Rearrangement and Scission of Terminal Alkynes in Dimolybdenum Complexes on Reaction with Ruthenium Carbonyl: Formation of Trinuclear Vinylidene and Hexanuclear Bis(alkylidyne) Clusters

Harry Adams, Louise J. Gill, and Michael J. Morris*,†

Department of Chemistry, University of Sheffield, Sheffield S3 7HF, U.K.

Received March 27, 1996⊗

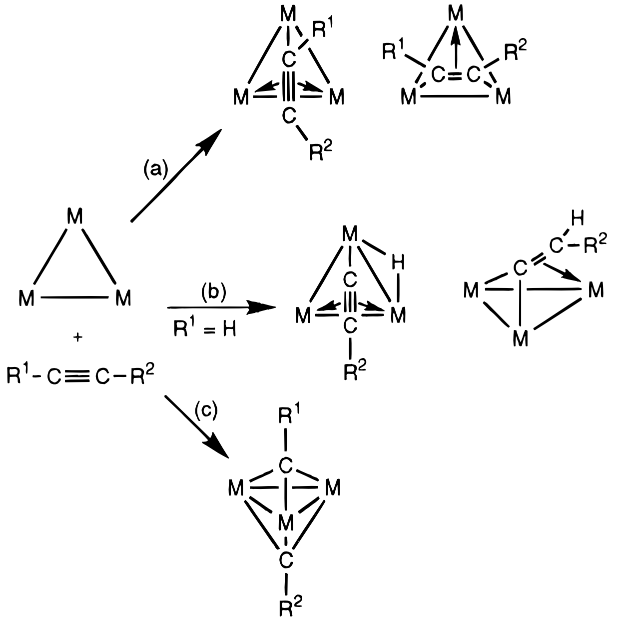
The reaction of the dimolybdenum alkyne complexes $Mo_2(CO)_4(\mu\text{-}R^1C{\equiv}CR^2)Cp_2$ (Cp = $\eta\text{-}C_5H_5$; R^1= H, R^2 = H, Me, Ph, CO_2Me; **1a−d**) with $Ru_3(CO)_{12}$ in refluxing toluene or heptane affords reasonable yields of the orange μ_3-vinylidene clusters $[Mo_2Ru(\mu_3\text{-}C{=}CHR^2)(CO)_7Cp_2]$ (**2a−d**). The crystal structure of $Mo_2Ru(\mu_3\text{-}C{=}CHMe)(CO)_7Cp_2$ (**2b**) has been determined and shows that the metal triangle is capped by a vinylidene ligand which is formally σ-bound to the two molybdenum atoms and π-bound to the ruthenium. Low to moderate yields of the blue-turquoise hexanuclear bis(alkylidyne) clusters $Mo_2Ru_4(\mu_3\text{-}CR^1)(\mu_3\text{-}CR^2)(CO)_{12}Cp_2$ (**3a−d**) are formed in addition to the vinylidene clusters, especially if the reaction is carried out in heptane. The synthesis of **3a** is particularly noteworthy, as it represents the first example of the scission of ethyne into two methylidyne fragments on a metal cluster. The disubstituted alkyne complex **1e** ($R^1 = R^2$ = Me) leads to the corresponding hexanuclear cluster **3e** in either solvent, but complexes of bulkier disubstituted alkynes **1f** and **1g** ($R^1 = R^2$ = Et, CO_2Me) do not give analogous products. The X-ray crystal structure of the cluster $Mo_2Ru_4(\mu_3\text{-}CMe)_2(CO)_{12}Cp_2{\cdot}CH_2Cl_2$ (**3e**·CH_2Cl_2) reveals an octahedral metal core in which the two MoCp fragments occupy adjacent positions, with the two alkylidyne groups formed by scission of the alkyne ligand capping the two Mo_2Ru faces. Unusually for octahedral clusters, complexes of type **3** have 84 cluster valence electrons.

Introduction

The interaction of alkynes with di- and polynuclear metal carbonyls has been under investigation for over 35 years now and is still a subject of considerable research interest.[1] In such complexes, alkynes almost always coordinate as bridging ligands, such as the well-known $\mu_3,\eta^2\text{-}\perp$ and $\mu_3,\eta^2\text{-}\parallel$ bonding modes observed on metal triangles (Scheme 1, path a). Apart from simple coordination, however, they are known to undergo a variety of additional activation processes, e.g. coupling reactions with other ligands present on the cluster, most commonly hydride, CO, or further alkynes, but also alkylidynes and phosphinidenes.[1] Moreover, terminal alkynes often undergo rearrangement to form cluster-bound vinylidenes (i.e. $HC{\equiv}CR \rightarrow {=}C{=}CHR$) or oxidative addition to form alkynyl hydrides ($HC{\equiv}CR \rightarrow HMC{\equiv}CR$) (Scheme 1, path b).[2]

A much rarer form of activation involves the cleavage of the C≡C bond of disubstituted alkynes to produce two alkylidyne ligands (Scheme 1, path c). About 15 examples of this process have been reported since it was first observed; they encompass reactions on, or at least leading to, dinuclear, trinuclear, tetranuclear, hexanuclear, and heptanuclear clusters with both homo- and heterometallic frameworks.[3−5] The reverse process (coupling of two alkylidynes to form an alkyne) is also known,[6] and indeed some of the alkyne scission reactions are reversible. Often the C≡C bond rupture is induced by elimination of a CO ligand from the cluster, either by heating or by use of Me_3NO, and can subsequently be reversed simply by exposure to CO. Recently, the scission of an acetylide ligand into alkylidyne

Scheme 1



---

† E-mail: M.Morris@sheffield.ac.uk.

⊗ Abstract published in *Advance ACS Abstracts,* September 1, 1996.

[1] (a) Hübel, W. In *Organic Syntheses via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Wiley-Interscience: New York, 1968; Chapter 2, p 273. (b) Sappa, E.; Tiripicchio, A.; Braunstein, P. *Chem. Rev.* **1983**, *83*, 203. (c) Sappa, E.; Tiripicchio, A.; Braunstein, P. *Coord. Chem. Rev.* **1985**, *65*, 219. (d) Raithby, P. R.; Rosales, M. J. *Adv. Inorg. Chem. Radiochem.* **1985**, *29*, 169.

[2] (a) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59. (b) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197.

and carbide has been described in the reaction of $WRu_2(\mu_3\text{-}C{\equiv}CPh)(CO)_8Cp$ with $Ru_3(CO)_{12}$ to give $WRu_4(\mu_5\text{-}C)(\mu\text{-}CPh)(CO)_{12}Cp$ and $WRu_5(\mu_6\text{-}C)(\mu\text{-}CPh)(CO)_{14}Cp$; this can also be reversed under CO pressure.[7]

Prior to the work we describe here, only one instance was known of the scission of a terminal alkyne on a metal cluster, specifically the thermal reaction of $Co(CO)_2Cp$ with $HC{\equiv}CSiMe_3$ to give $Co_3(\mu_3\text{-}CH)(\mu_3\text{-}CSiMe_3)Cp_3$, from which the parent bis(methylidyne) cluster $Co_3(\mu_3\text{-}CH)_2Cp_3$ could be obtained by protodesilylation.[8] In most cases, activation of the C$-$H bonds of terminal alkynes is evidently much more favorable than C$\equiv$C scission. One would instinctively expect this on bond strength grounds,[9] but it is somewhat unfortunate, as scission reactions would provide a useful route to clusters containing the simplest hydrocarbon fragment: the methylidyne ligand, μ_3-CH. Methylidyne complexes are of interest as model systems for the behavior of this important species on the catalyst surface during the Fischer$-$Tropsch reaction, where it is thought to be formed by the reduction of the surface carbide resulting from the cleavage of CO;[10] for example, surface methylidyne ligands have been directly detected after hydrogenation of predeposited carbide on a Ru(001) surface.[11] Few general routes to methylidyne clusters exist and usually involve reduction of a CO ligand, modification of a methylene group, or dehalogenation of a C_1 halocarbon such as $CHCl_3$.[12]

This paper reports thermal reactions of the dimolybdenum alkyne complexes **1** with $Ru_3(CO)_{12}$ which apparently involve competing processes of C$-$H and C$-$C activation. By control of the conditions, alkyne scission can be induced in several terminal alkynes, including acetylene itself, to give octahedral Mo_2Ru_4 clusters with methylidyne ligands, albeit in fairly modest yields. A preliminary account of this work has appeared as a communication.[13]

Experimental Section

General experimental techniques were as described in recent papers from this laboratory.[14,15] Infrared spectra were recorded in CH_2Cl_2 solution on a Perkin-Elmer 1600 FT-IR machine using 0.5 mm NaCl cells. UV/visible spectra were recorded in CH_2Cl_2 solution on a Unicam UV2 spectrometer in glass cuvettes of path length 1 cm. ^1H and ^{13}C NMR spectra were obtained in $CDCl_3$ solution on a Bruker AC250 machine with automated sample changer or an AMX400 spectrometer. Chemical shifts are given on the δ scale relative to $SiMe_4$ (0.0 ppm). The $^{13}C\{^1H\}$ NMR spectra were routinely recorded using an attached proton test technique (JMOD pulse sequence). Mass spectra were recorded on a Fisons/BG Prospec 3000 instrument operating in the fast atom bombardment mode with *m*-nitrobenzyl alcohol as matrix. Elemental analyses were carried out by the Microanalytical Service of the Department of Chemistry.

