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Synthesis and Characterization of Alkyne Derivatives of $Ru_6C(CO)_{17}$

Ruth L. Mallors,[†] Alexander J. Blake,[†] Paul J. Dyson,[‡]
Brian F. G. Johnson,*[,§] and Simon Parsons[†]

Department of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, U.K., Department of Chemistry, Imperial College of Science, Technology, and Medicine, South Kensington, London SW7 2AY, U.K., and Department of Chemistry, The University of Cambridge, Lensfield Road, Cambridge CB2 1EW, U.K.

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The cluster−alkyne complexes $Ru_6C(CO)_{15}(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_2Me_2)$ (**2**), $Ru_6C(CO)_{14}(\mu\text{-}\eta^2{:}\eta^2\text{-}C_2Me_2)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_2Me_2)$ (**3**), $Ru_6C(CO)_{13}(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_2Me_2)_2$ (**4**), and $Ru_6C(CO)_{12}(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_2Me_2)_3$ (**5**) have been prepared from $Ru_6C(CO)_{17}$ (**1**) in a stepwise fashion using chemical activation methods. In **3**, the octahedral metal skeleton common to **1**, **2**, **4**, and **5** has undergone rearrangement to a monocapped square pyramid. The mixed-alkyne cluster, $Ru_6C(CO)_{14}(\mu\text{-}\eta^2{:}\eta^2\text{-}C_2Ph_2)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_2Me_2)$ (**6**), closely related to **3**, has also been prepared. The molecular structures of **3**, **5**, and **6** have been established in the solid state by single-crystal X-ray diffraction analysis.

Introduction

There is an established and well-developed coordination chemistry of alkyne ligands in transition metal cluster complexes, and the subject has been reviewed on several occasions.[1−3] A wide variety of bonding modes have been recorded for the alkyne (or alkyne-derived ligands), with coordination to three metal centers being the most common, although interactions with up to five metal atoms have been observed. The structure of an alkyne ligand, R−C≡C−R, alters markedly upon coordination to a cluster unit, *viz.* elongation of the C−C bond and loss of linearity of the R−C≡C−R system.[4] These physical changes are reflected in the marked changes in reactivity, which may well depend critically on the nature of the coordination mode adopted by the ligand. Reactions such as carbonyl insertion[5,6] and oligomerization[7] have been observed. In a recent example, cleavage of a C≡C alkyne bond under ambient conditions was observed in the reaction between $Ru_6C(CO)_{17}$ and phenylacetylene, yielding $Ru_6C(CO)_{13}(\eta^5\text{-}C_5H_3Ph_2)(\mu_3\text{-}CPh)$.[8] This cluster contains both a diphenylcyclopentadienyl ligand and an alkylidyne C−Ph ligand, the formation of which requires the cleavage of the acetylene triple bond together with cyclization to form the five-membered ring.

Continuing our studies in the organometallic chemistry of the hexaruthenium−carbido cluster, $Ru_6C(CO)_{17}$ (**1**),[9] we report some new alkyne derivatives prepared by chemical activation using Me_3NO under mild conditions.

Results and Discussion

The reaction of $Ru_6C(CO)_{17}$ (**1**) with 2 equiv of Me_3NO in the presence of but-2-yne (C_2Me_2) results in the formation of $Ru_6C(CO)_{15}(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_2Me_2)$ (**2**) in a moderate yield together with the more highly substituted cluster $Ru_6C(CO)_{14}(\mu\text{-}\eta^2{:}\eta^2\text{-}C_2Me_2)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_2Me_2)$ (**3**) in a lower yield (Scheme 1). Purification of these clusters was achieved chromatographically on silica using 20% dichloromethane−hexane as the eluent. Spectroscopic data of **2** and **3** (and the other compounds reported herein) are listed in Table 1. The mass spectrum of **2** comprises a strong molecular ion at *m*/*z* 1990 (calcd 1992) followed by peaks corresponding to the sequential loss of 15 carbonyl ligands. Similarly, the mass spectrum of **3** has a strong molecular ion peak at *m*/*z* 1116 (1118) together with successive loss of several carbonyls. Clearly, if the two alkyne ligands in **3** supply four electrons each to cluster bonding, the total electron count for the cluster would be 88, which is two more than that required for an octahedron. A polyhedral rearrangement would account for this anomaly, and a single-crystal X-ray diffraction analysis of 3 reveals that the ruthenium skeleton has rearranged to a monocapped square-based pyramid (*vide infra*). The ^1H NMR spectrum of **2** contains a singlet at δ 3.00, and in **3**, two singlets of equal relative intensity are observed at δ 3.29 and 2.88 all of which may be assigned to the methyl group protons of the alkyne ligands.

[†] The University of Edinburgh.

[‡] Imperial College of Science, Technology, and Medicine.

[§] The University of Cambridge.

