Scission of Ethyne into Two Methylidyne Ligands: C≡C *vs.* C–H Bond Activation

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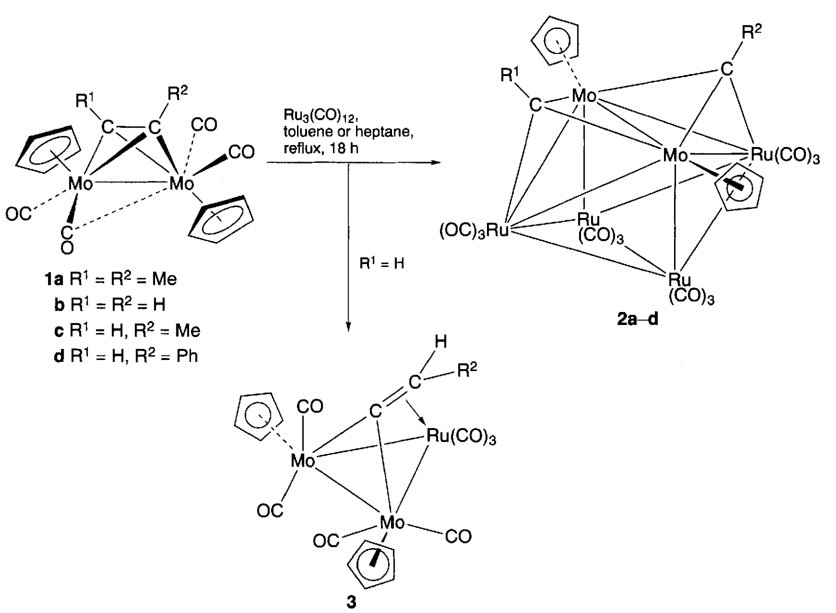
The dimolybdenum alkyne complexes $[Mo_2(CO)_4(\mu\text{-}R^1C_2R^2)(\eta\text{-}C_5H_5)_2]$ ($R^1 = R^2 = Me$; $R^1 = H$, $R^2 = H$, Me, Ph) react with $[Ru_3(CO)_{12}]$ in refluxing toluene or heptane to give the hexanuclear bis(alkylidyne) clusters $[Mo_2Ru_4(\mu_3\text{-}CR^1)(\mu_3\text{-}CR^2)(CO)_{12}(\eta\text{-}C_5H_5)_2]$; this represents the first reported transformation of ethyne into two methylidyne ligands on a metal cluster.

The reactivity of alkynes coordinated to polynuclear metal centres has been the subject of considerable research attention.[1] Activation of the C–H bonds of terminal alkynes is well established, *e.g.* rearrangement into vinylidene ligands by a hydrogen shift or into alkynyl hydride complexes by oxidative addition. Over the past 15 years, however, there have been a number of reports of the activation of alkynes by scission of the C≡C bond to give two alkylidyne fragments. Most of these take place on, or at least lead to, trinuclear complexes,[2] though there are also examples on tetranuclear frameworks[3] and one in a hexaosmium cluster.[4] Virtually all of these reactions involve disubstituted alkynes often with electron-withdrawing substituents such as CF_3, CO_2Me or Ph. Only in one case has such a process been demonstrated for a terminal alkyne: reaction of $[Co(CO)_2(\eta\text{-}C_5H_5)]$ with $HC\equiv CSiMe_3$ gave $[Co_3(\mu_3\text{-}CH)(\mu_3\text{-}CSiMe_3)(\eta\text{-}C_5H_5)_3]$ from which the parent bis(methylidyne) cluster $[Co_3(\mu_3\text{-}CH)_2(\eta\text{-}C_5H_5)_3]$ could then be obtained by protodesilylation.[5] Here we report a unique example of an alkyne scission reaction which occurs for both disubstituted and terminal alkynes, including, remarkably, ethyne itself.

The dimolybdenum alkyne complexes **1** are readily obtained in 75–80% yield from $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ *via* $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$.[6] Thermolysis of the disubstituted derivative **1a** ($R^1 = R^2 = Me$) with 1.5 equiv. of $[Ru_3(CO)_{12}]$ in refluxing toluene for 18 h produces a moderate yield (28%) of the blue, air-stable hexanuclear cluster $[Mo_2Ru_4(\mu_3\text{-}CMe)_2(CO)_{12}(\eta\text{-}C_5H_5)_2]$ **2a** (Scheme 1) which can be isolated by column chromatography. The other products of the reaction are various ruthenium clusters, including $[Ru_6C(CO)_{14}(\eta\text{-}C_6H_5Me)]$, which are also formed when $[Ru_3(CO)_{12}]$ is heated in toluene with no other added reagent.[7]