The complex $Mo_2(CO)_6Cp_2$ was prepared by a literature method.[16] The alkyne complexes **1a**$-$**g** were prepared by a slight modification of the literature procedure, described below.[17]

Synthesis of $Mo_2(CO)_4(\mu\text{-}R^1C_2R^2)Cp_2$ (1a$-$g). A solution of $Mo_2(CO)_6Cp_2$ (3 g, 6.12 mmol) in toluene (200$-$300 mL) was refluxed for 24 h with a stream of argon bubbling slowly through it to form $Mo_2(CO)_4Cp_2$. After the mixture was cooled to room temperature, 5 equiv of the appropriate alkyne was added; gaseous alkynes ($HC{\equiv}CH$, $HC{\equiv}CMe$) were bubbled through the solution for a few minutes. After this mixture was stirred overnight, the solvent was removed and the products isolated by column chromatography. Small amounts of unreacted $Mo_2(CO)_6Cp_2$ can sometimes be separated before elution of the product as a dark red band. Typical yields are 75$-$80%; we find that improved yields are consistently ob-

---

(3) Examples on, or leading to, trinuclear clusters are as follows. Co_3: (a) Fritch, J. R.; Vollhardt, K. P. C.; Thomson, M. R.; Day, V. W. *J. Am. Chem. Soc.* **1979**, *101*, 2768. (b) Eaton, B.; O'Connor, J. M.; Vollhardt, K. P. C. *Organometallics* **1986**, *5*, 394. (c) King, R. B.; Murray, R. M.; Davis, R. E.; Ross, P. K. *J. Organomet. Chem.* **1987**, *330*, 115. (d) Yamazaki, H.; Wakatsuki, Y.; Aoki, K. *Chem. Lett.* **1979**, 1041. (e) Quenec'h, P.; Rumin, R.; Pétillon, F. Y. *J. Organomet. Chem.* **1994**, *479*, 93. Co_3 and Rh_3: (f) King, R. B.; Harmon, C. A. *Inorg. Chem.* **1976**, *15*, 879. Co_3, Rh_3 and Ir_3: (g) Clauss, A. D.; Shapley, J. R.; Wilker, C. N.; Hoffmann, R. *Organometallics* **1984**, *3*, 619. Fe_3: (h) Cabrera, E.; Daran, J. C.; Jeannin, Y. *J. Chem. Soc., Chem. Commun.* **1988**, 607. W_2Os: (i) Chi, Y.; Shapley, J. R. *Organometallics* **1985**, *4*, 1900. W_2Ru: (j) Stone, F. G. A.; Williams, M. L. *J. Chem. Soc., Dalton Trans.* **1988**, 2467.

(4) Examples on, or leading to, tetranuclear clusters are as follows. WOs_3: (a) Park, J. T.; Shapley, J. R.; Churchill, M. R.; Bueno, C. *J. Am. Chem. Soc.* **1983**, *105*, 6182. (b) Park, J. T.; Shapley, J. R.; Bueno, C.; Ziller, J. W.; Churchill, M. R. *Organometallics* **1988**, *7*, 2307. (c) Park, J. T.; Woo, B. W.; Chung, J.-H.; Shim, S. C.; Lee, J.-H.; Lim, S.-S.; Suh, I.-H. *Organometallics* **1994**, *13*, 3384. W_2Ir_2: (d) Shapley, J. R.; McAteer, C. H.; Churchill, M. R.; Biondi, L. V. *Organometallics* **1984**, *3*, 1595. WIr_3: (e) Shapley, J. R.; Humphrey, M. G.; McAteer, C. H. *ACS Symp. Ser.* **1993**, *No. 517*, 127. Co_2Fe_2: (f) Rumin, R.; Robin, F.; Pétillon, F. Y.; Muir, K. W.; Stevenson, I. *Organometallics* **1991**, *10*, 2274. Mo_2Ni_2 and Mo_4Co_3: (g) Shaposhnikova, A. D.; Drab, M. V.; Kamalov, G. L.; Pasynskii, A. A.; Eremenko, I. L.; Nefedov, S. E.; Struchkov, Y. T.; Yanovsky, A. I. *J. Organomet. Chem.* **1992**, *429*, 109. (h) Pasynskii, A. A.; Eremenko, I. L.; Nefedov, S. E.; Kolobkov, B. I.; Shaposhnikova, A. D.; Stadnitchenko, R. A.; Drab, M. V.; Struchkov, Y. T.; Yanovsky, A. I. *New J. Chem.* **1994**, *18*, 69.

(5) Examples leading to higher nuclearity clusters are as follows. Ru_6: (a) Haggitt, J. L.; Johnson, B. F. G.; Blake, A. J.; Parsons, S. *J. Chem. Soc., Chem. Commun.* **1995**, 1263. Os_6: (b) Gomez-Sal, M. P.; Johnson, B. F. G.; Kamarudin, R. A.; Lewis, J.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1985**, 1622. (c) Fernandez, J. M.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *Acta Crystallogr., Sect. B* **1978**, *34B*, 3086. (d) Eady, C. R.; Fernandez, J. M.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Sheldrick, G. M. *J. Chem. Soc., Chem. Commun.* **1978**, 421. Os_7: (e) Johnson, B. F. G.; Lewis, J.; Lunniss, J. A.; Braga, D.; Grepioni, F. *J. Chem. Soc., Chem. Commun.* **1988**, 972. (f) Braga, D.; Grepioni, F.; Johnson, B. F. G.; Lewis, J.; Lunniss, J. A. *J. Chem. Soc., Dalton Trans.* **1991**, 2223. (g) Braga, D.; Grepioni, F.; Johnson, B. F. G.; Lewis, J.; Lunniss, J. A. *J. Chem. Soc., Dalton Trans.* **1992**, 1101.

(6) For examples on closely related W_2Ru clusters see: (a) Busetto, L.; Green, M.; Hessner, B.; Howard, J. A. K.; Jeffery, J. C.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1983**, 519. (b) Howard, J. A. K.; Laurie, J. C. V.; Johnson, O.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1985**, 2017. Other examples: (c) Nuel, D.; Dahan, F.; Mathieu, R. *Organometallics* **1985**, *4*, 1436. (d) Lentz, D.; Michael, H. *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 845. (e) Vollhardt, K. P.; Wolfgruber, M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 929.

(7) Chiang, S.-J.; Chi, Y.; Su, P.-C.; Peng, S.-M.; Lee, G.-H. *J. Am. Chem. Soc.* **1994**, *116*, 11181.

(8) Fritch, J. R.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 559. A further example was observed in solution, but the product was not isolated: Hriljac, J. A.; Shriver, D. F. *J. Am. Chem. Soc.* **1987**, *109*, 6011.

(9) Estimates of the C$-$H and C$\equiv$C bond strengths in acetylene are 535 and 960 kJ mol^{-1}, respectively. Even when allowance is made for the weakening of the C$\equiv$C bond on coordination of the alkyne to a dimolybdenum center, it is still the stronger of the two; for example in complexes **1** the C$\equiv$C bond length is around 1.33 Å, similar to that in ethylene (1.337 Å), where the C$=$C bond strength is 719 kJ mol^{-1}. Data from: Weast, R. C., Ed. *Handbook of Chemistry and Physics*; CRC Press: Boca Raton, FL, 1977.

(10) (a) Muetterties, E. L.; Rhodin, T. N.; Band, E.; Brucker, C. F.; Pretzer, W. R. *Chem. Rev.* **1979**, *79*, 91. (b) Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479. (c) Rofer-DePoorter, C. K. *Chem. Rev.* **1981**, *81*, 447. (d) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 117.

(11) Barteau, M. A.; Feulner, P.; Stengl, R.; Broughton, J. Q.; Menzel, D. *J. Catal.* **1985**, *94*, 51.

(12) Akita, M.; Noda, K.; Moro-oka, Y. *Organometallics* **1994**, *13*, 4145 and references therein.

(13) Adams, H.; Gill, L. J.; Morris, M. J. *J. Chem. Soc., Chem. Commun.* **1995**, 899; see also correction on p 1309.

(14) Adams, H.; Gill, L. J.; Morris, M. J. *Organometallics* **1996**, *15*, 464.

(15) Adams, H.; Bailey, N. A.; Gill, L. J.; Morris, M. J.; Wildgoose, F. A. *J. Chem. Soc., Dalton Trans.* **1996**, 1437.

(16) King, R. B. *Organometallic Syntheses*; Academic Press: New York, 1965; Vol. 1, p 109.

