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Synthesis and X-ray Structure of the Carbido−Oxo Cluster $Mo_2Ru_4(\mu_6\text{-}C)(\mu\text{-}O)(CO)_{12}Cp_2$

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Summary: The unusual heterometallic carbido−oxo cluster $Mo_2Ru_4(\mu_6\text{-}C)(\mu\text{-}O)(CO)_{12}Cp_2$ ($Cp = \eta\text{-}C_5H_5$) has been isolated in moderate yield from the reaction of $Mo_2(CO)_4Cp_2$ with $Ru_3(CO)_{12}$ in refluxing toluene. The X-ray crystal structure of the complex unexpectedly reveals the presence of two isomeric molecules in the unit cell: both have octahedral metal cores with a carbon atom in the center and an oxo ligand bridging the molybdenum−molybdenum bond, but one molecule has two bridging carbonyl ligands on Mo−Ru edges whereas the other has two additional carbonyls weakly semibridging Ru−Ru edges.

Introduction

The dissociative chemisorption of carbon monoxide on metal surfaces to produce surface carbide groups is established as an integral step in important catalytic processes such as the Fischer−Tropsch reaction. Consequently the synthesis and study of metal clusters containing carbido ligands remains an active area of research in organometallic chemistry.[1] The bonding modes available for the carbido ligand include μ_4-bridging on a butterfly of metal atoms (exposed), μ_5-bridging in the basal plane of a square pyramid of metals (semiexposed), and, most commonly, μ_6, interstitial in a metal octahedron. The last of these is particularly stable, especially for ruthenium, and a substantial chemistry of octahedral Ru_6C carbonyl derivatives has been developed from $Ru_6C(CO)_{17}$, $Ru_6C(CO)_{14}(\eta\text{-arene})$, and related species.[2]

Carbido clusters are most prevalent for metals of group 8 and are often formed in pyrolysis reactions of the metal carbonyls, though careful control of the conditions, and sometimes the presence of reducing agents, is necessary to obtain good yields.[3] The source of the carbide carbon in the pyrolysis reactions is generally assumed to be cleavage of a CO ligand, and in some cases this has been established by isotopic labeling techniques.[4] In one of the most carefully studied reactions, Johnson and Lewis demonstrated that the formation of $Ru_6C(CO)_{14}(\eta\text{-}C_6H_3Me_3)$ by pyrolysis of $Ru_3(CO)_{12}$ in hydrocarbon solvents containing mesitylene proceeds *via* the intermediate open-framework cluster $Ru_6(\mu_4,\eta^2\text{-}CO)_2(CO)_{13}(\eta\text{-}C_6H_3Me_3)$, presumably by cleavage of one of the activated bridging carbonyls.[5] In such reactions the carbonyl oxygen atom is generally thought to be expelled as CO_2, which in some cases has been detected and quantified. Adams and co-workers have shown that the carbido ligand in $Ru_6C(CO)_{16}(CN^tBu)$ arises from cleavage of a coordinated isonitrile in the starting cluster $Ru_5(CO)_{14}(CN^tBu)(\mu_5\text{-}CN^tBu)$ and suggested that the imido fragment is lost as $^tBuN{=}C{=}O$, which was detected by GC analysis.[6] Very recently Chi and co-workers have prepared WRu_4 and WRu_5 clusters by the reaction of $WRu_2(\mu\text{-}C{\equiv}CPh)(CO)_8Cp$ with additional $Ru_3(CO)_{12}$; cleavage of the acetylide ligand occurs to give a carbide and a μ_2-phenylalkylidyne group, which both remain coordinated to the metal framework.[7]

It should be noted that, because of the relative lack of rational synthetic methods for carbido clusters, heterometallic examples are much rarer than homometallic ones. Most of those known have been made by capping the pentanuclear $[M_5C(CO)_{14}]^{2-}$ clusters (M = Fe, Ru) with an appropriate additional vertex from a mononuclear dicationic metal complex,[8] but recently the formation of $Mo_4Co_3(\mu_6\text{-}C)(\mu_3\text{-}OH)(\mu_3\text{-}CPh)_2(CO)_6Cp_4$ from the pyrolysis of $Mo_2(CO)_6Cp_2$ with $Co_2(\mu\text{-}C_2Ph_2)(CO)_6$ was reported by Russian workers; this compound contains a carbide ligand encapsulated in a Mo_3Co_3 octahedron and a hydroxo ligand triply bridging a Mo_3 face, both assumed to arise through cleavage of a CO.[9] Here we describe the preparation of a new heterometallic Mo_2Ru_4 carbido cluster in which the triple bond of a CO ligand has been cleaved, with both resulting fragments retained in the product.