Spectroscopic data† permitted the identification of the new cluster; the characteristic low-field resonance of the μ_3-alkylidyne groups (δ 353.9) in the ^{13}C NMR spectrum is particularly diagnostic. The X-ray crystal structure of **2a**‡ was determined and is shown in Fig. 1. The metal atoms form an octahedral core with the two $Mo(\eta\text{-}C_5H_5)$ units in adjacent positions; each ruthenium atom bears three carbonyl ligands. The two ethylidyne groups, formed by the scission of the initial but-2-yne ligand, cap the two Mo_2Ru faces of the octahedron. Unusually for an octahedral cluster, **2a** has 84 cluster valence electrons as opposed to the more common 86, but overall it does obey the 18-electron rule. Surprisingly, it is only the second octahedral cluster with a capping alkylidyne ligand to be characterised;[8] the other example is $[Ru_6\text{-}C(\mu_3\text{-}CH)(\mu\text{-}PPh_2)_2(CO)_{10}(\eta\text{-}C_5H_5)]$.[9] Other hexanuclear alkylidyne clusters are rare, but include octahedral $[WRu_5C(\mu\text{-}CPh)(CO)_{14}(\eta\text{-}C_5H_5)]$, in which the alkylidyne bridges a Ru–W edge,[10] and $[Os_6(CO)_{16}(\mu_3\text{-}CPh)(\mu_4\text{-}CPh)]$, which adopts a capped square pyramidal geometry.[4]

Similar reactions between the terminal alkyne complexes **1b–d** ($R^1 = H$, $R^2 = H$, Me, Ph) and $[Ru_3(CO)_{12}]$ in refluxing toluene gave analogous blue clusters only in very low yields, or not at all. Instead, the major products were the orange trinuclear vinylidene clusters **3** (Scheme 1), which will be described elsewhere.[11] However, we found that by changing the solvent to heptane and extending the reaction time to approximately 28 h, low yields (< 10%) of the hexanuclear clusters could be obtained as well, though **3** remained the major product. Complexes **2b–d** were isolated as stable blue solids and characterised by their spectroscopic data. Of particular interest is the bis(methylidyne) cluster **2b**, formed by the unprecedented scission of ethyne; the methylidyne carbons resonate at δ 323.4 in the ^{13}C NMR spectrum and were confirmed as μ_3-CH groups by an attached proton test technique. The intramolecular nature of the alkyne cleavage reaction is confirmed by the fact that the unsymmetrical complexes are the sole products of their respective reactions with no trace of the symmetrical scrambling products, *i.e.* **2c** is formed from **1c**, but **2a** and **2b** are not. The ^{13}C NMR spectra of unsymmetrical **2c** and **2d** show two



Scheme 1

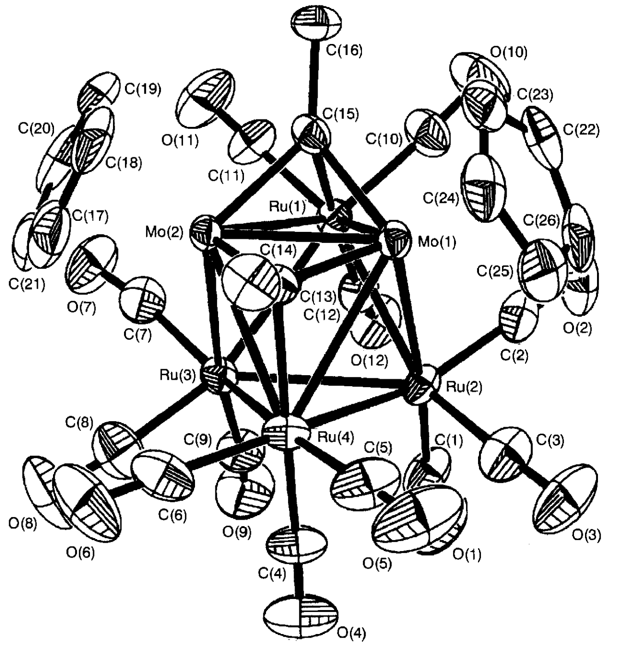


Fig. 1 Molecular structure of [$Mo_2Ru_4(\mu_3\text{-CMe})_2(CO)_{12}(\eta\text{-}C_5H_5)_2$]. Important bond lengths (Å): Ru(1)–Ru(2) 2.8316(9), Ru(1)–Ru(3) 2.8488(8), Ru(2)–Ru(3) 2.9484(8), Ru(2)–Ru(4) 2.8345(8), Ru(3)–Ru(4) 2.8337(8), Mo(1)–Ru(1) 2.9451(8), Mo(1)–Ru(2) 2.8126(9), Mo(1)–Ru(4) 2.9398(9), Mo(1)–Mo(2) 2.5792(8), Mo(2)–Ru(1) 2.9498(8), Mo(2)–Ru(3) 2.8229(9), Mo(2)–Ru(4) 2.9256(9), av. Mo–μ_3-C 2.028, av. Ru–μ_3-C 2.225.

signals for the two different alkylidyne groups, assigned using the attached proton test. The clusters are clearly fluxional in that the symmetrical complexes **2a** and **2b** display three CO resonances in their ^{13}C NMR spectra in an approximate 2 : 4 : 6 ratio, whereas **2c** and **2d** show five signals in a 1 : 1 : 2 : 2 : 6 pattern; the most likely explanation is that the CO ligands bonded to the two ruthenium atoms which bear the alkylidyne ligands are static on the NMR timescale, whereas those attached to the other two ruthenium atoms are undergoing tripodal rotation.