(17) Bailey, W. I., Jr.; Chisholm, M. H.; Cotton, F. A.; Rankel, L. A. *J. Am. Chem. Soc.* **1978**, *100*, 5764.

tained by stirring the second stage of the reaction overnight as opposed to the 4 h recommended previously.[17]

Synthesis of $Mo_2Ru(\mu_3\text{-}C{=}CH_2)(CO)_7Cp_2$ (2a). A solution of **1a** (250 mg, 0.543 mmol) and $Ru_3(CO)_{12}$ (521 mg, 0.815 mmol) in 175 mL of toluene was heated to reflux. The reaction was monitored by TLC until the starting material had disappeared. After 22 h, silica (5 g) was added, the solvent was removed on a rotary evaporator, and the residue was loaded onto a chromatography column. Elution with petroleum ether and then petroleum ether/CH_2Cl_2 (19:1) removed a yellow band containing $Ru_3(CO)_{12}$ followed by faint orange, pink, pink, and blue bands, the last of these consisting of minute quantities of **3a**. Careful elution with petroleum ether/CH_2Cl_2 (9:1) produced an orange band of **2a** (137 mg, 0.212 mmol, 39.0%) followed by a darker red-brown zone of $Ru_6(\mu_6\text{-}C)(CO)_{14}(\eta\text{-}C_6H_5Me)$ (31 mg, 0.028 mmol, 7.0%).

2a: IR ν(CO) 2058 s, 2001 s, 1983 m, 1961 m, 1916 w, 1840 m cm^{-1}; ^{1}H NMR δ 5.21 (s, 10 H, Cp), 4.61 (s, 2 H, CH_2); ^{13}C NMR δ 295.9 (μ_3-C), 231.0 (Mo—CO), 226.9 (Mo—CO), 198.5 (Ru—CO), 195.2 (2 Ru—CO), 91.1 (Cp), 71.2 (CH_2); MS *m/e* 646 (M$^+$). Anal. Calcd for $C_{19}H_{12}O_7Mo_2Ru$: C, 35.35; H, 1.75. Found: C, 35.18; H, 1.75.

Synthesis of $Mo_2Ru(\mu_3\text{-}C{=}CHMe)(CO)_7Cp_2$ (2b). In a manner similar to that above, a mixture of **1b** (1.95 g, 4.07 mmol) and $Ru_3(CO)_{12}$ (2.56 g, 4.00 mmol) in toluene (150 mL) was heated to reflux for 18 h. Chromatography, with petroleum ether as eluent, gave a small amount of $Ru_3(CO)_{12}$ followed by $H_2Ru_4(CO)_{13}$ (117.4 mg). Subsequent elution with petroleum ether/CH_2Cl_2 (19:1) afforded a blue band of **3b** (114.1 mg, 0.103 mmol, 2.6%). Elution with petroleum ether/CH_2Cl_2 (4:1 and then 3:1) produced two major fractions, orange-red **2b** (1.1684 g, 1.77 mmol, 44.3%) and red-brown $Ru_6(\mu_6\text{-}C)(CO)_{14}(\eta\text{-}C_6H_5Me)$ (155.3 mg, 0.142 mmol, 3.6%). A large black band (300 mg), which presumably consists of higher nuclearity ruthenium clusters judging from the absence of any Cp signals in its ^{1}H NMR spectrum, could be eluted in CH_2Cl_2 but was not investigated further.

2b: IR ν(CO) 2056 s, 1998 s, 1982 m, 1962 m, 1909 w, 1841 m cm^{-1}; ^{1}H NMR δ 5.21 (q, J = 6 Hz, 1 H, CH), 5.15 (s, 5 H, Cp), 5.08 (s, 5 H, Cp), 1.83 (d, J = 6 Hz, 3 H, Me); ^{13}C NMR δ 290.6 (μ_3-C), 233.8, 230.7, 229.5, 222.8 (all Mo—CO), 198.4, 197.2, 193.5 (all Ru—CO), 91.5 (Cp), 91.1 (*C*HMe), 90.5 (Cp), 29.3 (Me); MS *m/e* 660 (M$^+$). Anal. Calcd for $C_{20}H_{14}O_7Mo_2Ru$: C, 36.42; H, 2.12. Found: C, 36.42; H, 1.99.

Synthesis of $Mo_2Ru(\mu_3\text{-}C{=}CHPh)(CO)_7Cp_2$ (2c). A solution of **1c** (0.75 g, 0.93 mmol) and $Ru_3(CO)_{12}$ (0.894 g, 1.40 mmol) in toluene was heated to reflux for 18 h. The reaction mixture was subjected to chromatographic workup as before. Petroleum ether eluted small amounts of $Ru_3(CO)_{12}$ and $H_2Ru_4(CO)_{13}$. After descent of a faint pink band, a blue band of **3c** (35 mg, 0.03 mmol, 3.2%) was eluted with petroleum ether/CH_2Cl_2 (9:1), followed by an unidentified yellow-green zone and then orange **2c** (204 mg, 0.28 mmol, 30.4%). Finally, a small amount of $Ru_6(\mu_6\text{-}C)(CO)_{14}(\eta\text{-}C_6H_5Me)$ was collected.

2c: IR ν(CO) 2058 s, 2001 s, 1983 m, 1964 m, 1911 w, 1845 m cm^{-1}; ^{1}H NMR δ 7.40−7.19 (m, 5 H, Ph), 6.28 (s, 1 H, CH), 5.25 (s, 5 H, Cp), 5.12 (s, 5 H, Cp); ^{13}C NMR δ 290.6 (μ_3-C), 233.7, 229.9, 229.6, 222.5 (all Mo—CO), 198.3, 197.7, 192.2 (all Ru—CO), 143.9 (C_{ipso}), 128.1, 127.7, 127.0 (all Ph), 98.9 (*C*HPh), 92.5 (Cp), 91.2 (Cp); MS *m/e* 722 (M$^+$). Anal. Calcd for $C_{25}H_{16}O_7Mo_2Ru$: C, 41.61; H, 2.22. Found: C, 41.58; H, 2.13.

Synthesis of $Mo_2Ru(\mu_3\text{-}C{=}CHCO_2Me)(CO)_7Cp_2$ (2d) and $Mo_2Ru_4(\mu_3\text{-}CH)(\mu_3\text{-}CCO_2Me)(CO)_{12}Cp_2$ (3d). A solution of **1d** (300 mg, 0.58 mmol) and $Ru_3(CO)_{12}$ (550 mg, 0.86 mmol) in heptane was heated to reflux for 24 h. Column chromatography of the products yielded two major fractions: blue **3d** (110.3 mg, 0.10 mmol, 16.6%), which was eluted by petroleum ether/CH_2Cl_2 (3:1), and then orange **2d** (177.5 mg, 0.25 mmol, 43.6%), which was eluted by a 3:2 mixture of the same solvents.

2d: IR ν(CO) 2062 s, 2006 s, 1989 m, 1967 m, 1923 w cm^{-1}; ^{1}H NMR δ 5.29 (s, 5 H, Cp), 5.17 (s, 5 H, Cp), 5.11 (s, 1 H, CH), 3.69 (s, 3 H, Me); ^{13}C NMR δ 299.1 (μ_3-C), 231.5, 229.4, 228.8, 222.3 (all Mo—CO), 197.8, 196.5, 193.1 (all Ru—CO), 172.0 (*C*O$_2$Me), 93.2 (Cp), 90.8 (Cp), 79.5 (CH), 51.6 (Me); MS *m/e* 705 (M$^+$). Anal. Calcd for $C_{21}H_{14}O_9Mo_2Ru{\cdot}CH_2Cl_2$: C, 33.50; H, 2.03. Found: C, 33.92; H, 1.78.

3d: IR ν(CO) 2071 w, 2046 s, 2019 s, 1980 w, 1955 w cm^{-1}; UV/vis λ_{max} 312 nm (ϵ 14 430 dm^3 mol^{-1} cm^{-1}), 589 nm (ϵ 2290 dm^3 mol^{-1} cm^{-1}); ^{1}H NMR δ 16.32 (s, 1 H, μ_3-CH), 5.16 (s, 10 H, Cp), 3.96 (s, 3 H, Me); ^{13}C NMR δ 324.7 (μ_3-CH), 317.3 (μ_3-CCO$_2$Me), 204.9 (CO), 203.8 (CO), 201.7 (6 CO), 192.6 (2 CO), 192.5 (2 CO), 182.6 (*C*O$_2$Me), 96.1 (Cp), 52.7 (Me); MS *m/e* 1147 (M$^+$). Anal. Calcd for $C_{26}H_{14}O_{14}Mo_2Ru_4$: C, 27.23; H, 1.22. Found: C, 27.14; H, 1.23.

