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Synthesis of the Tetranuclear Clusters $RuM_3H(C\equiv CFc)(CO)_{12}$ (M = Ru, Os; Fc = Ferrocenyl), Containing a Fluxional μ_4-Acetylide Ligand. Structure of a Mixed Crystal Containing Tetranuclear ($Ru_4H(C\equiv CFc)(CO)_{12}$) and Trinuclear ($Ru_3H(C\equiv CFc)(CO)_9$) Ruthenium Complexes

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Reactions of acetylide clusters $M_3H(C\equiv CFc)(CO)_9$ (**1a**, M = Ru; **1b**, M = Os; Fc = ferrocenyl) with $Ru_3(CO)_{12}$ in refluxing hexane yield the tetranuclear clusters $RuM_3H(C\equiv CFc)(CO)_{12}$ (**2a,b**) with a butterfly metal core. The μ_4-acetylide ligand of these complexes undergoes migration, indicated by variable-temperature ^1H and ^{13}C NMR studies. Compounds **2a** and **2b** are relatively unstable in solution as well as in the solid state and decompose with formation of corresponding trinuclear acetylide precursors and $Ru_3(CO)_{12}$. The molecular structures of **1a** and **2a** were established by the X-ray diffraction study of a mixed crystal, which contains both clusters in a 1:1 ratio.

Introduction

Transformations of hydrocarbons on polymetallic centers of transition-metal clusters continue to attract considerable attention, demonstrating a variety of bonding modes of hydrocarbon ligands and unusual stereodynamic behavior of the organometallic complexes formed.[1] Although the reactions of alkynes with metal carbonyl clusters have been sufficiently well studied,[2] introduction of heteroatom-substituted[3] and functionalized alkynes[4] into these reactions considerably enriched this field of organometallic chemistry, allowing homo- and heteronuclear transition-metal cluster compounds with unusual types of ligands to be obtained.

Earlier, while studying the reactions of mononuclear acetylide derivatives of transition metals with trinuclear metal carbonyls, we observed transformations of alkyne ligands into μ_3-carbene,[3b,c] μ_2-carbyne,[3c,d] μ_2-alkenyl,[3e] and μ_2-acetylide[3b,c] species and detected the fluxional behavior of a μ-η^1:η^2-acetylide ligand in the $Os_3H(C\equiv CPh)(CO)_{10}$ cluster.[5] In the present work we describe the reactions of *trinuclear* acetylide clusters $M_3H(C\equiv CFc)(CO)_9$ (**1a**, M = Ru; **1b**, M = Os; Fc = ferrocenyl) with $Ru_3(CO)_{12}$. These reactions give the tetranuclear butterfly clusters $RuM_3H(C\equiv CFc)(CO)_{12}$ (**2a**, M = Ru; **2b**, M = Os) which contain a multisite-bound μ_4-acetylide ligand. The ferrocenylacetylide ligand in **2a** and **2b** undergoes fast migration, as has been shown by variable-temperature ^1H and ^{13}C NMR studies.[6] Parts of this work were published in preliminary communications.[6] Simultaneously with us, Chi and co-

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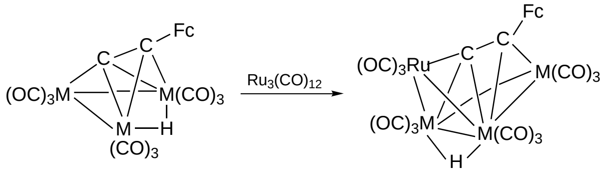
Scheme 1



1a, M = Ru
1b, M = Os

2a, M = Ru
2b, M = Os

workers reported on the similar migration of the μ_4-acetylide ligand in the heterometallic cluster (C_5Me_5)$WOs_3(C{\equiv}CCH_2OMe)(CO)_{11}$ (**3**).[7]

Results and Discussion

Synthesis and Characterization. Reaction of $Ru_3H(C{\equiv}CFc)(CO)_9$ (**1a**) with $Ru_3(CO)_{12}$ in refluxing hexane gives the deep green compound $Ru_4H(C{\equiv}CFc)(CO)_{12}$ (**2a**) in yields up to 52% (Scheme 1). Compound **2a** was purified by TLC on silica gel and separated from unreacted **1a** and $Ru_3(CO)_{12}$. Complex **2a** may be obtained also in the direct reaction of $Ru_3(CO)_{12}$ with excess ferrocenylacetylene; however, in this case the yield of **2a** is very low, because the reaction is complicated by the formation of the binuclear complexes $Ru_2(HC_2Fc)_2(CO)_6$ and $Ru_2[(HC_2Fc)_2CO](CO)_6$[8a] and the trinuclear carbyne cluster $Ru_3H(CFc)(CO)_{10}$[8b] along with complexes **1a** and **2a**. Compound **2a** is relatively unstable in solution as well as in the solid state and slowly decomposes, with the formation of starting orange complex **1a** and $Ru_3(CO)_{12}$. The reaction of the trinuclear osmium complex $Os_3H(C{\equiv}CFc)(CO)_9$ (**1b**) with $Ru_3(CO)_{12}$ proceeds in a similar way, giving the deep green heteronuclear cluster $RuOs_3H(C{\equiv}CFc)(CO)_{12}$ (**2b**) (Scheme 1).