Results and Discussion

We have recently shown that heating the alkyne complexes $Mo_2(\mu\text{-}R^1C{\equiv}CR^2)(CO)_4Cp_2$ with 1−1.5 equiv

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(1) Bradley, J. S. *Adv. Organomet. Chem.* **1982**, *22,* 1. Tachikawa, M.; Muetterties, E. L. *Prog. Inorg. Chem.* **1981**, *28,* 203.

(2) Ma, L.; Williams, G. K.; Shapley, J. R. *Coord. Chem. Rev.* **1993**, *128,* 261.

(3) For high-yield syntheses of Ru carbido clusters, see: Hayward, C.-M. T.; Shapley, J. R. *Inorg. Chem.* **1982**, *21,* 3816. Hayward, C.-M. T.; Shapley, J. R.; Churchill, M. R.; Bueno, C.; Rheingold, A. L. *J. Am. Chem. Soc.* **1982**, *104,* 7347. Chihara, T.; Komoto, R.; Kobayashi, K.; Yamazaki, H.; Matsuura, Y. *Inorg. Chem.* **1989**, *28,* 964. Bailey, P. J.; Johnson, B. F. G.; Lewis, J.; McPartlin, M.; Powell, H. R. *J. Organomet. Chem.* **1989**, *377,* C17. Johnson, B. F. G.; Lewis, J.; Nicholls, J. N.; Puga, J.; Raithby, P. R.; Rosales, M. J.; McPartlin, M.; Clegg, W. *J. Chem. Soc., Dalton Trans.* **1983**, 277. Bradley, J. S.; Ansell, G. B.; Hill, E. W. *J. Organomet. Chem.* **1980**, *184,* C33.

(4) Eady, C. R. Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1975**, 2606. Johnson, B. F. G.; Johnston, R. D.; Lewis, J. *J. Chem. Soc. A* **1968**, 2865.

(5) Anson, C. E.; Bailey, P. J.; Conole, G.; Johnson, B. F. G.; Lewis, J.; McPartlin, M.; Powell, H. R. *J. Chem. Soc., Chem. Commun.* **1989,** 442. Bailey, P. J.; Duer, M. J.; Johnson, B. F. G.; Lewis, J.; Conole, G.; McPartlin, M.; Powell, H. R.; Anson, C. E. *J. Organomet. Chem.* **1990**, *383,* 441.

(6) Adams, R. D.; Mathur, P.; Segmüller, B. E. *Organometallics* **1983**, *2,* 1258.

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

(8) Tachikawa, M.; Geerts, R. L.; Muetterties, E. L. *J. Organomet. Chem.* **1981**, *213,* 11. Gomez-Sal, M. P.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Wright, A. H. *J. Chem. Soc., Chem. Commun.* **1985**, 1682. Adams, R. D.; Wu, W. *J. Cluster Sci.* **1991**, *2,* 271.

(9) 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. 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.

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Table 1. Crystal Data and Structure Refinement for 1

identification code	lg11x
empirical formula	$C_{23}H_{10}Mo_2O_{13}Ru_4$
fw	1090.47
temp	293(2) K
wavelength	0.710 73 Å
cryst system	triclinic
space group	$P\bar{1}$
unit cell dimens	$a = 9.7910(10)$ Å, $\alpha = 92.490(10)°$ $b = 16.041(3)$ Å, $\beta = 95.330(10)°$ $c = 17.853(3)$ Å, $\gamma = 96.190(10)°$
V	2771.5(8) Å^3
Z	4
D(calcd)	2.613 Mg/m^3
abs coeff	3.067 mm^{-1}
F(000)	2048
cryst size	0.73 × 0.45 × 0.23 mm
θ range for data collcn	1.76−22.51°
index ranges	$-1 \leq h \leq 10$, $-17 \leq k \leq 17$, $-19 \leq l \leq 19$
reflcns collcd	8645
indpdt reflcns	7245 ($R_{\text{int}} = 0.0368$)
refinement method	full-matrix-block least squares on F^2
data/restraints/params	7245/0/757
goodness-of-fit on F^2	1.087
final R indices [$I > 2\sigma(I)$]	$R1 = 0.0811$, w$R2 = 0.2090$
R indices (all data)	$R1 = 0.0848$, w$R2 = 0.2151$
largest diff peak and hole	1.989 and −4.813 e Å^{-3}