Synthesis of $Mo_2Ru_4(\mu_3\text{-}CH)_2(CO)_{12}Cp_2$ (3a). A solution of **1a** (1.00 g, 2.17 mmol) and $Ru_3(CO)_{12}$ (1.389 g, 2.17 mmol) in heptane (175 mL) was heated to reflux for 24 h. After this time TLC indicated the presence of unreacted dimolybdenum complex; a further 0.5 equiv of $Ru_3(CO)_{12}$ was added and heating continued for a further 20 h. The mixture was then absorbed onto silica and chromatographed. Elution with petroleum ether gave a yellow band of $Ru_3(CO)_{12}$ followed by an orange band of $H_4Ru_4(CO)_{12}$ (351 mg, 0.471 mmol, 10.9%). After a faint pink band, the blue cluster **3a** (106.3 mg, 0.098 mmol, 4.5%) was separated by careful elution with petroleum ether/CH_2Cl_2 (19:1). Orange **2a** (538.1 mg, 0.834 mmol, 38.4%) was then eluted with petroleum ether/CH_2Cl_2 (5:1).

3a: IR ν(CO) 2068 w, 2039 s, 2012 s, 1980 w, 1949 w cm^{-1}; UV/vis λ_{max} 317 nm (ϵ 8700 dm^3 mol^{-1} cm^{-1}), 589 nm (ϵ 1440 dm^3 mol^{-1} cm^{-1}); ^{1}H NMR δ 16.58 (s, 2 H, μ_3-CH), 5.06 (s, 10 H, Cp); ^{13}C NMR δ 323.4 (μ_3-CH), 204.7 (2 CO), 202.3 (6 CO), 192.8 (4 CO), 94.2 (Cp); MS *m/e* 1089 (M$^+$). Anal. Calcd for $C_{24}H_{12}O_{12}Mo_2Ru_4$: C, 26.47; H, 1.10. Found: C, 25.99; H, 1.03.

Synthesis of $Mo_2Ru_4(\mu_3\text{-}CH)(\mu_3\text{-}CMe)(CO)_{12}Cp_2$ (3b). A solution of **1b** (850 mg, 1.79 mmol) and $Ru_3(CO)_{12}$ (1.71 g, 2.69 mmol) in heptane (200 mL) was refluxed for 33 h. Chromatographic separation of the product mixture, with petroleum ether as eluent, gave a small amount of $Ru_3(CO)_{12}$ and 400 mg of $H_2Ru_4(CO)_{13}$. Careful elution with petroleum ether/CH_2Cl_2 (19:1) produced a blue band of **3b** (182 mg, 0.165 mmol, 9.2%). Finally, an orange band of **2b** (656.9 mg, 1.00 mmol, 55.8%) was removed with petroleum ether/CH_2Cl_2 (4:1).

3b: IR ν(CO) 2064 m, 2036 s, 2013 s, 1980 w, 1949 w cm^{-1}; UV/vis λ_{max} 313 nm (ϵ 15 360 dm^3 mol^{-1} cm^{-1}), 589 nm (ϵ 2550 dm^3 mol^{-1} cm^{-1}); ^{1}H NMR δ 16.60 (s, 1 H, μ_3-CH), 5.04 (s, 10 H, Cp), 4.07 (s, 3 H, Me); ^{13}C NMR δ 353.3 (μ_3-CMe), 323.1 (μ_3-CH), 206.2 (CO), 204.0 (CO), 202.4 (6 CO), 194.6 (2 CO), 192.4 (2 CO), 95.7 (Cp), 51.4 (Me); MS *m/e* 1103 (M$^+$). Anal. Calcd for $C_{25}H_{14}O_{12}Mo_2Ru_4$: C, 27.22; H, 1.27. Found: C, 27.06; H, 1.18.

Synthesis of $Mo_2Ru_4(\mu_3\text{-}CH)(\mu_3\text{-}CPh)(CO)_{12}Cp_2$ (3c). A solution of **1c** (500 mg, 0.93 mmol) and $Ru_3(CO)_{12}$ (894 mg, 1.40 mmol) in heptane (150 mL) was heated to reflux for 30 h and subjected to chromatographic workup as above. After elution of $Ru_3(CO)_{12}$ and **1c**, cluster **3c** was eluted with CH_2Cl_2/petroleum ether (1:4) as a blue band (81 mg, 0.07 mmol, 7.5%). Further elution with a 2:3 mixture of the same solvents produced an orange band of **2c** (402 mg, 37.0%).

3c: IR ν(CO) 2066 m, 2038 s, 2016 s, 1986 w, 1922 w cm^{-1}; UV/vis λ_{max} 308 nm (ϵ 17 820 dm^3 mol^{-1} cm^{-1}), 605 nm (ϵ 3670 dm^3 mol^{-1} cm^{-1}); ^{1}H NMR δ 16.86 (s, 1 H, CH), 7.31−6.68 (m, 5 H, Ph), 4.96 (s, 10 H, Cp); ^{13}C NMR δ 348.5 (μ_3-CPh), 327.7 (μ_3-CH), 207.4 (CO), 202.6 (CO), 202.1 (6 CO), 195.3 (2 CO), 192.1 (2 CO), 166.6 (C_{ipso}), 128.2, 125.4 (Ph), 97.1 (Cp); MS *m/e* 1163 (M$^+$). Anal. Calcd for $C_{30}H_{16}O_{12}Mo_2Ru_4$: C, 30.93; H, 1.37. Found: C, 30.63; H, 1.31.

Synthesis of $Mo_2Ru_4(\mu_3\text{-}CMe)_2(CO)_{12}Cp_2$ (3e). A solution of **1e** (250 mg, 0.51 mmol) and $Ru_3(CO)_{12}$ (491 mg, 0.77 mmol) in toluene was refluxed for 18 h. Chromatography produced a weak red band of dimolybdenum starting material followed by a blue band due to **3e** (158.7 mg, 0.14 mmol, 27.8%), which

Table 1. Summary of Crystallographic Data for Complexes 2b and 3e·CH$_2$Cl$_2$

	2b	**3e**·CH$_2$Cl$_2$
identification code	lg123x	lg514
formula	$C_{20}H_{14}Mo_2O_7Ru$	$C_{27}H_{18}Cl_2Mo_2O_{12}Ru_4$
fw	659.26	1201.47
temp, K	293(2)	293(2)
wavelength, Å	0.710 73	0.710 73
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
unit cell dimens	$a = 9.3070(10)$ Å, $b = 16.190(2)$ Å, $c = 13.9550(10)$ Å, $\beta = 96.350\ (10)°$	$a = 15.126(3)$ Å, $b = 14.672(2)$ Å, $c = 15.196(2)$ Å, $\beta = 91.810(10)°$
V, Å^3	2089.8 (4)	3370.7 (9)
Z	4	4
density (calcd), Mg/m^3	2.095	2.368
abs coeff, mm^{-1}	1.934	2.685
$F(000)$	1272	2280
cryst size, mm	0.65 × 0.44 × 0.35	0.65 × 0.40 × 0.40
θ range for data collection, deg	1.93−22.5	1.87−22.51
index ranges	$-1 \leq h \leq 10$, $-1 \leq k \leq 17$, $-15 \leq l \leq 15$	$-1 \leq h \leq 14$, $-1 \leq k \leq 15$, $-16 \leq l \leq 16$
no. of rflns collected	3435	5365
no. of indep rflns	2715 ($R_{int} = 0.0450$)	4316 ($R_{int} = 0.0233$)
refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2
no. of data/restraints/params	2715/0/271	4315/0/424
goodness of fit on F^2	1.274	1.224
final R indices (I > 2$\sigma(I)$)	R1 = 0.0476, wR2 = 0.1205	R1 = 0.0384, wR2 = 0.0985
R indices (all data)	R1 = 0.0498, wR2 = 0.1225	R1 = 0.0436, wR2 = 0.1018
largest diff peak and hole, e Å^{-3}	0.722 and −2.711	0.683 and −2.035

was eluted in petroleum ether/CH$_2$Cl$_2$ (9:1). A small band of $Ru_6(\mu_6\text{-}C)(CO)_{14}(\eta\text{-}C_6H_5Me)$ was also collected. The reaction can also be performed in heptane with no significant change in yield.

3e: IR ν(CO) 2063 m, 2034 s, 2012 s, 1980 w, 1949 w cm^{-1}; UV/vis λ_{max} 310 nm (ϵ 15 430 dm^3 mol^{-1} cm^{-1}), 582 nm (ϵ 3030 dm^3 mol^{-1} cm^{-1}); ^{1}H NMR δ 5.15 (s, 10 H, Cp), 4.11 (s, 6 H, Me); ^{13}C NMR δ 353.9 (μ_3-C), 205.5 (2 CO), 202.5 (6 CO), 194.4 (4 CO), 97.3 (Cp), 52.4 (Me); MS m/e 1117 (M$^+$). Anal. Calcd for $C_{26}H_{16}O_{12}Mo_2Ru_4$: C, 27.96; H, 1.43. Found: C, 27.81; H, 1.36.