IR spectra of compounds **2a**,**b** in the carbonyl region indicate the presence of only terminal CO groups. The ^{1}H NMR spectrum (C_6D_6, 25 °C) of compound **2a** contains a single hydride resonance at δ −22.16 (1H) and three signals for the ferrocenyl group at δ 4.20 (5H), 4.58 (2H), and 5.44 (2H), the last resonance being considerably broadened. The spectral pattern of compound **2b** is similar. The spectra of compounds **2a** and **2b** show that these complexes have rather unusual structures and, moreover, that both complexes exhibit some kind of fluxionality. It was therefore necessary to obtain direct structural information on these complexes by means of an X-ray diffraction study.

Crystal Structure. Owing to the relative instability of compound **2a**, the numerous attempts to grow its single crystals suitable for X-ray diffraction study were unsuccessful. At the initial stage of the present work we obtained a deep green sample (**I**) of compound **2a** and performed an X-ray diffraction study, which allowed us to establish the molecular structure of this compound.[6] However, the poor quality of single crystals **I** did not allow us to obtain the geometric parameters of molecule **2a** with sufficient accuracy, and this stimulated us to continue attempts to grow a more adequate crystalline sample. Finally, we found a stable brownish green crystal, which, as it turned out, contained molecules **1a** and **2a** in the ratio of 1:1. It is noteworthy that orange single crystals of **1a** also precipitated from the same hexane solution. Thus, we isolated three different types of single crystals from one system, viz., crystals **I** built of molecules **2a**, **II** containing the 1:1 mixture of **2a** and **1a**, and crystals **III**, built exclusively of molecules **1a**.

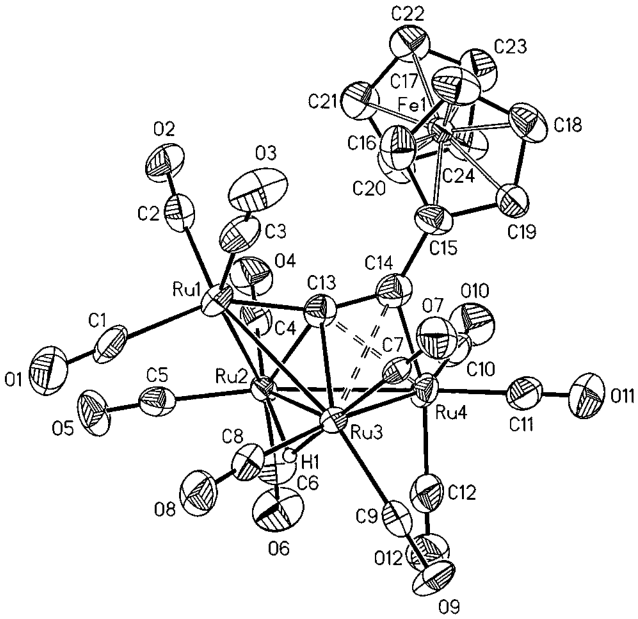


Figure 1. Molecular structure of complex 2a in the crystal of II.

Further discussion of structural peculiarities of molecule **2a** is based on the results obtained in the study of a single crystal of **II**. The molecular structure of **2a** is shown in Figure 1. Selected bond distances and angles in structure **II** are listed in Table 1.

The molecule of **2a** features the Ru_4 butterfly metal core, with three terminal CO groups bonded to each Ru atom and a hydride ligand bridging the hinge Ru(2) and Ru(3) atoms; the bridging hydride atom was directly located in the X-ray diffraction study. The Ru(1)Ru(2)Ru(3) triangle is isosceles, with exactly equal Ru(1)−Ru(2) and Ru(1)−Ru(3) bonds and a slightly longer Ru(2)−Ru(3) edge. Another triruthenium wing of the butterfly core is less symmetrical, the Ru(2)−Ru(4) bond being markedly longer than Ru(3)−Ru(4). The dihedral angle formed by the two butterfly wings is 127.6°; the dihedral angles Ru(1)Ru(2)Ru(3)/Ru(2)H(1)Ru(3) and Ru(2)Ru(3)Ru(4)/Ru(2)H(1)Ru(3) are equal to 129.9 and 102.5°, respectively. The four-membered Ru(2)Ru(3)H(1)C(13) cycle is almost ideally planar, the folding angle along the Ru(2)-Ru(3) line not exceeding 2.5°.