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for 1

	x	y	z	U(eq)[a]
Mo(1)	1814(1)	1426(1)	4143(1)	22(1)
Mo(2)	−567(1)	2296(1)	4399(1)	23(1)
Mo(3)	−3911(1)	6529(1)	1870(1)	24(1)
Mo(4)	−6340(1)	6405(1)	785(1)	25(1)
Ru(1)	3(1)	3349(1)	3114(1)	27(1)
Ru(2)	−343(1)	1581(1)	2868(1)	25(1)
Ru(3)	2342(1)	2528(1)	2853(1)	26(1)
Ru(4)	2203(1)	3276(1)	4325(1)	25(1)
Ru(5)	−6454(1)	8246(1)	1037(1)	30(1)
Ru(6)	−4156(1)	8352(1)	2145(1)	27(1)
Ru(7)	−3907(1)	7685(1)	636(1)	31(1)
Ru(8)	−6515(1)	7197(1)	2294(1)	26(1)
O(1)	385(7)	1421(4)	4802(4)	29(2)
O(2)	−3052(10)	3578(8)	3049(8)	95(4)
O(3)	977(11)	5131(6)	3683(6)	66(3)
O(4)	142(11)	3850(7)	1503(6)	72(3)
O(5)	4929(11)	4311(7)	4172(6)	71(3)
O(6)	1726(10)	4549(5)	5558(5)	51(2)
O(7)	3636(11)	4146(6)	2255(6)	69(3)
O(8)	5063(11)	1803(8)	2771(7)	84(4)
O(9)	1391(11)	1707(7)	1294(5)	70(3)
O(10)	−2352(12)	1935(7)	1552(6)	86(4)
O(11)	−200(11)	−196(6)	2242(6)	69(3)
O(12)	3901(10)	2401(5)	5463(5)	58(3)
O(13)	−2774(8)	815(5)	3610(5)	49(2)
O(14)	−1746(13)	9183(7)	520(7)	89(4)
O(15)	−4094(15)	7215(9)	−1029(6)	103(5)
O(16)	−9315(11)	8004(8)	219(8)	97(4)
O(17)	−1486(10)	6671(7)	777(7)	76(3)
O(18)	−3559(12)	10189(5)	1864(6)	79(4)
O(19)	−7073(13)	9942(7)	1677(6)	82(3)
O(20)	−6319(10)	6334(6)	3793(5)	55(2)
O(21)	−5452(12)	9123(6)	−318(6)	73(3)
O(22)	−9063(10)	8053(7)	2535(6)	68(3)
O(23)	−1589(10)	8513(6)	3266(6)	62(3)
O(24)	−5587(9)	8763(5)	3530(4)	44(2)
O(25)	−8613(10)	5707(6)	1848(5)	65(3)
O(26)	−5053(7)	5717(4)	1223(4)	29(2)
C(1)	−1802(14)	3324(7)	4888(8)	56(4)
C(2)	−951(14)	3049(7)	5500(7)	44(3)
C(3)	−1406(13)	2220(8)	5602(7)	43(3)
C(4)	−2518(13)	1951(8)	5055(7)	44(3)
C(5)	−2753(13)	2619(8)	4599(8)	46(3)
C(6)	1719(15)	−13(7)	3924(9)	55(4)
C(7)	2850(18)	370(9)	3587(8)	64(4)
C(8)	3787(12)	755(8)	4155(8)	50(4)
C(9)	3238(15)	600(7)	4836(8)	51(4)
C(10)	1983(14)	110(7)	4682(9)	52(4)
C(11)	−1914(15)	3502(8)	3088(9)	57(4)
C(12)	763(13)	4441(7)	3538(7)	42(3)
C(13)	96(13)	3662(7)	2097(7)	41(3)
C(14)	3885(12)	3921(7)	4203(6)	42(3)
C(15)	1894(12)	4055(7)	5113(6)	36(3)
C(16)	3166(13)	3516(8)	2484(7)	44(3)
C(17)	4065(13)	2056(8)	2823(7)	43(3)
C(18)	1537(13)	1949(8)	1904(8)	46(3)
C(19)	−1611(13)	1785(7)	2044(7)	41(3)
C(20)	−232(12)	462(8)	2495(6)	40(3)
C(21)	−1779(12)	1268(7)	3544(6)	34(3)
C(22)	3113(11)	2445(7)	4936(6)	32(2)
C(23)	927(9)	2404(5)	3615(5)	19(2)
C(24)	−6463(14)	5874(9)	−465(6)	52(3)
C(25)	−7460(15)	6448(8)	−390(6)	54(4)
C(26)	−8435(12)	6084(7)	83(7)	42(3)
C(27)	−8021(13)	5330(7)	277(6)	44(3)
C(28)	−6838(14)	5195(8)	−70(7)	53(3)
C(29)	−3701(13)	5724(8)	2917(7)	48(3)
C(30)	−3191(14)	5276(8)	2351(7)	51(3)
C(31)	−2052(14)	5742(9)	2147(8)	56(4)
C(32)	−1836(11)	6500(8)	2596(8)	50(3)
C(33)	−2870(14)	6469(8)	3087(7)	55(4)
C(34)	−4037(14)	7404(9)	−420(7)	55(4)
C(35)	−5584(13)	8729(7)	177(7)	46(3)
C(36)	−2497(12)	6904(8)	945(7)	47(3)
C(37)	−8273(14)	8065(9)	515(8)	59(4)
C(38)	−2548(14)	8608(9)	576(8)	61(4)
C(39)	−6826(14)	9287(8)	1442(6)	48(3)
C(40)	−6381(11)	6667(7)	3229(6)	38(3)
C(41)	−7691(11)	6194(6)	1765(6)	34(3)
C(42)	−5324(12)	8451(7)	2986(6)	36(3)
C(43)	−2517(12)	8409(7)	2822(6)	42(3)
C(44)	−5197(9)	7397(6)	1452(5)	25(2)
C(45)	−3771(13)	9496(7)	1973(7)	46(3)
C(46)	−8088(12)	7746(7)	2441(6)	38(3)