Crystal Structure Determinations of 2b and 3e. The crystal data for the two structures are summarized in Table 1. Three-dimensional, room-temperature X-ray data were collected on a Siemens P4 diffractometer by the ω-scan method. The independent reflections for which $|F|/\sigma(|F|) > 4.0$ were corrected for Lorentz and polarization effects, but not for absorption. The structures were solved by direct methods and refined by full-matrix least squares on F^2. Hydrogen atoms were included in calculated positions and refined in the riding mode. Refinement converged at the final R values shown with allowance for the thermal anisotropy of all non-hydrogen atoms. Weighting schemes $w = 1/[\sigma^2(F_o{}^2) + (0.0748P)^2 + 1.57P]$ (for **2b**) and $w = 1/[\sigma^2(F_o{}^2) + (0.0564P)^2 + 2.98P]$ (for **3e**), where $P = (F_o{}^2 + 2F_c{}^2)/3$, were used in the latter stages of refinement. Complex scattering factors were taken from the program package SHELXL93,[18] as implemented on the Viglen 486dx computer.

Results and Discussion

Synthesis of Vinylidene Clusters 2a−d. The dimolybdenum alkyne complexes $Mo_2(CO)_4(\mu\text{-}R^1C{\equiv}CR^2)Cp_2$ (**1a−g**) can be conveniently prepared in 75−80% yield by a one-pot process from $Mo_2(CO)_6Cp_2$.[17] The incorporation of the alkyne ligand greatly modifies the reactivity of the dimolybdenum center compared to $Mo_2(CO)_6Cp_2$ and $Mo_2(CO)_4Cp_2$, both of which have been extensively studied.[19] As a result, we and others have shown previously that the alkyne compounds can act as useful starting materials for further reactions with phosphines, thiols, or elemental sulfur and that the products obtained often retain the alkyne ligands.[20] Moreover, their identities depend on the electronic and steric properties of R^1 and R^2, the alkyne substituents. For this reason we always tend to explore the reactions of a range of such compounds rather than just a single example.

One of the established routes to higher nuclearity alkyne clusters is the reaction of preformed alkyne complexes with suitable metal fragments. Initially our objective in this work was to explore whether compounds of type **1** could be used as precursors to higher nuclearity alkyne clusters, since similar cluster-forming reactions are already known for related alkyne complexes such as $Co_2(CO)_6(\mu\text{-}R^1C_2R^2)$, $Ni_2(\mu\text{-}C_2Ph_2)Cp_2$, and recently $Ru_2(\mu\text{-}CO)(\mu\text{-}C_2R_2)Cp_2$ (R = Ph, CF$_3$).[3e,4f−h,21]

Scheme 2 shows the reactions carried out in the present work. Heating the terminal alkyne complexes **1a−d** (R^1 = H, R^2 = H, Me, Ph, CO$_2$Me) in toluene with 1−1.5 equiv of $Ru_3(CO)_{12}$ resulted in the gradual disappearance of the red dimolybdenum compound and the formation of two major products (one orange and one slightly darker red), as monitored by TLC. Separation by careful column chromatography provided the vinylidene clusters $Mo_2Ru(\mu_3\text{-}C{=}CHR^2)(CO)_7Cp_2$ (**2a−d**) as air-stable orange-red solids in moderate yields (30−45%). In each case the second product obtained was the hexanuclear carbido cluster $Ru_6(\mu_6\text{-}C)(CO)_{14}(\eta\text{-}C_6H_5Me)$, which is known to be formed when $Ru_3(CO)_{12}$ is heated

---

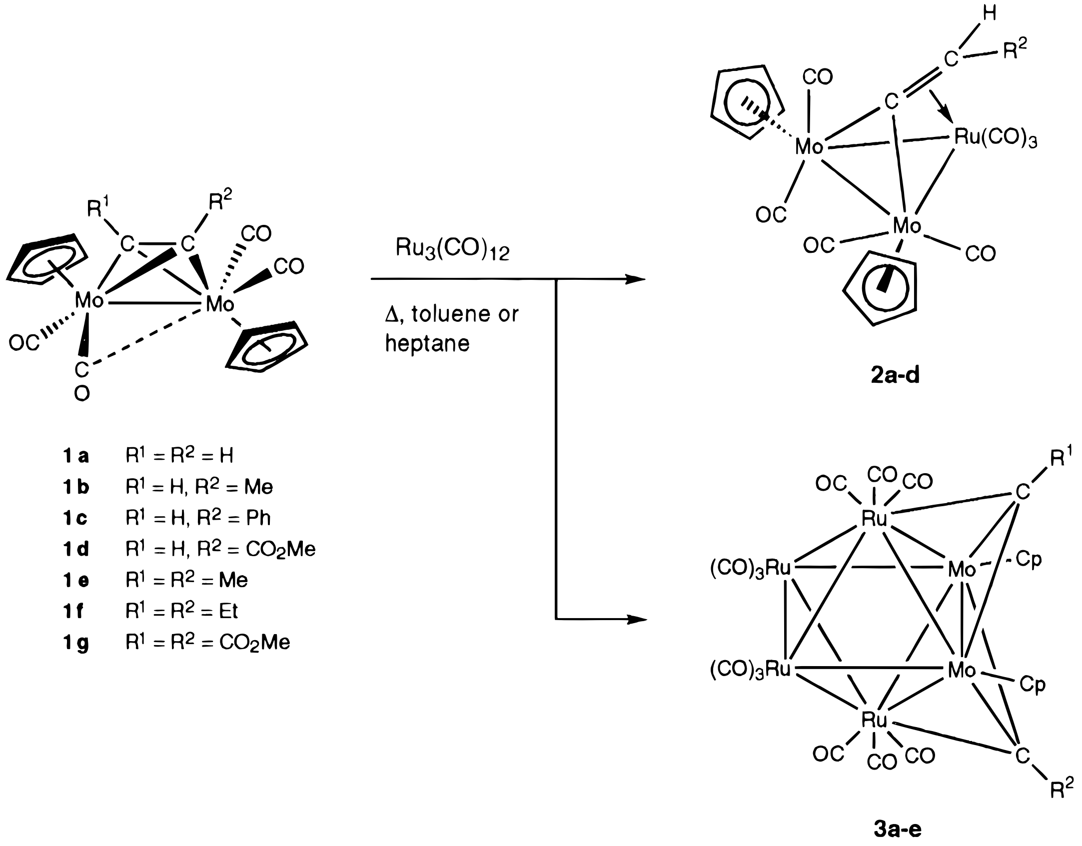
[18] Sheldrick, G. M. SHELXL93, an Integrated System for Solving and Refining Crystal Structures from Diffraction Data (Revision 5.1); University of Göttingen: Göttingen, Germany, 1993.

[19] (a) Curtis, M. D. *Polyhedron* **1987**, *6*, 759. (b) Winter, M. J. *Adv. Organomet. Chem.* **1989**, *29*, 101. (c) Morris, M. J. In *Comprehensive Organometallic Chemistry II*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 5, Chapter 7.

[20] (a) Doel, G. R.; Feasey, N. D.; Knox, S. A. R.; Orpen, A. G.; Webster, J. *J. Chem. Soc., Chem. Commun.* **1986**, 542. (b) Conole, G.; Hill, K. A.; McPartlin, M.; Mays, M. J.; Morris, M. J. *J. Chem. Soc., Chem. Commun.* **1989**, 688. (c) Conole, G.; McPartlin, M.; Mays, M. J.; Morris, M. J. *J. Chem. Soc., Dalton Trans.* **1990**, 2359. (d) Adams, H.; Bailey, N. A.; Gay, S. R.; Hamilton, T,; Morris, M. J. *J. Organomet. Chem.* **1995**, *493*, C25. (e) Abbott, A.; Bancroft, M. N.; Gill, L. J.; Morris, M. J.; Hogarth, G.; Redmond, S. Manuscript in preparation.

[21] (a) Robin, F.; Rumin, R.; Pétillon, F. Y.; Foley, K.; Muir, K. W. *J. Organomet. Chem.* **1991**, *418*, C33. (b) Adams, K. J.; Barker, J. J.; Charmant, J. P. H.; Ganter, C.; Klatt, G.; Knox, S. A. R.; Orpen, A. G.; Ruile, S. *J. Chem. Soc., Dalton Trans.* **1994**, 477.

Scheme 2



in toluene.[22] In some reactions (particularly those of **1c**), low yields (*i.e.* traces) of the hexanuclear bis(alkylidyne) clusters **3** described below were also obtained.

The vinylidene clusters **2a**−**d** were characterized by their IR, ^{1}H and ^{13}C NMR, and mass spectra. All show a similar pattern of six peaks in the IR spectrum consisting of two sharp absorptions, which we ascribe to the Ru(CO)$_3$ unit, and four broader peaks at lower wavenumber, which we assign to the Mo−CO groups. The presence of the vinylidene ligand is evident from the NMR spectra; thus, the ^{1}H NMR spectrum of **2b** shows a doublet and a quartet ($J = 6$ Hz) characteristic of a =CHMe group, and the ^{13}C spectra of all four compounds contain a peak between 290 and 296 ppm due to the μ_3-C atom and a peak between 70 and 100 ppm due to the β-carbon. The spectra were recorded with an attached proton test technique (JMOD spectrum), which enabled this peak to be identified as a CH$_2$ (for **2a**) or CHR^2 carbon (for **2b**−**d**) as appropriate. In addition, the ^{13}C NMR spectra display two groups of carbonyl peaks, those between 220 and 235 ppm assigned to the Mo−CO groups and others in the range 190−200 ppm assigned to the CO ligands on Ru. Complex **2a** evidently has a symmetrical structure in solution, leading to four CO peaks in a ratio of 2:2:2:1, whereas in the unsymmetrical compounds **2b**−**d**, all seven CO ligands are inequivalent. This asymmetry is also reflected in the Cp signals in both ^{1}H and ^{13}C NMR spectra. The complexes all gave clear molecular ion peaks in their FAB mass spectra, with peaks corresponding to CO losses also present.

