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Preliminary communication

PROTONATION OF μ-ALKYNE-DIMOLYBDENUM COMPLEXES: X-RAY STRUCTURE OF $[Mo_2\{OC(O)CF_3\}(CO)_4(\mu\text{-}CHCH_2)(\eta\text{-}C_5H_5)_2]$

JANE A. BECK, SELBY A.R. KNOX, GEOFFREY H. RIDING, GRAHAM E. TAYLOR, and MARK J. WINTER

Department of Inorganic Chemistry, The University, Bristol BS8 1TS (Great Britain)

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Summary

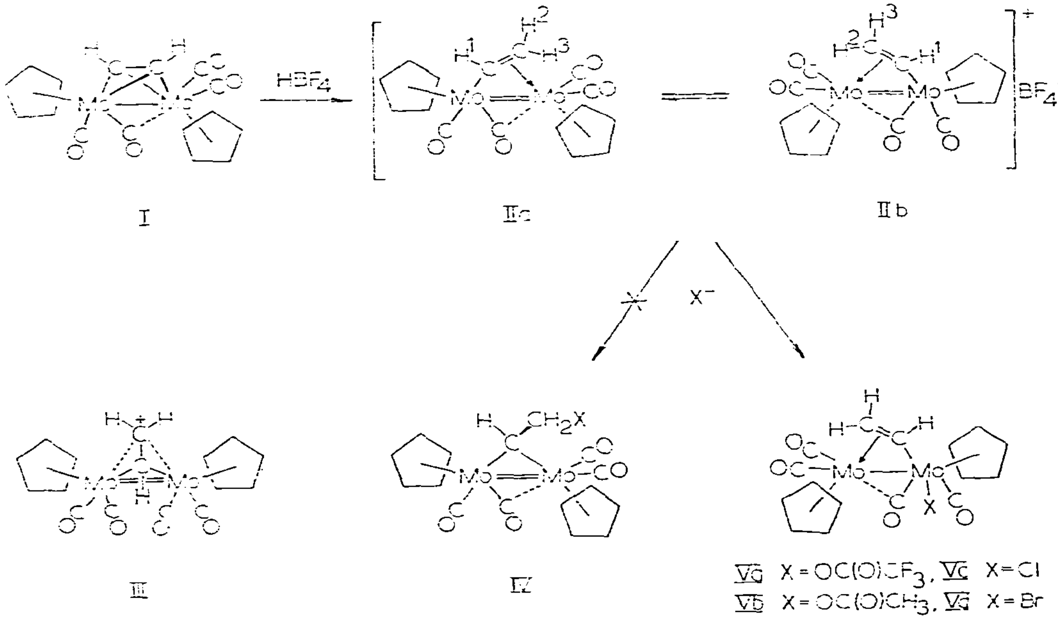
Protonation of the μ-ethyne complex $[Mo_2(CO)_4(\mu\text{-}CHCH)(\eta\text{-}C_5H_5)_2]$ with HBF_4 yields the fluxional μ-vinyl cation $[Mo_2(CO)_4(\mu\text{-}CHCH_2)(\eta\text{-}C_5H_5)_2]^+$ which is attacked at molybdenum by various nucleophiles X^- (X = $OC(O)CF_3$, OC(O)Me, Cl, Br) to produce $[Mo_2(X)(CO)_4(\mu\text{-}CHCH_2)(\eta\text{-}C_5H_5)_2]$; the structure of $[Mo_2\{OC(O)CF_3\}(CO)_4(\mu\text{-}CHCH_2)(\eta\text{-}C_5H_5)_2]$ has been determined by X-ray diffraction.

We recently described [1] the synthesis of μ-carbene complexes of iron and ruthenium through hydride attack upon μ-vinyl cations. The latter were obtained by protonation of complexes derived from alkynes. The existence of μ-alkyne-dimolybdenum complexes such as $[Mo_2(CO)_4(\mu\text{-}CHCH)(\eta\text{-}C_5H_5)_2]$ (I) [2,3] led us to extend our studies to the protonation of these species and their subsequent reactions with nucleophiles. The aim was to obtain μ-carbene-dimolybdenum complexes; we believe [4] such carbenes could have a role in alkene metathesis, which often involves molybdenum catalysts. This aim was not realised. Although an intermediate μ-vinyl cation was formed on protonation of I, this either suffered deprotonation or attack at the metal when subjected to nucleophiles.