[a] U(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

of $Ru_3(CO)_{12}$ in toluene or heptane solution results in cleavage of the alkyne C≡C bond and formation of the hexanuclear clusters $Mo_2Ru_4(\mu_3\text{-}CR^1)(\mu_3\text{-}CR^2)(CO)_{12}Cp_2$. This occurs to some extent even when the alkyne involved is a terminal one ($R^1 = H$), including acetylene itself, though the major products in these cases are the trinuclear vinylidene clusters $Mo_2Ru(\mu_3\text{-}C{=}CHR^2)(CO)_7Cp_2$.[10] In an attempt to gain further insight into the mechanism of this reaction, in particular the nuclearity of the cluster in which the alkyne scission step occurs, we examined some possible routes to other mixed-metal MoRu clusters. An obvious first choice seemed to be the reaction of the well-known $Mo_2(CO)_4Cp_2$, which contains a reactive Mo≡Mo bond, with ruthenium carbonyl. Several previous cluster-forming reactions have been reported for $Mo_2(CO)_4Cp_2$, as well as others which start from $Mo_2(CO)_6Cp_2$ under conditions where decarbonylation to the tetracarbonyl is strongly implied as an initial step.[11] We were however mindful of the fact that $Mo_2(CO)_4Cp_2$ reacts rapidly with CO, and hence, scavenging of CO released from $Ru_3(CO)_{12}$ might simply regenerate $Mo_2(CO)_6Cp_2$.

In the event, heating a toluene solution of $Mo_2(CO)_4Cp_2$ [generated *in situ* by decarbonylation of $Mo_2(CO)_6Cp_2$] with 1 equiv of $Ru_3(CO)_{12}$ afforded the new cluster $Mo_2Ru_4(\mu_6\text{-}C)(\mu\text{-}O)(CO)_{12}Cp_2$ (**1**) in 41% yield after column chromatography. Only a small amount of $Mo_2(CO)_6Cp_2$ was isolated, and the only other product was an unidentified cluster formed in low yield.