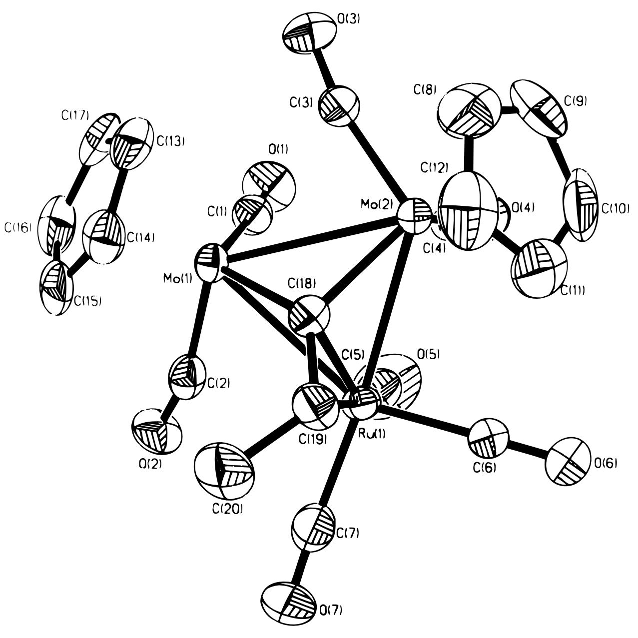


Figure 1. ORTEP plot of the molecular structure of Mo$_2$Ru(μ_3-C=CHMe)(CO)$_7$Cp$_2$ (**2b**) in the crystal.

The structure of **2b**, derived from propyne, has been determined by X-ray diffraction. A perspective view of the molecule is shown in Figure 1 with selected bond lengths and angles given in Table 2.

The structure is based on a triangle of two molybdenum atoms and one ruthenium atom. The two Mo−Ru bonds are slightly unequal in length, with Mo(1)−Ru(1) being slightly longer than Mo(2)−Ru(1) (2.9272(7) as opposed to 2.8935(7) Å), but both are within the range found in other Mo−Ru clusters.[23] The Mo(1)−Mo(2)

---

[22] (a) Johnson, B. F. G.; Johnston, R. D.; Lewis, J. *J. Chem. Soc. A* **1968**, 2856. (b) Eady, C. R.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1975**, 2606.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 2b

Mo(1)–C(2)	1.979(7)	Mo(1)–C(1)	1.992(7)
Mo(1)–C(18)	2.088(6)	Mo(1)–Ru(1)	2.9272(7)
Mo(1)–Mo(2)	3.0277(8)	Ru(1)–C(6)	1.893(7)
Ru(1)–C(5)	1.911(8)	Ru(1)–C(7)	1.916(8)
Ru(1)–C(18)	2.123(6)	Ru(1)–C(19)	2.325(7)
Ru(1)–Mo(2)	2.8935(7)	Mo(2)–C(3)	1.956(7)
Mo(2)–C(4)	1.979(8)	Mo(2)–C(18)	2.090(6)
C(18)–C(19)	1.380(9)	C(19)–C(20)	1.515(9)

Ru(1)–Mo(1)–Mo(2)	58.11(2)	Mo(2)–Ru(1)–Mo(1)	62.68(2)
Ru(1)–Mo(2)–Mo(1)	59.20(2)	O(1)–C(1)–Mo(1)	175.6(5)
O(2)–C(2)–Mo(1)	165.9(5)	O(3)–C(3)–Mo(2)	168.0(6)
O(4)–C(4)–Mo(2)	173.7(6)	O(5)–C(5)–Ru(1)	177.1(7)
O(6)–C(6)–Ru(1)	177.2(6)	O(7)–C(7)–Ru(1)	175.9(7)
C(19)–C(18)–Mo(1)	132.4(5)	C(19)–C(18)–Mo(2)	131.7(5)
Mo(1)–C(18)–Mo(2)	92.9(2)	C(19)–C(18)–Ru(1)	80.1(4)
Mo(1)–C(18)–Ru(1)	88.1(2)	Mo(2)–C(18)–Ru(1)	86.7(2)
C(18)–C(19)–Ru(1)	64.1(4)		

bond length is 3.0277(8) Å. The metal triangle is spanned by a triply bridging methylvinylidene fragment which is formally σ-bound to the two molybdenum atoms and π-bound to ruthenium; the μ_3-C atom C(18) caps the triangle virtually symmetrically. The C(18)–C(19) bond length of 1.380(9) Å is typical for μ_3-vinylidene ligands.[2] The ruthenium atom bears three CO ligands, which are all virtually linear. Each molybdenum atom bears two carbonyls, one of which is closer to linearity than the other; CO ligands C(2)–O(2) and C(3)–O(3) are the most nonlinear with angles of 165.9(5) and 168.0(6)°, respectively. These deviations are large enough to designate these ligands semibridging (they have asymmetry parameters of 0.364 and 0.462, respectively)[24] and do not appear to result from crystal-packing effects, since similar nonlinearity is observed in the substituted analogue $Mo_2Ru(\mu_3\text{-}C{=}CHMe)(CO)_6(PPh_2Me)$.[25] Moreover, the structure of **2b** bears a striking resemblance to that of $Mo_2Ru(\mu_3\text{-}S)(CO)_7Cp_2$, which has a capping sulfur atom in place of the vinylidene ligand.[26] The metal frameworks of the two clusters are almost identical, and it is interesting to note that the two Mo–Ru bond lengths in the sulfur-capped cluster were also unequal (2.9129(8) and 2.8989(9) Å). A slightly different pattern of semibridging carbonyls was present, though the maximum deviation from linearity was similar to that in the present case.

The formation of triply bridging vinylidene ligands by the rearrangement of alkyne ligands in dinuclear complexes on reaction with metal carbonyls is well established, e.g. the synthesis of $FeCo_2(\mu_3\text{-}C{=}CHR)(CO)_9$ (R = H, Me, Ph, ^{t}Bu) from $Co_2(\mu\text{-}HC{\equiv}CR)(CO)_6$ and $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$. In some cases the initial product was the corresponding μ_3-alkyne cluster, which then rearranged to the vinylidene on heating.[27] In agreement with this, in a study of interconvertible triply bridging terminal alkyne, vinylidene, and (by hydrogenation) alkylidyne ligands on a range of trinuclear metal cluster centers, Vahrenkamp found that the vinylidene was the favored form.[28] No evidence for the formation of alkyne clusters was obtained in the present work, though given the conditions of the reaction it is possible that they were formed as intermediates.

Synthesis of Bis(alkylidyne) Clusters 3a–e. Realizing that dimolybdenum complexes of disubstituted alkynes would be unable to undergo rearrangement to form vinylidene clusters, we also investigated the behavior of the but-2-yne complex **1e** ($R^1 = R^2 =$ Me) toward ruthenium carbonyl under the same reaction conditions. Two major products were formed, the second of which was again $Ru_6(\mu_6\text{-}C)(CO)_{14}(\eta\text{-}C_6H_5Me)$. The first was royal blue and was characterized as the hexanuclear bis(ethylidyne) cluster $Mo_2Ru_4(\mu_3\text{-}CMe)_2(CO)_{12}Cp_2$ (**3e**), as described below. The reaction can also be carried out in heptane with little alteration in the yield of the product, which was a reasonable 28%. However, when we tried to extend the reaction to complexes of bulkier disubstituted alkynes, namely $EtC{\equiv}CEt$ (**1f**) and $MeO_2CC{\equiv}CCO_2Me$ (**1g**), no tractable products were obtained in either case.

Since the hexaruthenium toluene complex is an unwanted side product in the synthesis of the vinylidene clusters described above, we also investigated the reaction of **1a–d** with $Ru_3(CO)_{12}$ in heptane. As expected, this strategy for eliminating the arene cluster was successful, and good yields of **2a–d** were still obtained; however, an unforeseen bonus was that the blue bis(alkylidyne) clusters **3a–d**, which were generally formed in only trace amounts or not at all in toluene solution, were now produced in somewhat increased yields (ranging from 4.5% for **3a** to 16% for **3d**), which enabled their complete characterisation.

