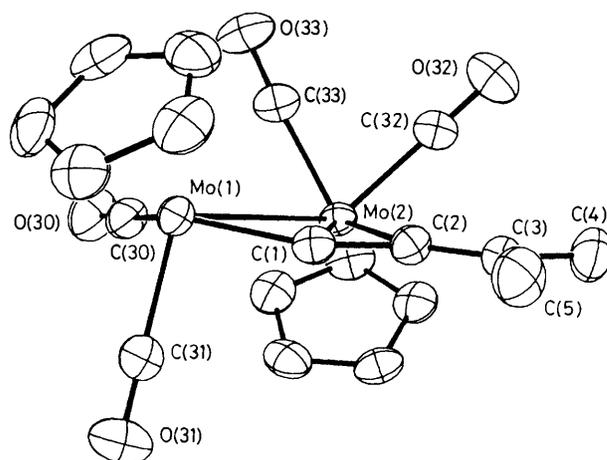


Figure 1. Molecular structure of $[\text{Mo}_2(\mu\text{-}\sigma,\eta^2\text{-C}=\text{CMe}_2)(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ (3), with hydrogen atoms omitted for clarity. Important geometric parameters include: bond lengths (\AA): Mo(1)–Mo(2) 3.145(1), Mo(1)–C(1) 1.912(3), Mo(2)–C(1) 2.209(3), Mo(2)–C(2) 2.240(3), C(1)–C(2) 1.336(3), C(2)–C(3) 1.348(4); bond angles ($^\circ$): Mo(1)–C(1)–Mo(2) 99.3(1), Mo(1)–C(1)–C(2) 167.2(2), C(1)–C(2)–C(3) 144.5(3).

ambient temperature site exchange is slowly occurring. It is possible that this involves a $\mu\text{-}\sigma,\eta^2$ -allenylidene to $\mu\text{-}\sigma,\sigma$ -allenylidene transformation and this is being investigated in detail.

Clearly it was also important to establish the solid state structure of these μ -allenylidenes. A single crystal *X*-ray study[‡] of (3) was therefore undertaken, and revealed the molecular geometry depicted in Figure 1. This shows the unique asymmetrical bonding mode of the allenylidene ligand across the Mo–Mo single bond [Mo(1)–Mo(2) 3.145(1) \AA]. In this conformation the ligand acts as a four-electron donor to the Mo_2 centre by binding to Mo(1) via a Mo=C double bond [Mo(1)–C(1) 1.912(3) \AA] and to Mo(2) via the interaction of the C(1)–C(2) double bond [Mo(2)–C(1) 2.209(3), Mo(2)–C(2) 2.240(3) \AA] the substituents at C(3) lying close to the $\text{Mo}_2(\mu\text{-C}_2)$ plane. The C_3 allenylidene fragment is distinctly kinked [Mo(1)–C(1)–C(2) 167.2(2), C(1)–C(2)–C(3) 144.5(3) $^\circ$] compared with the strictly linear arrangement adopted by $\mu\text{-}\sigma,\sigma$ -bonded allenylidenes. It is also interesting to compare this molecule with the related asymmetrically bridged Mo_2 vinylidene $[\text{Mo}_2\{\mu\text{-}\sigma,\eta^2\text{-C}=\text{C}(\text{Ph})\text{R}\}(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ [R = $(\text{CH}_2)_4\text{OH}$] where both the Mo(2)–C(2) [2.240(3) vs. 2.443(6) \AA] and C(1)–C(2) [1.336(3) vs. 1.380(7) \AA] distances are shorter.²

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[‡] *Crystal Data* for (3): $\text{C}_{19}\text{H}_{16}\text{Mo}_2\text{O}_4$, $M = 500.2$, triclinic, space group $P\bar{1}$ (No. 2), $a = 8.138(2)$, $b = 10.022(2)$, $c = 11.495(3)$ \AA , $\alpha = 85.41(2)$, $\beta = 84.35(2)$, $\gamma = 73.54(2)^\circ$, $U = 893.3(3)$ \AA^3 , $Z = 2$, $D_c = 1.867$ g cm^{-3} , $F(000) = 491.79$, graphite monochromated, Mo- K_α *X*-radiation, $\lambda = 0.71069$ \AA , $\mu(\text{Mo-}K_\alpha) = 13.9$ cm^{-1} . Intensity data were collected on a Nicolet P3m diffractometer, at ambient temperature, for a unique portion of reciprocal space in the range $4 < 2\theta < 55^\circ$. Structure solution was by Patterson and difference Fourier methods. Least squares refinement gave final residuals $R(R_w)$ 0.031 (0.033) for 3750 unique, absorption corrected, observed [$I > 1.5\sigma(I)$] intensity data.

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, 1986.

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