The remarkable feature of the structure of **2a** is the coordination of the acetylide ligand, which is bound to four ruthenium atoms. The C(13) carbon atom is almost symmetrically disposed above the plane of the isosceles triangle Ru(1)Ru(2)Ru(3), forming bonds with all its vertices. Another acetylene carbon atom C(14) forms the only Ru−C bond with the Ru(4) atom. There are also two additional contacts between the atoms of the acetylide ligand and the metal atoms, Ru(4)···C(13) = 2.58(1) Å and Ru(3)···C(14) = 2.76(1) Å. Taking into account that tetranuclear carbonyl clusters with a butterfly metal core have typically 62e, we may expect

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

Ru(1)−Ru(2)	2.817(1)	Fe(1)−C	2.01−2.07	Ru(2)−H(1)	1.74(7)	Ru(6)−C(34)	2.21(1)
Ru(1)−Ru(3)	2.818(1)	C(13)−C(14)	1.34(1)	Ru(3)−Ru(4)	2.843(1)	Ru(6)−C(35)	2.26(1)
Ru(1)−C(1)	2.00(1)	C(14)−C(15)	1.47(1)	Ru(3)−C(7)	1.90(1)	Ru(6)−H(2)	1.70(7)
Ru(1)−C(2)	1.89(1)	Ru(5)−Ru(6)	2.799(1)	Ru(3)−C(8)	1.94(1)	Ru(7)−C(31)	1.91(1)
Ru(1)−C(3)	1.90(1)	Ru(5)−Ru(7)	2.820(1)	Ru(3)−C(9)	1.93(1)	Ru(7)−C(32)	1.92(1)
Ru(1)−C(13)	1.97(1)	Ru(5)−C(25)	1.96(1)	Ru(3)−C(13)	2.18(1)	Ru(7)−C(33)	1.94(1)
Ru(2)−Ru(3)	2.825(1)	Ru(5)−C(26)	1.91(1)	Ru(3)−C(14)	2.76(1)	Ru(7)−C(34)	2.22(1)
Ru(2)−Ru(4)	2.881(1)	Ru(5)−C(27)	1.92(1)	Ru(3)−H(1)	1.60(8)	Ru(7)−C(35)	2.24(1)
Ru(2)−C(4)	1.89(1)	Ru(5)−C(34)	1.96(1)	Ru(4)−C(10)	1.87(1)	Ru(7)−H(2)	1.71(7)
Ru(2)−C(5)	1.94(1)	Ru(6)−Ru(7)	2.799(1)	Ru(4)−C(11)	1.90(1)	Fe(2)−C	2.02−2.06
Ru(2)−C(6)	1.93(1)	Ru(6)−C(28)	1.92(1)	Ru(4)−C(12)	1.97(1)	C(34)−C(35)	1.30(1)
Ru(2)−C(13)	2.17(1)	Ru(6)−C(29)	1.92(1)	Ru(4)−C(13)	2.58(1)	C(35)−C(36)	1.46(1)
Ru(2)−C(14)	3.10(1)	Ru(6)−C(30)	1.93(1)	Ru(4)−C(14)	2.07(1)		