Compounds **3a–e** are all blue, air-stable solids which were initially characterized spectroscopically. The observation of molecular ions in their mass spectra, together with 12 successive CO loss peaks, indicated that hexanuclear clusters had been formed. Confirmation of alkyne scission in **3a–e** was obtained from their ^{1}H and ^{13}C NMR spectra. The ^{1}H spectra consist of one peak for the equivalent Cp ligands together with appropriate signals for R^1 and R^2; in the symmetrical complexes **3a** and **3e** the two alkylidyne substituents are clearly equivalent. For the methylidyne complexes **3a–d**, the ^{1}H NMR peaks due to the μ_3-CH groups occur at around δ 16.5, which is typical for such ligands.[12,29] The ^{13}C NMR spectra also show the low-field resonances characteristic of μ_3-alkylidyne ligands between 320 and 360 ppm. Again for the symmetrical compounds **3a** and **3e** only one peak is observed, showing that the two alkylidyne ligands are in equivalent environments. For

---

(23) (a) Cazanoue, M.; Lugan, N.; Bonnet, J.-J.; Mathieu, R. *Organometallics* **1988**, *7*, 2480. (b) Wang, J.-C.; Chi, Y.; Peng, S.-M.; Lee, G.-H.; Shyu, S.-G.; Tu, F.-H. *J. Organomet. Chem.* **1994**, *481*, 143. (c) Chi, Y.; Su, C.-J.; Farrugia, L. J.; Peng, S.-M.; Lee, G.-H. *Organometallics* **1994**, *13*, 4167.

(24) (a) Curtis, M. D.; Han, K. R.; Butler, W. M. *Inorg. Chem.* **1980**, *19*, 2096; (b) Klingler, R. J.; Butler, W. M.; Curtis, M. D. *J. Am. Chem. Soc.* **1978**, *100*, 5034. The long M–CO distances in **2b** are C(2)–Ru(1) = 2.700 Å and C(3)–Mo(1) = 2.860 Å.

(25) Adams, H.; Bailey, N. A.; Gill, L. J.; Morris, M. J.; Sadler, N. D. manuscript in preparation.

(26) (a) Richter, F.; Roland, E.; Vahrenkamp, H. *Chem. Ber.* **1984**, *117*, 2429. (b) Adams, R. D.; Babin, J. E.; Tasi, M. *Organometallics* **1988**, *7*, 219. (c) Adams, R. D.; Babin, J. E.; Tasi, M.; Wang, J.-G. *Organometallics* **1988**, *7*, 755. (d) Adams, R. D.; Babin, J. E.; Tasi, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 685. (e) Adams, R. D.; Babin, J. E.; Tasi, M. *Organometallics* **1987**, *6*, 2247.

(27) Albiez, T.; Bernhardt, W.; von Schnering, C.; Roland, E.; Bantel, H.; Vahrenkamp, H. *Chem. Ber.* **1987**, *120*, 141.

(28) Bernhardt, W.; Schacht, H.-T.; Vahrenkamp, H. *Z. Naturforsch., B* **1989**, *44*, 1060.

(29) For examples of $Ru_3(\mu_3\text{-}CH)$ complexes, see: (a) Kakigano, T.; Suzuki, H.; Igarishi, M.; Moro-oka, Y. *Organometallics* **1990**, *9*, 2192. (b) Keister, J. B.; Horling, T. L. *Inorg. Chem.* **1980**, *19*, 2304. (c) Morris, M. J. Ph.D. Thesis, University of Bristol, 1984. For mixed-metal systems, see: (d) Duffy, D. N.; Kassis, M. M.; Rae, A. D. *J. Organomet. Chem.* **1993**, *460*, 97. (e) Schacht, H. T.; Vahrenkamp, H. *J. Organomet. Chem.* **1990**, *381*, 261.

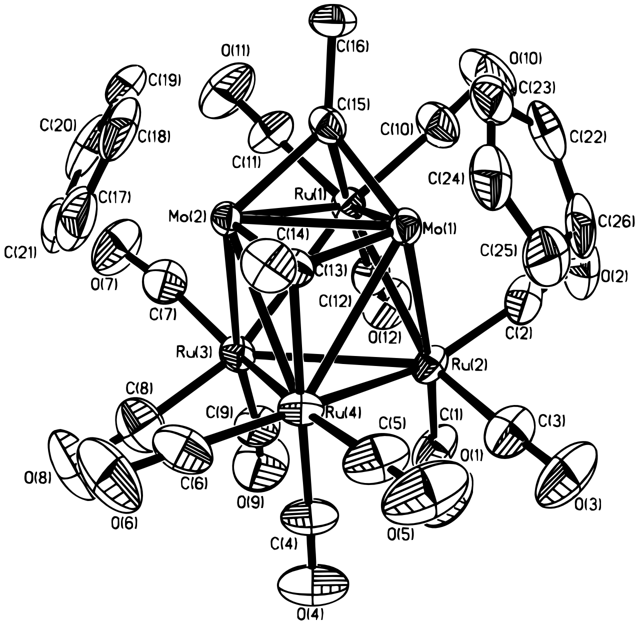


Figure 2. ORTEP plot of the molecular structure of $Mo_2Ru_4(\mu_3\text{-}CMe)_2(CO)_{12}Cp_2$ (**3e**) in the crystal. The dichloromethane of crystallization is not shown.

the unsymmetrical complexes **3b**−**d**, two such signals are observed and can be distinguished by the JMOD technique: the μ_3-CH carbon consistently occurs at approximately 325 ppm.

The carbonyl regions of the ^{13}C NMR spectra of the symmetrical clusters **3a** and **3e** contain three peaks in an approximate intensity ratio of 2:6:4, whereas the unsymmetrical **3b**−**d** each show five peaks in a 1:1:6:2:2 pattern. The most likely explanation for this is that the CO ligands bonded to the two ruthenium atoms which are bonded to the alkylidyne ligands are static on the NMR time scale, whereas those attached to the other two ruthenium atoms are undergoing rapid tripodal rotation. The latter pair of metals remain equivalent even when the two alkylidyne ligands are different, whereas the former become inequivalent. Owing to the limited solubility of the clusters at low temperature, we did not investigate this phenomenon further.

The X-ray crystal structure of the bis(ethylidyne) cluster **3e** was determined, and a view of the molecule is shown in Figure 2. Selected bond lengths and angles are collected in Table 3.

The molecule consists of an octahedral metal core in which the two molybdenum atoms, each bearing a Cp ligand, are situated in adjacent positions. The Mo(1)−Mo(2) bond is rather short (2.5792(8) Å) compared to that of 2.980(1) Å in the alkyne complex **1a**,[17] though it is not as short as the 2.448(1) Å found for the Mo≡Mo bond in $Mo_2(CO)_4Cp_2$.[24b] It may therefore be indicative of some degree of multiple bonding, formally a double bond, as indicated by electron counting (vide infra). However, it should be pointed out that related Mo_2Ru clusters in which the Mo−Mo bond is bridged by organic fragments can also display rather short Mo−Mo distances. For example, $Mo_2Ru\{\mu_3\text{-}HCC(Ph)CHC(Ph)CHC(Ph)\}(\mu_3\text{-}S)(CO)_2Cp_2$ and $Mo_2Ru(\mu\text{-}PhCCHCPh)(\mu_3\text{-}HCCPhCH)(\mu_3\text{-}S)(CO)_2Cp_2$, which were both made by oligomerization of phenylacetylene on the face of $Mo_2Ru(\mu_3\text{-}S)(CO)_7Cp_2$, have very similar Mo−Mo bond lengths of 2.663(1) and 2.679(2) Å, respectively, even though the first is formally electron deficient whereas the latter is electron precise.[25]

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 3e·CH_2Cl_2

Ru(1)−C(15)	2.228(7)	Ru(1)−Ru(2)	2.8316(9)
Ru(1)−Ru(3)	2.8488(8)	Ru(1)−Mo(1)	2.9451(8)
Ru(1)−Mo(2)	2.9498(8)	Ru(2)−Mo(1)	2.8126(9)
Ru(2)−Ru(4)	2.8345(8)	Ru(2)−Ru(3)	2.9484(8)
Ru(3)−Mo(2)	2.8229(9)	Ru(3)−Ru(4)	2.8337(8)
Ru(4)−C(13)	2.221(7)	Ru(4)−Mo(2)	2.9256(9)
Ru(4)−Mo(1)	2.9398(9)	Mo(1)−C(13)	2.031(7)
Mo(1)−C(15)	2.044(7)	Mo(1)−Mo(2)	2.5792(8)
Mo(2)−C(13)	2.007(7)	Mo(2)−C(15)	2.029(6)
C(13)−C(14)	1.548(9)	C(15)−C(16)	1.504(10)
Ru−CO (av)	1.897(8)		