Compound **1** is a brown-black air-stable solid. The presence of molybdenum in the product was inferred from the ^1H NMR spectrum, which showed a singlet at δ 5.66 for the Cp ligands; moreover analytical data indicated a formula of $Mo_2Ru_4(CO)_{13}Cp_2$, and a molecular ion was observed in the FAB mass spectrum. At room temperature the ^{13}C NMR spectrum shows only one signal for the Cp ligands and two broad peaks for the carbonyls at 220.1 and 205.2 ppm in an apparent 1:2 intensity ratio; at 223 K the lower field CO peak

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

(11) Curtis, M. D. *Polyhedron* **1987**, *6*, 759. Winter, M. J. *Adv. Organomet. Chem.* **1989**, *29*, 101.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 1

Mo(1)−O(1)	1.910(7)	Mo(1)−C(22)	2.304(11)
Mo(1)−Mo(2)	2.9052(12)	Mo(1)−Ru(4)	2.9502(12)
Mo(1)−Ru(2)	2.9956(12)	Mo(1)−Ru(3)	3.0111(12)
Mo(2)−O(1)	1.899(7)	Mo(2)−C(1)	2.333(12)
Mo(2)−C(21)	2.341(11)	Mo(2)−Ru(2)	2.9554(12)
Mo(2)−Ru(1)	2.9661(12)	Mo(2)−Ru(4)	3.0013(12)
Mo(3)−O(26)	1.896(7)	Mo(3)−C(44)	2.092(10)
Mo(3)−C(36)	2.310(12)	Mo(3)−Mo(4)	2.9085(12)
Mo(3)−Ru(7)	2.9403(13)	Mo(3)−Ru(6)	2.9821(13)
Mo(3)−Ru(8)	3.0158(12)	Mo(4)−O(26)	1.900(7)
Mo(4)−C(44)	2.099(9)	Mo(4)−C(41)	2.306(10)
Mo(4)−Ru(8)	2.9559(12)	Mo(4)−Ru(5)	2.9830(13)
Mo(4)−Ru(7)	3.0114(13)	Ru(1)−Ru(3)	2.8266(12)
Ru(1)−Ru(2)	2.8293(12)	Ru(1)−Ru(4)	2.9221(12)
Ru(2)−C(21)	1.976(12)	Ru(2)−Ru(3)	2.8933(11)
Ru(3)−Ru(4)	2.8615(12)	Ru(4)−C(22)	1.991(11)
Ru(5)−Ru(6)	2.8413(12)	Ru(5)−Ru(8)	2.8646(13)
Ru(5)−Ru(7)	2.8811(13)	Ru(5)−C(35)	1.972(13)
Ru(6)−C(42)	1.981(11)	Ru(6)−Ru(8)	2.8412(12)
Ru(6)−Ru(7)	2.8966(12)	Ru(7)−C(36)	2.017(13)
Ru(7)−C(35)	2.576(13)	Ru(8)−C(46)	1.888(12)
Ru(8)−C(41)	2.018(10)	Ru(8)−C(42)	2.439(11)
Mo(2)−O(1)−Mo(1)	99.4(3)	Mo(3)−O(26)−Mo(4)	100.0(3)
Ru(2)−C(21)−Mo(2)	86.0(4)	Ru(4)−C(22)−Mo(1)	86.4(4)
Ru(5)−C(35)−Ru(7)	77.4(4)	Ru(7)−C(36)−Mo(3)	85.3(4)
Ru(8)−C(41)−Mo(4)	86.0(4)	Ru(6)−C(42)−Ru(8)	79.3(4)

