'Side-on' Co-ordination of Vinylidene at a Dimolybdenum Centre

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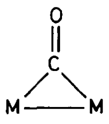
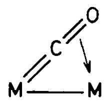
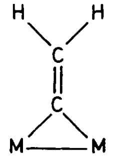
Ethyne reacts with $[Mo_2(CO)_4(\eta\text{-}C_5Me_5)_2]$ under u.v. irradiation to yield $[Mo_2(CO)_4(\mu\text{-}\eta^1,\eta^2\text{-}CCH_2)(\eta\text{-}C_5Me_5)_2]$, containing vinylidene bound side-on to the dimolybdenum centre as a four-electron ligand; this new species undergoes thermal isomerisation to μ-ethyne, reacts with diazomethane to give μ-allene, and is step-wise protonated to afford μ-vinyl then μ-ethylidene.

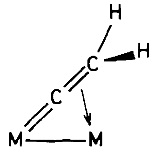
In addition to its common μ_2-bridging mode (**1**), carbon monoxide is also seen occasionally to bridge in the side-on manner (**2**),[1] *i.e.* as a four- rather than two-electron ligand. Vinylidene, on the other hand, is known to bridge a dinuclear metal centre only in the symmetrical way (**3**).[2] We now report that this hydrocarbon can also bridge side-on, as in (**4**), and that its reactivity is markedly different from (**3**) when in this situation.

U.v. irradiation (250 W mercury lamp, water-cooled Pyrex flask, 7 h) of a tetrahydrofuran solution of triply metal–metal bonded $[Mo_2(CO)_4(\eta\text{-}C_5Me_5)_2]$ (**5**) while purging with ethyne gives air-stable blue-black crystalline $[Mo_2(CO)_4(\mu\text{-}\eta^1,\eta^2\text{-}CCH_2)(\eta\text{-}C_5Me_5)_2]$ (**6**)† in *ca.* 40% yield (Scheme 1). *X*-Ray diffraction studies‡ on (**6**) were not definitive, but the nature of the bridging vinylidene ligand was unequivocally established by n.m.r. spectroscopy. Thus, unlike vinylidene ligands of type (**3**), the protons of which have typically olefinic chemical shifts of δ 6—7, the CH_2 group of (**6**) is seen as an AB quartet centred at δ 2.6, a value characteristic of a co-ordinated olefinic unit. In accord, the ^{13}C n.m.r. signal for the CH_2 group also appears at much higher field (δ 45.3) than is typical of (**3**) (*ca.* δ 125). Moreover, the very low field shift (δ 337.3) of the μ-*C*CH₂ carbon in (**6**) indicates the μ-alkylidyne character which is expected for side-on co-ordination, emphasised by the representation (**6b**); for type (**3**) vinylidenes μ-alkylidene-like shifts of δ 240—280 are observed.


(**1**)


(**2**)


(**3**)


(**4**)

The generation of vinylidene ligands from ethyne is well known and the mechanism of the process has been discussed.[3] However, (**6**) provides the first example of the reverse of this transformation; both in the solid state (slowly) and in solution (within 5 min in boiling $[^2H_8]$toluene) isomerisation to the μ-ethyne complex $[Mo_2(CO)_4(\mu\text{-}C_2H_2)(\eta\text{-}C_5Me_5)_2]$ (**7**)† occurs smoothly in an apparently intramolecular manner. Recently, two examples of μ-alkylidyne to μ-vinyl rearrangement ($\mu\text{-C-CHR}_2 \rightarrow \mu\text{-CH=CR}_2$) have been reported,[4] involving a 1,2-hydrogen shift to electron-deficient carbon, and we see the rearrangement of $\mu\text{-}\eta^1,\eta^2$-vinylidene to μ-ethyne ($\mu\text{-C=CH}_2 \rightarrow \mu\text{-CH}\equiv\text{CH}$) as a very related process, consistent with the alkylidyne character of the μ-carbon in (**6**).

Vinylidene ligands (**3**) mono-protonate to form either μ-ethylidyne[5] or μ-vinyl[6] cations. Addition of one equivalent of CF_3CO_2H to (**6**) also results in mono-protonation, yielding the μ-vinyl complex $[Mo_2(CO)_4(\sigma\text{-}O_2CCF_3)(\mu\text{-}CHCH_2)(\eta\text{-}C_5Me_5)_2]$ (**8**),† but with an excess of the acid a second protonation occurs to afford the μ-ethylidene complex $[Mo_2(CO)_4(\mu\text{-}O_2CCF_3)(\mu\text{-}CHMe)(\eta\text{-}C_5Me_5)_2][H(CO_2CF_3)_2]$ (**9**),† involving a change in trifluoroacetate co-ordination from mono- to bi-dentate. Treatment of (**7**) with CF_3CO_2H also provides (**8**) and (**9**) in sequence, whereas the $\eta\text{-}C_5H_5$ analogue of (**7**) gave only the analogue of (**8**),[7] a difference attributable to the greater electron-donor power of $\eta\text{-}C_5Me_5$ compared with $\eta\text{-}C_5H_5$. No products were isolated when (**6**) and (**7**) were acidified with $HBF_4{\cdot}OEt_2$.