Ru(2)−Ru(1)−Ru(3)	62.54(2)	Ru(2)−Ru(1)−Mo(1)	58.23(2)
Ru(3)−Ru(1)−Mo(1)	86.02(2)	Ru(2)−Ru(1)−Mo(2)	85.70(2)
Ru(3)−Ru(1)−Mo(2)	58.23(2)	Mo(1)−Ru(1)−Mo(2)	51.89(2)
Mo(1)−Ru(2)−Ru(1)	62.90(2)	Mo(1)−Ru(2)−Ru(4)	62.74(2)
Ru(1)−Ru(2)−Ru(4)	95.73(2)	Mo(1)−Ru(2)−Ru(3)	86.61(2)
Ru(1)−Ru(2)−Ru(3)	59.02(2)	Ru(4)−Ru(2)−Ru(3)	58.64(2)
Mo(2)−Ru(3)−Ru(4)	62.29(2)	Mo(2)−Ru(3)−Ru(1)	62.67(2)
Ru(4)−Ru(3)−Ru(1)	95.36(2)	Mo(2)−Ru(3)−Ru(2)	85.88(2)
Ru(4)−Ru(3)−Ru(2)	58.67(2)	Ru(1)−Ru(3)−Ru(2)	58.45(2)
Ru(3)−Ru(4)−Ru(2)	62.69(2)	Ru(3)−Ru(4)−Mo(2)	58.68(2)
Ru(2)−Ru(4)−Mo(2)	86.10(2)	Ru(3)−Ru(4)−Mo(1)	86.39(2)
Ru(2)−Ru(4)−Mo(1)	58.27(2)	Mo(2)−Ru(4)−Mo(1)	52.17(2)
Mo(2)−Mo(1)−Ru(2)	93.57(2)	Mo(2)−Mo(1)−Ru(4)	63.63(2)
Ru(2)−Mo(1)−Ru(4)	58.99(2)	Mo(2)−Mo(1)−Ru(1)	64.15(2)
Ru(2)−Mo(1)−Ru(1)	58.86(2)	Ru(4)−Mo(1)−Ru(1)	91.12(2)
Mo(1)−Mo(2)−Ru(3)	93.94(2)	Mo(1)−Mo(2)−Ru(4)	64.20(2)
Ru(3)−Mo(2)−Ru(4)	59.03(2)	Mo(1)−Mo(2)−Ru(1)	63.96(2)
Ru(3)−Mo(2)−Ru(1)	59.09(2)	Ru(4)−Mo(2)−Ru(1)	91.31(2)
C(14)−C(13)−Mo(2)	134.2(5)	C(14)−C(13)−Mo(1)	133.9(5)
Mo(2)−C(13)−Mo(1)	79.4(2)	C(14)−C(13)−Ru(4)	118.8(5)
Mo(2)−C(13)−Ru(4)	87.4(2)	Mo(1)−C(13)−Ru(4)	87.4(3)
C(16)−C(15)−Mo(2)	134.6(5)	C(16)−C(15)−Mo(1)	133.1(5)
Mo(2)−C(15)−Mo(1)	78.6(2)	C(16)−C(15)−Ru(1)	119.8(5)
Mo(2)−C(15)−Ru(1)	87.6(3)	Mo(1)−C(15)−Ru(1)	87.0(3)
Ru−C−O (av)	175.0(8)		

The Mo−Ru bonds involving Ru(1) and Ru(4), which are bonded to the capping alkylidynes, are all very similar and lie within the range 2.9256(9)−2.9498(8) Å. However, the Mo−Ru bonds involving Ru(2) and Ru(3) are somewhat shorter (2.8126(9) and 2.8229(9) Å). The Ru−Ru bonds between these two Ru atoms and Ru(1) and Ru(4) are all virtually the same length and lie in the range 2.8316(9)−2.8488(8) Å, whereas the Ru(2)−Ru(3) bond itself is somewhat longer (2.9484(8) Å). The two ethylidyne ligands symmetrically cap the two Mo_2Ru faces of the octahedron. The C(13)−C(15) distance, which in the alkyne complexes **1** is approximately 1.33 Å, has opened up to 2.944 Å, though it is interesting to note that this axis remains perpendicular to the Mo−Mo bond.

In terms of electron counting, compounds of type **3** have a total of 84 cluster valence electrons (corresponding to *n* pairs of skeletal electrons) instead of the 86 which is usual for octahedral clusters ($n + 1$ pairs of skeletal electrons, corresponding to a *closo* structure). This means that the cluster as a whole obeys the 18-electron rule rather than the Wade−Mingos rules.[30] The short Mo−Mo distance may be a consequence of this unsaturation. It is also interesting to compare **3e** with $Mo_2Ru_4(\mu_6\text{-}C)(\mu\text{-}O)(CO)_{12}Cp_2$, which if the oxo ligand acts as a 2-electron donor also has 84 electrons;[14] if bond length can be considered an accurate indicator of bond

---

(30) Mingos, D. M. P.; May, A. S. In *The Chemistry of Metal Cluster Complexes*; Shriver, D. F., Kaesz, H. D., Adams, R. D., Eds.; VCH: New York, 1990; Chapter 2, p 44.

order, the longer Mo—Mo distance of 2.9052(12) Å observed may mean that the deficiency is made up by further donation from the oxo ligand.

At present it is difficult to propose a mechanism for the formation of **3a**—**e** and we have been unable to isolate any intermediates, but it is reasonable to suppose that the alkyne scission occurs in a mixed-metal cluster. The intramolecular nature of this step is demonstrated by the fact that complexes **1b**—**d**, which contain unsymmetrical alkynes, give rise only to the corresponding unsymmetrical bis(alkylidyne) complexes **3b**—**d** with no trace of the symmetrical scrambling products, which would include **3a.** This rules out a mechanism involving dissociation of the starting complexes into two mononuclear $Mo(CO)_2(\equiv CR)Cp$ fragments, which would in any case be highly unlikely. Moreover, the reactions of the tungsten alkylidyne complexes $W(CO)_2(\equiv CR)Cp$ (R = p-C_6H_4Me, Me) with $Ru_3(CO)_{12}$ have already been studied by Stone and co-workers; they give rise to the trinuclear alkyne clusters $W_2Ru(\mu_3\text{-}C_2R_2)(CO)_7Cp_2$ by coupling of two alkylidyne fragments.[6] The complete absence of any products of this type in the current work, especially in the case of the disubstituted alkyne complex, indicates the operation of a mechanism in which alkyne cleavage is the only available pathway.

The structure of **3e**, and the fact that the bulkier alkyne complexes **1f,g** give no products at all, both indicate that the initial approach of the ruthenium atoms to the dimolybdenum center is toward the Mo_2C faces of the starting dimetallatetrahedrane. However, the successful reactions of **1c**,**d** show that if R^1 is small, R^2 can be quite large. Clearly, attachment of one $Ru(CO)_x$ unit is necessary in order to obtain the vinylidene complexes **2**, but treatment of **2** with further $Ru_3(CO)_{12}$ does not lead to **3** and it seems plausible to propose that initial interaction with (at least) two such $Ru(CO)_x$ fragments is necessary to proceed instead to alkyne scission and construction of the hexanuclear clusters **3**. Conceptually, it is easy to visualize the formation of **3** by the simple insertion of a Ru_4 butterfly into the Mo—Mo bond of **1**, accompanied by the "clicking open" of the carbon—carbon bond, but there is no evidence to suggest that this is what actually occurs in solution.

Conclusion

This work has demonstrated for the first time that scission of the C≡C bonds of simple terminal alkynes, including acetylene itself, to form two alkylidyne ligands is a process which can be observed in suitable metal clusters under appropriate conditions. A better understanding of the factors which influence this, as opposed to the more common C—H bond activation, may furnish useful routes to clusters containing the important methylidyne ligand. A theoretical study[31] has shown that the cleavage of alkynes is facilitated by charge transfer ($M \rightarrow \pi^*$) to the resulting alkylidyne ligands, which should be more effective from the MoCp fragments than from the $Ru(CO)_3$ groups, hence the preference of the μ_3-CR ligands in **3** for the Mo_2Ru faces. A further illustration is the fact that $Os_3(\mu_3\text{-}C_2R_2)(CO)_{10}$ does not undergo alkyne scission whereas $OsW_2(\mu_3\text{-}C_2R_2)(CO)_7Cp_2$ does so readily to give a product in which one alkylidyne caps the cluster but the other bridges the W—W edge; the formation of the strong W—C bonds is thought to drive the reaction forward.[3j] It seems reasonable to suggest that future examples of alkyne scission are most likely to be encountered by the incorporation of such fragments, and consequently we are currently exploring further routes to mixed-metal clusters using the alkyne complexes **1** as precursors.

Acknowledgment. We thank the EPSRC for a studentship to L.J.G. and Johnson Matthey plc for a generous loan of ruthenium trichloride. We also thank Dr. B. F. Taylor and Prof. B. E. Mann for assistance in recording and interpreting the NMR spectra and Dr. Yun Chi (National Tsing Hua University, Taiwan) for interesting discussions.

Supporting Information Available: Full tables of atomic coordinates, bond lengths and angles, H atom coordinates, and thermal parameters for complexes **2b** and **3e** (14 pages). Ordering information is given on any current masthead page. Tables of structure factors are available from the authors on request.

OM960235C

---

(31) Deshmukh, P.; Dutta, T. K.; Hwang, J. L.-S.; Housecroft, C. E.; Fehlner, T. P. *J. Am. Chem. Soc.* **1982**, *104*, 1740.