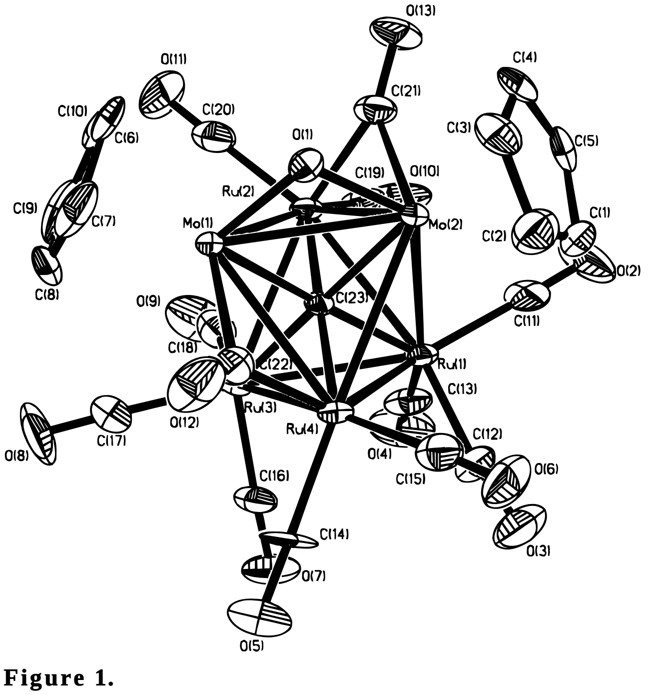


Figure 1.

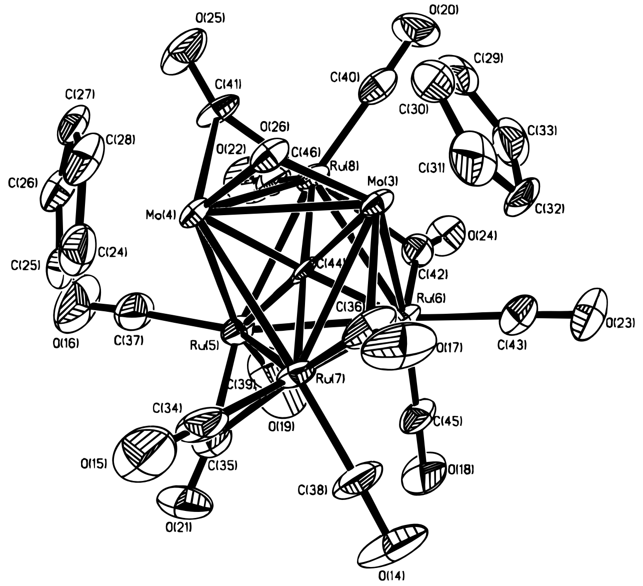
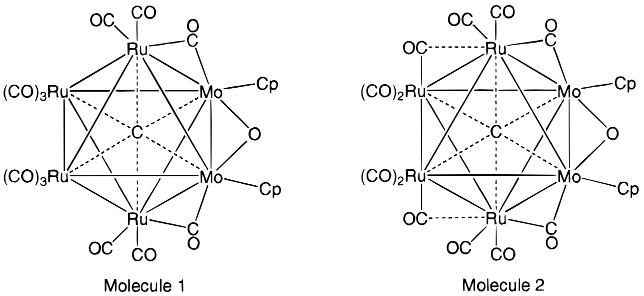


Figure 2.

Chart 1



had broadened into the baseline, indicating a fluxional process; however a low-temperature limiting spectrum could not be attained. A further feature of the low-temperature spectrum was that the resonance due to the carbido carbon atom could be detected at 438.7 ppm.

Suitable crystals of **1** were grown by diffusion of petroleum ether into a dichloromethane solution. The X-ray crystal structure unexpectedly revealed the presence of two isomeric molecules in the unit cell. Selected bond lengths and angles for each molecule are collected in Table 3, and ORTEP plots of their molecular structures are illustrated in Figures 1 and 2. The basic metal frameworks of the two molecules are very similar and they differ significantly only in the arrangement of the carbonyl ligands (Chart 1).

Considering molecule 1 first, the cluster consists of an octahedron of two molybdenum and four ruthenium atoms; the two molybdenums, which each bear a Cp ligand, occupy adjacent positions and are linked by a bond of length 2.9052(12) Å, which is typical for a single bond. The bonds between Mo and Ru all lie in the range 2.9502(12)−3.0111(12) Å, and those between two ruthenium atoms lie between 2.8266(12) and 2.9221(12) Å. Both of these ranges are typical for such bonds and compare favorably to those observed in other MoRu clusters.[12] A carbido carbon atom is situated virtually in the center of the octahedron; the bond lengths to all six metals are very similar, 2.030−2.116 Å, with those to Mo very slightly longer than those to Ru. The molybdenum−molybdenum bond is symmetrically bridged by an oxo ligand with bond lengths typical of such groups [Mo(1)−O(1) 1.910(7), Mo(2)−O(1) 1.899(7) Å]. The position of this ligand is in accord with the greater oxophilicity of molybdenum; the Mo(μ-O)Mo motif is a very common one in dinuclear complexes, but examples in organometallic clusters are much rarer.[13]

Ruthenium atoms Ru(1) and Ru(3) have three terminal carbonyl ligands, whereas Ru(2) and Ru(4) have two terminal carbonyls. In addition the Mo(1)−Ru(4) and Mo(2)−Ru(2) edges are spanned by the remaining two CO ligands which are rather unsymmetrically bonded: the two Mo−CO distances are 2.304(11) and 2.341(11) Å, respectively, whereas the corresponding Ru−CO distances are 1.991(11) and 1.976(12) Å.