Addition of an excess of HBF_4 to a dichloromethane solution of I, followed by ether, precipitated $[Mo_2(CO)_4(\mu\text{-}CHCH_2)(\eta\text{-}C_5H_5)_2][BF_4]$ (II) as a slightly air-sensitive brown microcrystalline powder in 85% yield. The IR spectrum of II shows a pattern of carbonyl bands (2034s, 1962s, 1896s(br) cm^{-1} (CH_2Cl_2)) similar to that of I, but shifted to higher frequencies as expected for a cation, and still with a band attributable to a semi-bridging carbonyl. The ^1H NMR spectrum has, in acetone-d_6 at −45°C, the signals characteristic [1] of a μ-vinyl group (δ 8.89 (dd, J 8 and 12 Hz, 1H), 4.07 (d, J 8 Hz, 1H), 3.29 (d, *J* 12 Hz, 1H)) and inequivalent cyclopentadienyls (δ 5.71 (s, 5H), 5.42 (s, 5H)). The structure II is therefore indicated, with a double metal—metal bond as required by the eighteen-electron rule.

The complex II is fluxional. On warming above −45°C the ^{1}H NMR spectrum varies such that the two C_5H_5 signals broaden and coalesce at 25°C, subsequently becoming a sharp singlet above 55°C. In concert with these changes the signals due to the methylenic protons H(2) and H(3) become very broad at 55°C, while the H(1) signal has merged from a double doublet to a sharp triplet. This clearly implies that, like the C_5H_5 groups, there is time-averaging of the H(2) and H(3) proton environments. However, the reactivity of II towards a wide variety of solvents prevented the observation of a high temperature limiting NMR spectrum. We tentatively attribute the spectral behaviour to the occurrence on NMR time scale of the process IIa ⇌ IIb illustrated. This will effect the required time-averaging of the cyclopentadienyl ligand environments and, provided there is synchronous rotation about the vinylic C—C bond, of the methylenic protons H(2) and H(3). Superficially, the process has features in common with the fluxionality of I [3] and of μ-vinyl ligands in general [1,5]. Previous to II, however, fluxionality of a μ-vinyl has always occurred with the methylenic protons retaining their distinct identities, i.e. without C—C bond rotation, suggesting a transition state in which the plane of the μ-vinyl is perpendicular to the metal—metal bond. For the process IIa ⇌ IIb a transitional species like III must be invoked, with the methylenic protons equivalent following a 90° rotation about the C—C bond. From the coalescence of the cyclopentadienyl NMR signals the free energy of activation is calculated to be ca. 62.5 kJ mol^{-1}.

Treatment of II with hydride, methoxide or cyanide did not provide μ-carbene complexes of type IV as had been hoped. Rather than add to the



μ-vinyl, as occurs for related diiron and diruthenium complexes [1], these nucleophiles effect proton abstraction and regenerate the μ-ethyne complex I. However, other nucleophiles X^- (trifluoroacetate, acetate, chloride, bromide) attack II at molybdenum, forming maroon crystalline complexes $[Mo_2(X)(CO)_4(\mu\text{-}CHCH_2)(\eta\text{-}C_5H_5)_2]$ (V) in good yield (e.g. Va: 65%; m.p. 145°C (decomp.); ν(CO) 2028s, 1958s, 1886s(br) cm^{-1} (CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 8.99 (dd, J 9 and 13 Hz, 1H), 5.29 (s, 5H), 5.13 (s, 5H), 3.99 (d, J 9 Hz, 1H), 3.30 (d, J 13 Hz, 1H); ^{19}F NMR ($CDCl_3$) δ −74.08 ppm (relative to $CFCl_3$)). Complexes Va and Vb may be obtained directly by stoichiometric addition of HX to a dichloromethane solution of I. The retention of the μ-vinyl in V and of a semi-bridging carbonyl group were clearly indicated by the spectra, and the consequential prospect of a monodentate ligand X led us to study the structure of Va by X-ray diffraction.

Crystal data. (Va): $C_{18}H_{13}F_3Mo_2O_6$, M 574.2, triclinic, space group $P\bar{1}$, a 11.769(3). b 8.592(2), c 10.306(2) Å, α 101.79(2), β 89.14(2), γ 107.00(2)°, U 974.4(3) $Å^3$, $Z = 2$, $F(000) = 560$, Mo-K_α X-radiation ($\bar{\lambda}$ 0.710 69 Å), μ(Mo-K_α) 13.15 cm^{-1}.