C(2)−Ru(1)−Ru(2)	99.5(3)	C(14)−C(13)−Ru(3)	100.9(6)	C(8)−Ru(3)−Ru(1)	77.5(3)	Ru(7)−Ru(6)−Ru(5)	60.50(3)
C(3)−Ru(1)−Ru(2)	151.0(3)	Ru(1)−C(13)−Ru(3)	85.4(3)	C(13)−Ru(3)−Ru(1)	44.3(2)	C(34)−Ru(7)−C(35)	33.9(3)
C(13)−Ru(1)−Ru(2)	50.1(3)	Ru(2)−C(13)−Ru(3)	81.1(3)	C(7)−Ru(3)−Ru(2)	143.6(2)	C(31)−Ru(7)−Ru(6)	110.7(3)
C(1)−Ru(1)−Ru(2)	107.7(3)	C(13)−C(14)−C(15)	126.9(10)	C(9)−Ru(3)−Ru(2)	112.3(3)	C(32)−Ru(7)−Ru(6)	141.7(3)
C(2)−Ru(1)−Ru(3)	150.6(3)	C(13)−C(14)−Ru(4)	96.1(7)	C(8)−Ru(3)−Ru(2)	106.6(3)	C(33)−Ru(7)−Ru(6)	108.7(3)
C(3)−Ru(1)−Ru(3)	97.8(3)	C(15)−C(14)−Ru(4)	136.5(8)	C(13)−Ru(3)−Ru(2)	49.3(2)	C(34)−Ru(7)−Ru(6)	50.6(2)
C(13)−Ru(1)−Ru(3)	50.4(3)	C(25)−Ru(5)−Ru(6)	100.4(3)	Ru(1)−Ru(3)−Ru(2)	59.90(3)	C(35)−Ru(7)−Ru(6)	51.7(2)
C(1)−Ru(1)−Ru(3)	107.6(3)	C(26)−Ru(5)−Ru(6)	99.9(3)	C(7)−Ru(3)−Ru(4)	102.6(3)	C(31)−Ru(7)−Ru(5)	88.4(3)
Ru(2)−Ru(1)−Ru(3)	60.17(3)	C(27)−Ru(5)−Ru(6)	158.3(3)	C(9)−Ru(3)−Ru(4)	79.6(3)	C(32)−Ru(7)−Ru(5)	91.8(3)
C(4)−Ru(2)−Ru(1)	99.8(3)	C(34)−Ru(5)−Ru(6)	51.7(2)	C(8)−Ru(3)−Ru(4)	163.6(3)	C(33)−Ru(7)−Ru(5)	168.1(3)
C(6)−Ru(2)−Ru(1)	163.1(3)	C(26)−Ru(5)−Ru(7)	155.5(3)	C(13)−Ru(3)−Ru(4)	60.1(2)	C(34)−Ru(7)−Ru(5)	43.9(2)
C(5)−Ru(2)−Ru(1)	73.2(3)	C(27)−Ru(5)−Ru(7)	102.0(3)	Ru(1)−Ru(3)−Ru(4)	102.68(4)	C(35)−Ru(7)−Ru(5)	76.8(2)
C(13)−Ru(2)−Ru(1)	44.3(2)	C(25)−Ru(5)−Ru(7)	101.3(3)	Ru(2)−Ru(3)−Ru(4)	61.10(3)	Ru(6)−Ru(7)−Ru(5)	59.76(3)
C(4)−Ru(2)−Ru(3)	142.3(3)	C(34)−Ru(5)−Ru(7)	51.6(3)	C(10)−Ru(4)−Ru(3)	161.3(3)	C(35)−C(34)−Ru(5)	152.5(7)
C(6)−Ru(2)−Ru(3)	114.9(3)	Ru(6)−Ru(5)−Ru(7)	59.74(3)	C(11)−Ru(4)−Ru(3)	100.5(3)	C(35)−C(34)−Ru(6)	75.0(5)
C(5)−Ru(2)−Ru(3)	108.2(3)	C(34)−Ru(6)−C(35)	33.9(3)	C(12)−Ru(4)−Ru(3)	97.4(3)	Ru(5)−C(34)−Ru(6)	84.1(3)
C(13)−Ru(2)−Ru(3)	49.6(2)	C(29)−Ru(6)−Ru(7)	140.3(3)	C(14)−Ru(4)−Ru(3)	66.3(3)	C(35)−C(34)−Ru(7)	74.0(5)
Ru(1)−Ru(2)−Ru(3)	59.93(3)	C(28)−Ru(6)−Ru(7)	112.7(3)	C(10)−Ru(4)−Ru(2)	106.4(3)	Ru(5)−C(34)−Ru(7)	84.5(3)
C(4)−Ru(2)−Ru(4)	99.1(3)	C(30)−Ru(6)−Ru(7)	108.1(3)	C(11)−Ru(4)−Ru(2)	159.4(3)	Ru(6)−C(34)−Ru(7)	78.4(3)
C(6)−Ru(2)−Ru(4)	87.2(4)	C(34)−Ru(6)−Ru(7)	51.0(2)	C(12)−Ru(4)−Ru(2)	91.3(3)	C(34)−C(35)−C(36)	143.6(8)
C(5)−Ru(2)−Ru(4)	167.2(3)	C(35)−Ru(6)−Ru(7)	51.3(2)	C(14)−Ru(4)−Ru(2)	75.5(3)	C(34)−C(35)−Ru(7)	72.1(5)
C(13)−Ru(2)−Ru(4)	59.4(2)	C(29)−Ru(6)−Ru(5)	92.4(3)	Ru(3)−Ru(4)−Ru(2)	59.14(3)	C(36)−C(35)−Ru(7)	135.2(6)
Ru(1)−Ru(2)−Ru(4)	101.74(4)	C(28)−Ru(6)−Ru(5)	88.1(3)	C(14)−C(13)−Ru(1)	151.9(8)	C(34)−C(35)−Ru(6)	71.1(5)
Ru(3)−Ru(2)−Ru(4)	59.76(3)	C(30)−Ru(6)−Ru(5)	168.5(3)	C(14)−C(13)−Ru(2)	122.3(7)	C(36)−C(35)−Ru(6)	130.2(6)
C(7)−Ru(3)−Ru(1)	97.0(3)	C(34)−Ru(6)−Ru(5)	44.2(2)	Ru(1)−C(13)−Ru(2)	85.6(4)	Ru(7)−C(35)−Ru(6)	77.0(3)
C(9)−Ru(3)−Ru(1)	167.5(3)	C(35)−Ru(6)−Ru(5)	77.0(2)				