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[12] Richter, F.; Roland, E.; Vahrenkamp, H. *Chem. Ber.* **1984**, *117*, 2429. Adams, R. D.; Babin, J. E.; Tasi, M. *Organometallics*, **1988**, *7*, 219. Adams, R. D.; Babin, J. E.; Tasi, M.; Wang, J.-G. *Organometallics* **1988**, *7*, 755. Adams, R. D.; Babin, J. E.; Tasi, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 685. Adams, R. D.; Babin, J. E.; Tasi, M. *Organometallics* **1987**, *6*, 2247. Chi, Y.; Su, C.-J.; Farrugia, L. J.; Peng, S.-M.; Lee, G.-H. *Organometallics* **1994**, *13*, 4167.

[13] Bottomley, F.; Sutin, L. *Adv. Organomet. Chem.* **1988**, *28*, 339.

The bond lengths of the metal framework, the carbido ligand, and the oxo ligand in molecule 2 are almost identical to those in molecule 1. However it differs in the arrangement of CO ligands, in that each ruthenium atom now has only two terminal carbonyls. Two carbonyls bridge the Mo(3)−Ru(7) and Mo(4)−Ru(8) edges; the Mo−CO distances of 2.306(10) and 2.310(12) Å are the same as in molecule 1, while the Ru−CO distances of 2.018(10) and 2.017(13) Å are possibly slightly longer, though not significantly so. The two remaining carbonyls bridge the Ru(5)−Ru(7) and Ru(6)−Ru(8) edges in a highly asymmetric manner; the bonds to Ru(5) and Ru(6) are short, 1.972(13) and 1.981(11) Å, respectively, whereas those to Ru(7) and Ru(8) are long, 2.576(13) and 2.439(11) Å, respectively. It therefore seems that the difference between the two molecules is simply that, in molecule 2, these two carbonyl ligands have "tipped over" from terminal to semibridging mode; clearly in this case there is very little energy difference between the two. The IR spectrum of **1** in CH_2Cl_2 solution showed peaks at 2057, 2017, 1974, and 1812 cm^{-1}. The solid-state IR spectrum (KBr) of the crystals used for the structure determination is more complex than in solution, and two peaks are observed in the region associated with bridging carbonyls, confirming the presence of two isomers. In solution, though, IR and NMR spectra both indicate the presence of a single fluxional species.

In terms of electron counting, if the oxo ligand acts as a two-electron donor, compound **1** has a total of 84 cluster valence electrons instead of the 86 which is more common for octahedral clusters ($n + 1$ pairs of skeletal electrons, corresponding to a *closo* structure).[14] It therefore disobeys the Wade−Mingos rules, but obeys the 18-electron rule overall. Comparison with the related $Mo_2Ru_4(\mu_3\text{-}CR^1)(\mu_3\text{-}CR^2)(CO)_{12}Cp_2$ clusters,[10] which also have 84 cluster valence electrons, reveals that both have a $Mo_2Ru_4(CO)_{12}Cp_2$ core providing a total of 78 electrons; in the case of the bis(alkylidyne) clusters, an additional 6 electrons are provided by the two μ_3-CR ligands which arise through cleavage of an alkyne; in the case of the carbido cluster, the additional 6 electrons are contributed by the interstitial carbide and an oxo ligand apparently formed by cleavage of a carbonyl ligand. The presence of the Cp ligand in larger clusters has been previously noted as a reason for unusual electron counts.[14]

Experimental Section

All reactions were carried out under dry argon using standard Schlenk techniques. The product described is relatively air stable, and workup procedures can be carried out without special precautions.