Vinylidenes of type (**3**) react in an olefin-like way with diazomethane to yield μ-cyclopropylidene complexes.[8] The unsaturation in complex (**6**), however, lies in a molybdenum–carbon rather than a carbon–carbon bond, and reaction with diazomethane introduces methylene at this site, giving the μ-allene complex $[Mo_2(CO)_4(\mu\text{-}CH_2CCH_2)(\eta\text{-}C_5Me_5)_2]$ (**10**)‡ in 15% yield. The latter is obtained in near-quantitative yield directly from (**5**) and allene. We are currently seeking to exploit the reactivity of the Mo=C double bond in (**6**) in other ways.

In view of the ease with which the four-electron μ-vinylidene ligand rearranges to four-electron μ-ethyne it is perhaps destined to remain a rare species, but $\mu\text{-}\eta^1,\eta^2\text{-}CCR_2$ (R ≠ H) derivatives, for which no such process is likely, may prove less elusive.

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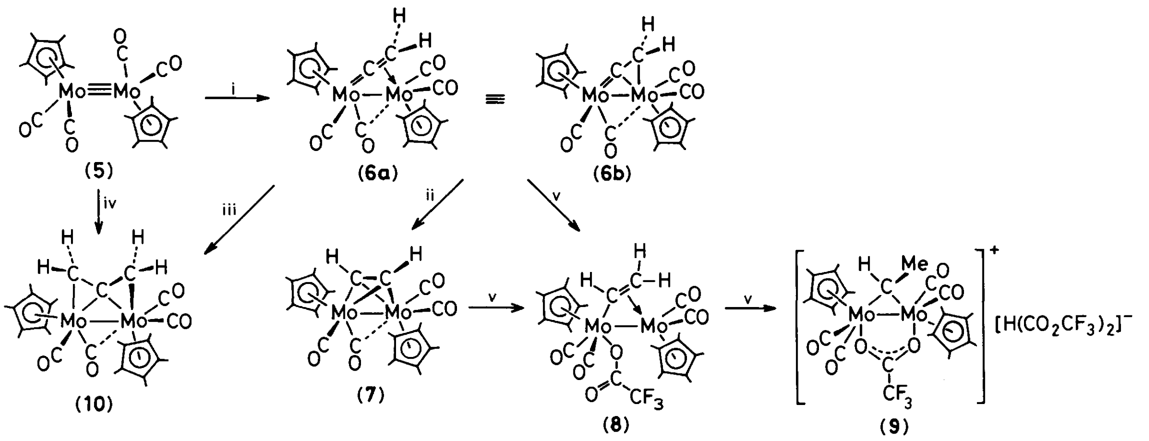
† The new complexes (**6**)—(**10**) were characterised by elemental analyses and mass, i.r., and n.m.r. spectroscopy. Selected spectroscopic data (i.r. in CH_2Cl_2, n.m.r. in $CDCl_3$ unless stated otherwise, coupling constants in Hz): (**6**), blue-black crystals, ν(CO) at 1 952w, 1 898s, 1 869w, and 1 825w cm^{-1}; ^1H n.m.r. δ 1.86 (s, 15 H), 1.87 (s, 15 H), 2.37 (d, *J* 14, 1 H), and 2.84 (d, *J* 14, 1 H); ^{13}C n.m.r. δ 45.3 (CH_2) and 337.3 (μ-C). (**7**), red crystals, ν(CO) at 1 966m, 1 887s, and 1 804m cm^{-1}; ^1H n.m.r. 1.93 (s, 30 H) and 3.74 (s, 2 H); ^{13}C n.m.r. δ 69.6(μ-C). (**8**), red-brown powder, ν(CO) at 2 010s, 1 937s, 1 883m, 1 865sh, and 1 688m (CO_2CF_3) cm^{-1}; ^1H n.m.r. δ 1.78 (s, 30 H), 2.58 (dd, *J* 1 and 9, 1 H), 2.92(dd, *J* 1 and 11, 1 H), and 7.68 (dd, *J* 9 and 11, 1 H). (**9**), orange crystals, ν(CO) at 2 041m, 1 993s, and 1 900m cm^{-1}; ^1H n.m.r. δ 1.85 (d, *J* 8, 3 H), 1.92 (s, 15 H), 2.07 (s, 15 H), and 7.08 (q, *J* 8, 1 H); ^{13}C n.m.r. δ 24.4 (μ-CH*Me*) and 145.5 (μ-*C*HMe); ^{19}F n.m.r. δ −73.8 (3 F) and −75.3 p.p.m. (6 F). (**10**), red crystals, ν(CO) at 1 935m, 1 896s, 1 856m, and 1 831m cm^{-1}; ^1H n.m.r. δ 1.79 (s, 30 H), 2.67 (m, 2 H), and 3.11 (m, 2 H); ^{13}C n.m.r. (in $[^2H_8]$toluene) δ 46.4 (CH_2) and 238.9 (μ-C).

‡ Crystals of (**6**) grown from a variety of solvents have been examined by *X*-ray diffraction at room temperature (ref. 9). The structure is severely disordered about a crystallographic 2-fold rotation axis. The only molecular dimension that can be approximately determined is the Mo–Mo distance [3.082(7) Å], all other atomic positions being very poorly determined. The observed features in electron density maps could not define the molecular structure unambiguously but were consistent with the formulation given in the text.



Scheme 1. *Reagents*, i, C_2H_2, u.v.; ii, boiling [$^2H_8$]toluene; iii, CH_2N_2; iv, allene (2 atm) ; v, CF_3CO_2H.

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