the acetylide ligand in complex **2a** to act as a 5e donor. Indeed, one may regard complex **2a** as an alkenyl derivative with the C(13)−C(14) double bond π-coordinated by the Ru(3) atom, the C(13) atom σ-bonded to both Ru(1) and Ru(2) atoms and the C(14) atom σ-bonded to Ru(4). At the same time, in the framework of this bonding scheme the rather short Ru(4)···C(13) contact should be treated as nonbonding, originating from the overall steric overcrowding in the molecule. (The alternative description of the C(13)−C(14) bond as a triple bond π-coordinated to both Ru(2) and Ru(3) atoms is inconsistent with the very long Ru(2)···C(14) distance of 3.10(1) Å.) Such coordination of the acetylide ligand in tetranuclear clusters has been found just in a few cases, viz., in the heteronuclear butterfly clusters $(C_5Me_5)WOs_3(C{\equiv}CCH_2OMe)(CO)_{11}$ (**3**) (with the W atom at the wingtip position),[7] $(C_5H_5)WOs_3(C{\equiv}CPh)(CO)_{11}$ (**4**) (with the W atom at the hinge position),[9] and $(C_5H_5)WRu_3(C{\equiv}CPh)(\mu\text{-}NPh)(CO)_9$ (**5**) (with the W atom at the hinge position).[10] In contrast to compounds **3**−**5**, cluster **2a** represents the first homonuclear complex of this type and contains only carbonyl and hydride ligands along with the μ_4-acetylide group.

The Ru(3)-C(14) distance in **2a** is consideraby longer than the corresponding M−C distances in complexes **3** (Os−C = 2.32(2) Å), **4** (W−C = 2.49(2) Å), and **5** (W−C = 2.39(1) Å), which may be due to the presence of electron-donating ligands at the metal core atoms in **3**−**5** and/or the influence of the ferrocenyl substituent at the acetylene carbon atom in **2a**. It may be noted in this respect that the C(14) atom in **2a** has an almost planar environment and deviates from the C(13)C(15)Ru(4) plane by no more than 0.06 Å. At the same time the C(14)-C(15) bond is noticeably inclined to the cyclopentadienyl plane (by 6.8°), so that the C(14) atom is displaced from the Cp plane toward the Fe(1) atom. This type of geometry of the exocyclic bond is typical for ferrocenyl carbocations,[11] wherein the inclination angle may vary in a wide range depending on the nature of the substituents at the carbocationic center, e.g. from 6.3° in ferrocenyldiphenylcyclopropenium[11c] to 20.7° in ferrocenyldiphenylmethylium[11d] ions. (It may be noted in this connection that the proton resonances of the ferrocenyl group in ^1H NMR spectra of **2a** and **2b** (see below) are observed at remarkably low field in comparison with their precursors **1a** and **1b**.) Although one may suggest that there exist interactions of two metal atoms with a “carbocationic” [12] acetylide atom, Ru(3)−C(14)···Fe(1), in **2a**, the distance Fe(1)···C(14) = 3.04(1) Å seems to be too long for any bonding interaction. At present we may just assume that there is some transfer of electron density from the ferrocenyl group to Ru_4 and $RuOs_3$ clusters.

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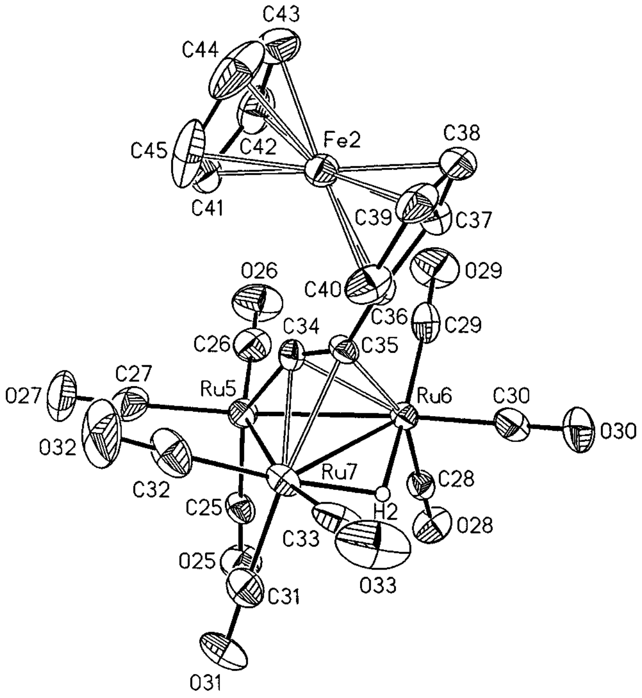


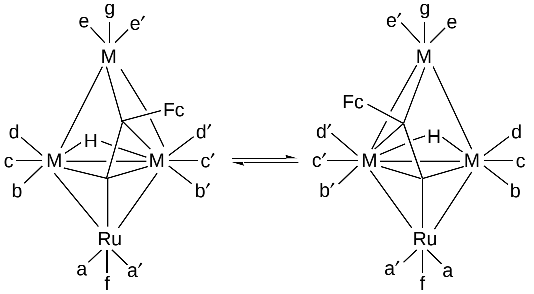
Figure 2. Molecular structure of complex **1a** in the crystal of **II**.