Toluene and light petroleum were dried by distillation from sodium. Light petroleum refers to the fraction boiling between 60 and 80 °C. Dichloromethane and other solvents were used as received unless otherwise stated. Chromatographic separations were performed under a slight positive pressure of argon on silica columns (Merck Kieselgel 60, 230−400 mesh) of varying length. Thin-layer chromatography (TLC) was carried out on commercial Merck plates coated with a 0.20 mm layer of silica.

Infrared spectra were recorded in CH_2Cl_2 solution on a Perkin-Elmer 1600 FT-IR machine using 0.5 mm NaCl cells. ^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 $\delta(SiMe_4) = 0.0$ ppm. The $^{13}C\{^1H\}$ NMR spectra were recorded using an attached proton test technique (JMOD pulse sequence). Mass spectra were recorded on a Fisons/BG Prospec 3000 instrument operating in fast atom bombardment mode with 3-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.[15]

Synthesis of $Mo_2Ru_4(\mu_6\text{-}C)(\mu\text{-}O)(CO)_{12}Cp_2$ (1). A solution of $Mo_2(CO)_6Cp_2$ (3.0 g) in 300 mL of toluene was refluxed for 24 h with a purge of argon passing through it. At the end of this period an aliquot of 40 mL was removed which was calculated to contain 265 mg (0.61 mmol) of $Mo_2(CO)_4Cp_2$, on the basis of a 75% yield for the decarbonylation step (the remaining 260 mL of solution was used for other purposes). To the aliquot was added $Ru_3(CO)_{12}$ (390 mg, 0.61 mmol), and the mixture was heated to reflux for 5 h with TLC monitoring. The solvent was removed in vacuo and the residue absorbed onto a small amount of silica and chromatographed. Small amounts of residual $Ru_3(CO)_{12}$ and $Mo_2(CO)_6Cp_2$ were removed with light petroleum. A 3:1 mixture of light petroleum and CH_2Cl_2 was used to elute a brown band of complex **1** (275.0 mg, 41.3%). An unidentified red band (104.7 mg) was then eluted with a 1:4 mixture of the same solvents [IR (CH_2Cl_2) ν(CO) 2075 m, 2035 s, 2020 s, 2006 s; MS *m/e* 1403]. Attempts to grow crystals of this compound were unsuccessful, but we believe it contains no molybdenum.

Data for **1**: IR (CH_2Cl_2) ν(CO) 2057 m, 2017 s, 1974 m, 1812 w cm^{-1}; IR (KBr) 2057 s, 2008 s, 1993 s, 1980 s, 1970 s, 1955 s, 1814 s, 1798 s cm^{-1}; ^1H NMR δ 5.66 (s, Cp); ^{13}C NMR (298 K) 220.1 (CO), 205.2 (CO), 106.4 (Cp); ^{13}C NMR (223 K) 438.7 (μ_6-C), 220.1 (CO), 205.7 (CO), 106.3 (Cp); MS *m/e* 1091 (M^+). Anal. Calcd for $C_{23}H_{10}O_{13}Mo_2Ru_4$: C, 25.32; H, 0.92. Found: C, 25.07; H, 0.83.

Crystal Structure Determination. Crystal data for **1** are collected in Table 1. 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 7245 independent reflections (of 8645 measured) for which $|F|/\sigma(|F|) > 4.0$ were corrected for Lorentz and polarization effects but not for absorption. The structure was solved by direct methods and refined by full-matrix blocked least squares on F^2. Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement converged at a final $R1 = 0.0811$ ($wR_2 = 0.20905$ for all 7245 unique data, 757 parameters, mean and maximum δ/σ 0.004, −0.0280), with allowance for the thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density was −4.815 and 1.995 e $Å^{-3}$. A weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.1793P)^2 + 4.599P]$, where $P = (F_o^2 + 2F_c^2)/3$, was used in the latter stages of refinement. Complex scattering factors were taken from the program package SHELXL93[16] as implemented on the Viglen 486dx computer.

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Supporting Information Available: Complete listings of bond lengths and angles, anisotropic thermal parameters, and hydrogen atom coordinates and thermal parameters for complex **1** (13 pages). Ordering information and Internet access instructions are given on any current masthead page.

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[14] 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.

[15] King, R. B. *Organometallic Syntheses;* Academic Press: New York, 1965; Vol. 1, p 109.

[16] Sheldrick, G. M. SHELXL93, An integrated system for solving and refining crystal structures from diffraction data, University of Gottingen, Germany, 1993.