Since none of the other reported reactions of **1** lead to alkyne scission, and there are no examples known on ruthenium clusters, we infer that the active species is probably a mixed-metal cluster. Previous heterometallic cases have involved W_2Os, W_2Ru, WOs_3, Mo_2Ni_2 and Co_2Fe_2 clusters, but this is the first time that alkyne scission has been observed in a Mo–Ru system.[2,3] At present, the mechanism of our reaction and the nuclearity of the species in which the alkyne scission step occurs are both matters of speculation. A further unusual feature is that the reaction appears to be sterically influenced: dimolybdenum complexes derived from hex-3-yne or dimethyl acetylenedicarboxylate did not give any tractable products under these conditions. Our results do, however, agree with those of other workers in that charge transfer (M → π*) from the Group 6 metals to the resulting alkylidyne ligands may be involved in facilitating the process of alkyne scission.[2,3,12] Further mechanistic investigations are currently under way.

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Footnotes

† *Spectroscopic data* (IR in CH_2Cl_2, NMR in $CDCl_3$, all signals are singlets. For mass spectra the highest intensity peak of the molecular ion envelope is reported. Satisfactory analyses were obtained for all new compounds): **2a**: ν(CO)/cm^{-1} 2063m, 2034s, 2012s, 1980w, 1949w; ^1H NMR δ 5.15 (10H, C_5H_5), 4.11 (6H, Me); ^{13}C NMR 353.9 (μ_3-C), 205.5 (2CO), 202.5 (6CO), 194.4 (4CO), 97.3 (C_5H_5), 52.4 (Me); MS *m/z* 1117. **2b**: ν(CO)/cm^{-1} 2068w, 2039s, 2012s, 1980w, 1949w; ^1H NMR 5.58 (2H, CH), 5.06 (10H, C_5H_5); ^{13}C NMR 323.4 (μ_3-CH), 204.7 (2CO), 202.3 (6CO), 192.8 (4CO), 94.2 (C_5H_5); MS *m/z* 1089. **2c**: ν(CO)/cm^{-1} 2064m, 2036s, 2013s, 1980w, 1949w; ^1H NMR 5.51 (1H, CH), 5.04 (10H, C_5H_5), 4.07 (3H, Me); ^{13}C NMR 353.3 (μ_3-CMe), 323.1 (μ_3-CH), 206.2 (CO), 204.0 (CO), 202.4 (6CO), 194.6 (2CO), 192.4 (2CO), 95.7 (C_5H_5), 51.4 (Me); MS *m/z* 1103. **2d**: ν(CO)/cm^{-1} 2066m, 2038s, 2016s, 1986w, 1922w; ^1H NMR 7.31–6.68 (5H, Ph), 5.23 (1H, CH), 4.96 (10H, C_5H_5); ^{13}C NMR 348.5 (μ_3-CPh), 327.7 (μ_3-CH), 207.4 (CO), 202.6 (CO), 202.1 (6CO), 195.3 (2CO), 192.1 (2CO), 166.6 (C_{ipso}), 128.2, 125.4 (Ph), 97.1 (C_5H_5); MS *m/z* 1163.

‡ *Crystal data* for **2a**·CH_2Cl_2: $C_{27}H_{18}Cl_2Mo_2O_{12}Ru_4$, M = 1201.47, monoclinic, space group $P2_1/n$ (a non standard setting of $P2_1/c$ C^5_{2h}, no. 14), a = 15.126(3), b = 14.672(2), c = 15.196(2) Å, β = 91.810(10)°, U = 3370.7(9) Å^3, $F(000)$ = 2280, Mo-Kα radiation ($\bar{\lambda}$ = 0.71073 Å), μ(Mo-Kα) = 2.685 mm^{-1}, Z = 4, D_c = 2.368 g cm^{-3}. Three-dimensional, room temperature X-ray data were collected in the range $3.5 < 2\theta < 45°$ on a Siemens P4 diffractometer by the ω-scan method. The 3861 independent reflections (of 4316 measured) for which $|F|/\sigma(|F|) > 4.0$ were corrected for Lorentz and polarisation effects, but not for absorption. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2. Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement converged at a final R = 0.0384 (wR_2 = 0.0985, for all 4316 data, 424 parameters, mean and maximum δ/σ 0.000, 0.340), with allowance for the thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density −2.035 and 0.683 e A^{-3}. A weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0564{*}P)^2 + 2.98{*}P]$ where $P = (F_o^2 + 2{*}F_c^2)/3$ was used in the latter stages of refinement. Complex scattering factors were taken from the program package SHELXL93[13] as implemented on the Viglen 486dx computer. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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