The structure of molecule **1a** as determined in the crystal of **II** is shown in Figure 2. Complexes of this type, including the osmium analog of **1a**, $Os_3H(C{\equiv}CFc)(CO)_9$ (**6**),[13] have been studied earlier by diffraction methods.[2] The Ru(5)-Ru(7) bond in **1a** is somewhat longer than the two other bonds in the metal triangle. There is no obvious explanation of this difference; it is just noteworthy that the same peculiarity was observed in complex **1b**.

Fluxional Behavior of 2a and 2b. Taking into account the results of the X-ray diffraction study of compound **2a**, one may assume that the broadening of the substituted cyclopentadienyl ring proton resonances may be due to degenerate rearrangement of the acetylide ligand, including the σ- and π-bond exchange between the Ru(2) and Ru(3) atoms. This assumption was confirmed by the variable-temperature ^1H and ^{13}C NMR study of cluster **2a**.

When the toluene-d_8 solution of **2a** is cooled to −60 °C, the protons of the substituted cyclopentadienyl ring of the ferrocene moiety become diastereotopic, giving four distinct resonances at δ 5.83, 5.23, 4.70, and 4.56; the protons of the unsubstituted cyclopentadienyl ring and the hydride ligand are observed at δ 4.36 (5H) and −22.20 (1H), respectively. The warming of this solution led to the broadening of the resonances of the H(2) and H(5) protons of the substituted cyclopentadienyl ring and then their collapse (at −5 °C); signals for the H(3) and H(4) protons coalesce at ca. −15 °C. Finally, at 50 °C resonances for the H(2,5) and H(3,4) protons are observed at δ 5.56 (2H) and 4.76 (2H), respectively, showing that at this temperature fast exchange of the acetylide ligand takes place (Scheme 2).

Scheme 2



2a, M = Ru
2b, M = Os

The following thermodynamic parameters of acetylide migration have been calculated from analysis of the ^1H NMR spectra of compound **2a**: $\Delta G_{298} = 12.5 \pm 0.1$ kcal/mol, $\Delta H = 12.0 \pm 0.1$ kcal/mol, $\Delta S_{298} = -1.8 \pm 0.9$ eu. The small negative entropy of activation indicates the low influence of steric factors in the transition state of the exchange process.

The ^{13}C NMR spectrum of the ^{13}CO-enriched sample **2a** in CD_2Cl_2 at −73 °C contains 12 carbonyl resonances of equal intensities at δ 199.3, 199.0, 198.9, 198.5, 196.6, 195.8, 192.0, 190.5, 189.0, 188.5 ($^2J_{CH} = 12.1$ Hz), 188.1, and 186.2 ($^2J_{CH} = 16.1$ Hz), which in accordance with the solid-state molecular structure indicates that the molecule does not possess any symmetry elements. When the solution is warmed to approximately −40 °C, three resonances at δ 198.9, 198.5, and 188.5 are broadened considerably; at −23 °C these resonances are broadened to the extent that they are no longer visible. At −25 °C only two resonances at the lowest field (δ 199.3 and 199.0) are sharp, whereas seven others are broadened to an approximately equal extent. Further warming leads to the appearance and subsequent sharpening of the resonance which originates from the averaging of two resonances at δ 189.0 and 188.1 observed in the low-temperature limiting spectrum. At 25 °C the resonance at the lowest field is very broad, while the neighboring resonance remains sharp in the temperature range from −73 to +25 °C. Finally, at 50 °C the spectrum in the toluene-d_8 solution contains three broadened signals at δ 201.9, 196.9, and 192.2 with relative intensities of 1:6:2, respectively.

This ^{13}C NMR spectral pattern may be interpreted as follows. The lowest energy process is the localized exchange of the three carbonyls at one of the hinge ruthenium atoms Ru(2) and Ru(3) (carbonyls b/c/d or b′/c′/d′, respectively), as one of the exchanged carbonyls is in a trans position relative to the bridging hydride ligand (its resonance is split with $^2J_{CH} = 12.1$ Hz). The next exchange process is the migration of the acetylide ligand, which generates the mirror plane and equilibrates pairwise all carbonyl ligands with the exception of carbonyls f and g. The observation of a resonance of relative intensity 6 indicates that localized exchange of each $Ru(CO)_3$ group at the hinge ruthenium atoms operates simultaneously with acetylide migration. The resonances of relative intensities 1 and 2 observed at 50 °C are assigned to one axial and two equatorial ligands, respectively, at one of the wingtip ruthenium atoms, Ru(1) and Ru(4). Another axial carbonyl group signal broadens considerably on raising the temperature to ca. 10 °C, evidently due to the exchange process; the process, however, is not sufficiently fast on the NMR time scale to bring about the coalescence of three resonances (in the low-temperature limiting spectrum

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they are observed at δ 199.3, 192.0 and 190.5) even at 50 °C.