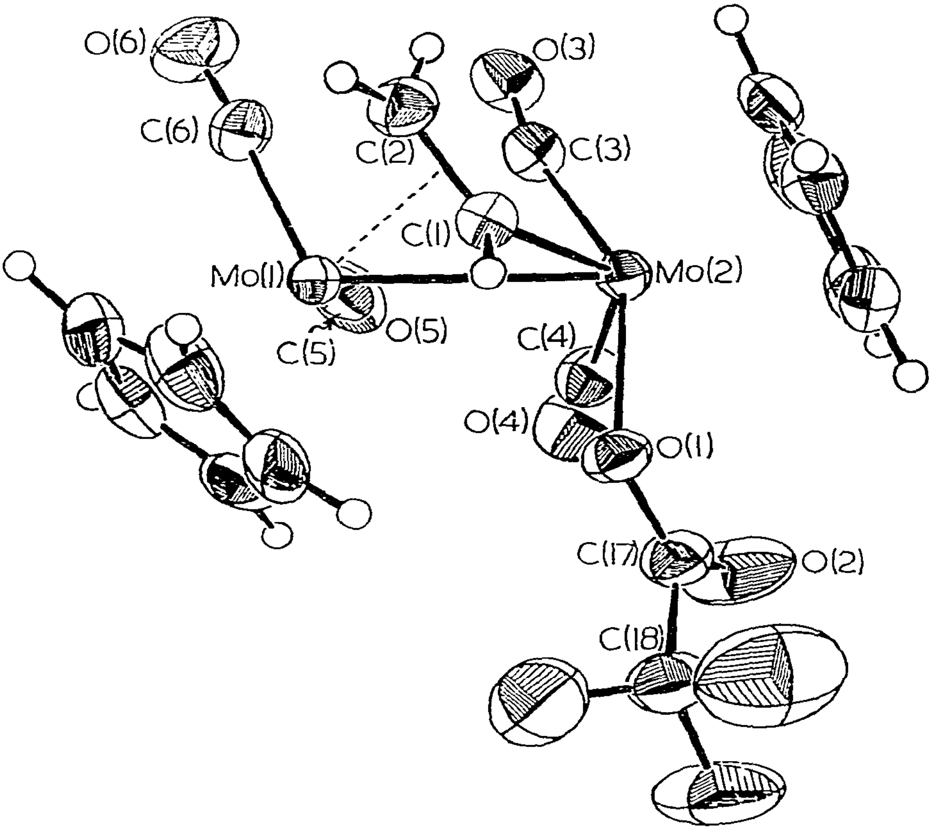


Fig. 1. Molecular structure of $[Mo_2\{OC(O)CF_3\}(CO)_4(\mu\text{-}CHCH_2)(\eta\text{-}C_5H_5)_2]$ (Va). Bond lengths: Mo(1)—Mo(2) 3.085(0), Mo(1)—C(1) 2.210(3), Mo(1)—C(2) 2.364(3), Mo(1)—C(3) 2.963, Mo(1)—C(5) 1.978(3), Mo(1)—C(6) 1.942(4), Mo(2)—C(1) 2.123(3), Mo(2)—C(3) 2.007(3), Mo(2)—C(4) 2.053(3), Mo(2)—O(1) 2.212(2), C(1)—C(2) 1.394(5), C(3)—O(3) 1.148(4), C(4)—O(4) 1.126(4), C(5)—O(5) 1.154(4), C(6)—O(6) 1.151(5), C(17)—O(1) 1.283(6), C(17)—O(2) 1.205(5), C(17)—C(18) 1.534(5), C—F (mean) 1.302(6) Å. Bond angle: Mo(2)—C(3)—O(3) 167.7(3)°.

The structure was solved by conventional heavy-atom methods from data collected to $2\theta = 55°$ at room temperature on a Syntex $P2_1$ diffractometer For a total of 4470 independent reflections collected, of which 3585 were deemed observed ($I > 2.5\sigma(I)$), R is 0.027.

The molecular structure of Va is presented in Fig. 1, together with some significant dimensions. The structure is based on two molybdenum atoms a single bond distance of 3.085 Å, bridged by a μ-vinyl ligand which may be garded as η^1-bonded to Mo(2) through C(1) and η^2-bonded to Mo(1) throug olefinic C(1)—C(2). The C(1)—C(2) length of 1.394(5) Å reflects π-donatio from Mo(1), being ca. 0.06 Å longer than an authentic double bond. Each molybdenum carries two carbonyl ligands and a cyclopentadienyl group, on of the carbonyls (C(3)—O(3)) on Mo(2) being, as expected, semi-bridging w bond lengths and angles comparable to the similar carbonyl in I [3]. In ad tion, Mo(2) bears a distinctly monodentate trifluoroacetate ligand, an unus feature of a binuclear metal complex.

A cation analogous to II is produced when $[Mo_2(CO)_4(\mu\text{-CHCMe})(\eta\text{-}C_5H$ is protonated, and this undergoes similar reactions with a range of nucleop Other efforts to obtain μ-carbene complexes of the chromium group met are in progress.

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