The ^1H NMR spectral pattern for the heteronuclear cluster **2b** is similar to that of cluster **2a**. At −70 °C in the toluene-d_8 solution, the spectrum contains four resonances of equal intensities at δ 5.97, 5.35, 4.65, and 4.78 due to the substituted cyclopentadienyl ring; resonances of C_5H_5 and μ-H ligands are observed at δ 4.53 and −23.88, respectively. At 50 °C the same solution gives resonances at δ 5.54 (2H), 4.77 (2H), 4.30 (5H), and −23.74 (1H); at this temperature the resonance at δ 5.54 is only slightly broadened. In the ^{13}C NMR spectrum of the sample of ^{13}CO-enriched **2b** in toluene-d_8 solution at −45 °C all 12 carbonyls are nonequivalent: δ 198.8, 195.0, 192.9, 182.8, 182.0, 181.4, 178.1, 176.8, 175.5, 175.2, 168.5 (d, $^2J_{CH} = 9.7$ Hz), and 165.9 (d, $^2J_{CH} = 11.1$ Hz). The lowest field signal should be assigned to the axial carbonyl f, and the next two resonances are attributed to equatorial ligands a and a′ of the $Ru(CO)_3$ moiety at the wingtip position of the cluster (Scheme 2). Resonances at δ 168.5 and 165.9 are assigned to the c and c′ ligands located in trans positions relative to the bridging hydride ligand. When the temperature of the solution was raised to 25 °C, only the resonance of axial carbonyl g at δ 182.61 remained sharp, whereas the signal of carbonyl f was slightly broadened; the other five resonances, each of relative intensity 2, at δ 194.0, 181.4, 176.3, 175.4, and 167.0 were broadened considerably. This spectral pattern indicates the fast migration of the acetylide ligand, which equilibrates the carbonyl environments pairwise (a/a′, b/b′, c/c′, d/d′, e/e′) with the exception of axial ligands f and g at the osmium and ruthenium atoms, respectively.

Conclusion

The formation of clusters **2a** and **2b** is quite remarkable, if we take into account that, notwithstanding extensive studies of the reactions of various alkynes with ruthenium and osmium carbonyls, acetylide butterfly complexes of this type have never been observed. In this connection one may raise the question of whether the formation of complexes **2a** and **2b** is due to the presence of the ferrocenyl substituent on the alkyne or whether similar acetylide clusters may have been formed in the earlier studied reactions, but their yields were too low, making their detection impossible. In order to establish the scope of the above reaction, we studied the interaction of other trinuclear acetylide clusters with $Ru_3(CO)_{12}$. According to the preliminary results the nature of the substituent on the alkyne may determine the type of product formed in the reaction. Thus, the thermal reaction of $Os_3H(C{\equiv}CMe)(CO)_9$ with $Ru_3(CO)_{12}$ yields the red tetranuclear butterfly complex $Os_3Ru(HC_2Me)(CO)_{12}$ with an alkyne rather than an acetylide ligand.[6a]

In contrast to the transition-metal complexes with bridging alkenyl ligands whose fluxionality was reliably established in a number of compounds,[14] the migration of the acetylide ligand has been elusive. The situation has changed over the last few years, since the migration of μ-η^1:η^2-acetylide ligands in triosmium[5] and dirhenium[15] clusters and rotation of μ_3-η^1:η^2:η^2-acetylide groups in trimetallic clusters[16] have been observed. It has now been found[6,7] that μ_4-η^1:η^1:η^1:η^2-acetylide ligands in butterfly clusters may also be fluxional. Thus, one may conclude that the acetylide ligands in transition-metal complexes may demonstrate not only a diversity of bonding possibilities but also various types of fluxional behavior.

Table 2. Crystal Data and Details of the X-ray Experiment for Crystal II

formula	$C_{45}H_{20}O_{21}Fe_2Ru_7$
mol wt	1715.80
cryst color and habit	brownish green needles
cryst size, mm	0.5 × 0.2 × 0.1
cryst syst	monoclinic
space group	$P2_1/c$
cell constants	
a, Å	9.412(3)
b, Å	35.254(10)
c, Å	15.563(5)
β, deg	91.13(3)
V, Å^3	5163(3)
Z	4
D_{calcd}, g cm^{-3}	2.207
diffractometer	Siemens P3/PC
temp, K	153
radiation (Å)	Mo Kα ($\lambda = 0.710\,73$), graphite monochromated
scan mode	$\theta - 2\theta$
$2\theta_{max}$, deg, (hkl signs)	50, ($-h$, $+h$; 0, k; 0, l)
abs coeff, μ(Mo Kα), cm^{-1}	26.09
no. of data collcd	9739
no. of unique data	9150
no. of params refined	684
R1 (on F for rflns with $I > 2\sigma(I)$)	0.0576 (6495 rflns)
wR2 (on F^2 for all rflns)	0.1305 (9097 rflns)

Experimental Section

General Procedures. All reactions were carried out under an argon atmosphere. Reagent grade solvents were purified by distillation under argon from appropriate drying agents. TLC separations were performed in air using silica gel on glass plates. IR spectra were recorded on a Bruker IFS-113v spectrometer and ^1H and ^{13}C NMR spectra on a Bruker AMX-400 instrument. The $Ru_3H(C{\equiv}CFc)(CO)_9$ and $Os_3H(C{\equiv}CFc)(CO)_9$ complexes were prepared according to published procedures.[8a,13] The ^{13}CO-enriched samples (*ca*. 40% ^{13}C) of compounds **2a** and **2b** were prepared by reaction of $Ru_3(^{13}CO)_{12}$ with **1a** and **1b**, respectively.

The kinetic data were obtained by dynamic ^1H NMR on the basis of comparison of experimental spectra with theoretical ones. For simplification of calculations it was suggested that exchange is of a two-site type. The difference in chemical shifts in the absence of exchange for calculation of τ values near collapse was extrapolated from low temperature. The τ values were determined within a −50 to +30 °C interval of temperature.

Reaction of $Ru_3H(C{\equiv}CFc)(CO)_9$ with $Ru_3(CO)_{12}$. A mixture of 60 mg of $Ru_3H(C{\equiv}CFc)(CO)_9$ (0.08 mmol) and 100 mg of the ruthenium carbonyl species (0.16 mmol) in 60 mL of hexane was refluxed for 10 h. The solvent was evaporated in vacuo and the residue was separated by TLC using hexane as solvent to yield (in order of elution) a red-orange band of

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unreacted $Ru_3(CO)_{12}$, an orange band of $Ru_3H(C{\equiv}CFc)(CO)_9$, and a green band of $Ru_4H(C{\equiv}CFc)(CO)_{12}$ (**2a**; (40 mg, 52%). IR (ν_{CO} in hexane, cm^{-1}) for **2a**: 2090 (w), 2062 (vs), 2052 (s), 2038 (w), 2019 (s), 1996 (w, br), 1979 (m, br). ^1H NMR (δ in $CDCl_3$, 23 °C) for **2a**: δ 5.54 (br, 2H), 5.17 (2H), 4.43 (5H), −22.18 (1H). ^{13}C NMR (δ in CD_2Cl_2, −73 °C, carbonyl region) for **2a**: 199.3, 199.0, 198.9, 198.5, 196.6, 195.8, 192.0, 190.5, 189.0, 188.5 (d, $^2J_{CH} = 12.1$ Hz), 188.1, 186.2 (d, $^2J_{CH} = 16.1$ Hz). Anal. Calcd for $C_{24}H_{10}FeO_{12}Ru_4$: C, 30.33; H, 1.06. Found: C, 30.58; H, 1.20.

Reaction of $Os_3H(C{\equiv}CFc)(CO)_9$ with $Ru_3(CO)_{12}$. The reaction was performed under the same conditions as detailed above, giving green $RuOs_3H(C{\equiv}CFc)(CO)_{12}$ (35%). IR (ν_{CO} in CH_2Cl_2, cm^{-1}): 2086 (w), 2054 (vs), 2009 (s), 1974 (m, br), 1938 (w, br). ^1H NMR (δ in $C_6D_5CD_3$, −60 °C); 5.97 (1H), 5.35 (1H), 4.65 (1H), 4.78 (1H), 4.53 (5H), −23.74 (1H). ^{13}C NMR (δ in $C_6D_5CD_3$, −45 °C): 198.8, 195.0, 192.9, 182.8, 182.0, 181.4, 178.1, 176.8, 175.5, 175.2, 168.5 (d, $^2J_{CH} = 9.7$ Hz), 165.9 (d, $^2J_{CH} = 11.1$ Hz). Anal. Calcd for $C_{24}H_{10}FeO_{12}Os_3Ru$: C, 23.67; H, 0.83. Found: C, 23.84; H, 1.08.

X-ray Data Collection, Structure Determination, and Refinement for II. Single crystals of **II** were grown slowly from a dilute solution in hexane at approximately −10 °C. Accurate unit cell parameters and orientation matrices were obtained by least-squares refinement of carefully centered 24 reflections in the $24 < 2\theta < 26°$ range. Data were corrected for Lorentz and polarization effects. The relatively low absorption coefficient value justified no necessity for absorption correction.

The structure was solved by direct methods and subsequent difference Fourier maps. All H atoms of the ferrocenylacetylide ligands were placed in geometrically calculated positions and included in the refinement using the riding model approximation with $U_{iso}(H) = 1.2U_{eq}(C)$; the bridging hydride atoms were located in the difference syntheses and refined in the isotropic approximation. All calculations were carried out on an IBM PC with SHELXTL PLUS 5 (gamma-version) programs. Crystal data and details of the X-ray experiments are given in Table 2.

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Supporting Information Available: Tables giving crystal data and structure refinement details, positional and thermal parameters, and bond distances and angles for **II** (10 pages). Ordering information is given on any current masthead page.

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