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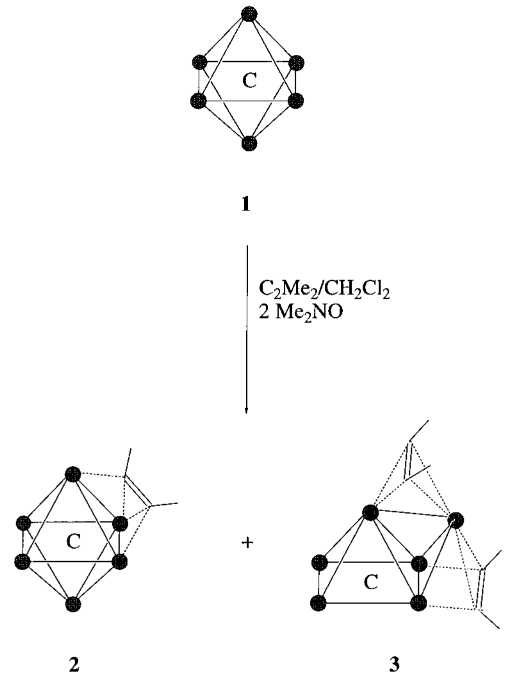
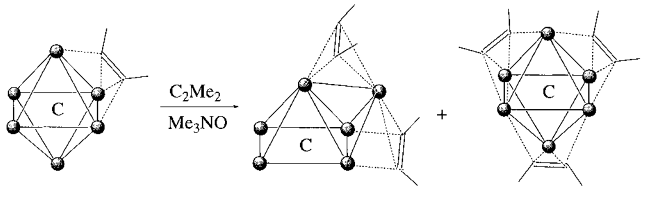
Table 1. Spectroscopic Details for Compounds 2−6

compound	IR (hexane, ν(CO), cm^{-1})	MS (m/z)	^1H NMR ($CDCl_3$, ppm)
2	2088 (w), 2044 (vs), 2036 (s, sh), 2021 (m), 2013 (m), 1944 (vw)	1090 (calcd 1092)	3.00 (s, 6H)
3	2083 (w), 2070 (vw), 2044 (sh), 2039 (vs), 2025 (s), 2012 (m), 2001 (vw), 1997 (vw), 1981 (vw), 1969 (vw)	1116 (calcd 1118)	3.29 (s, 6H), 2.88 (s, 6H)
4	2077 (m), 2042 (s), 2021 (vs), 1996 (w), 1978 (w)	1090 (calcd 1090)	2.98 (s, 12H)
5	2083 (w), 2074 (w), 2048 (vw), 2037 (sh), 2026 (vs), 2013 (sh), 2002 (sh), 1966 (w)	1116 (calcd 1116)	2.86 (s, 18H)
6	2082 (s), 2042 (vs), 2025 (s)	1242 (calcd 1242)	7.32 (m, 10H), 2.89 (s, 6H)

Scheme 1



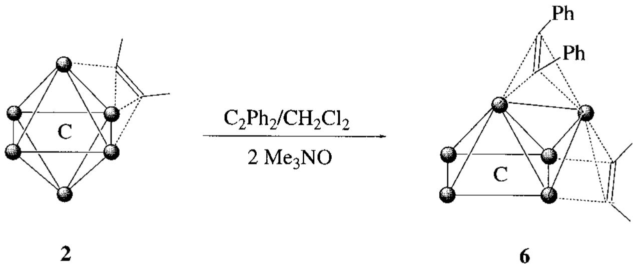
Scheme 2



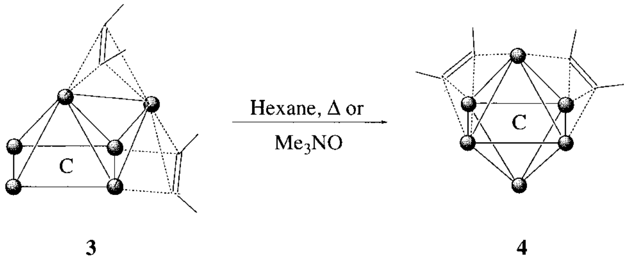
Further treatment of **2** with 2 equiv of Me_3NO in the presence of excess but-2-yne results in the formation of **3** and the new trisalkyne complex $Ru_6C(CO)_{12}(\mu_3\text{-}\eta^1:\eta^2:\eta^1\text{-}C_2Me_2)_3$ (**5**) in a low yield (Scheme 2). This cluster is in fact based on an octahedral geometry, as evidenced by a single-crystal X-ray diffraction study (*vide infra*), and has an electron count of 88 if each alkyne donates four electrons toward skeletal bonding. Compound **5** may also be produced in a much higher yield from the bisalkyne cluster **3** using an analogous method, *viz.* reaction with 2 equiv of Me_3NO in the presence of excess but-2-yne. The mass spectrum of **5** contains a parent peak at m/z 1116 (calcd 1116) with additional peaks arising from sequential CO loss from the otherwise intact cluster. The ^1H NMR spectrum exhibits a singlet resonance at δ 2.86, suggesting that all three alkynes are equivalent and bond to the cluster in a similar fashion.

In order to further our understanding of the conversion of **2** to **3**, cluster **2** was reacted with 2 equiv of Me_3NO in the presence of excess diphenylacetylene. The new cluster containing two different alkynes, $Ru_6C(CO)_{14}(\mu\text{-}\eta^2:\eta^2\text{-}C_2Ph_2)(\mu_3\text{-}\eta^1:\eta^2:\eta^1\text{-}C_2Me_2)$ (**6**), was produced (Scheme 3). The mass spectrum is comprised of a parent peak at m/z 1242 (calcd 1242) followed by a series of peaks, which may be attributed to the sequential loss of several CO ligands. The ^1H NMR spectrum of **6** exhibits a multiplet centered at δ 7.32 and a singlet resonance at δ 2.89, with relative intensities of 5:3. These signals may be assigned to the protons of the phenyl rings and methyl groups, respectively.

Scheme 3



Scheme 4



It has also been possible to expel one carbonyl ligand from **3** using either thermal or chemical techniques. Heating **3** in heptane for 1 h results in the formation of a new compound **4** (Scheme 4). The same compound is produced when **3** is treated with Me_3NO in an inert solvent, *viz.* dichloromethane. Characterization of **4** as $Ru_6C(CO)_{13}(\mu_3\text{-}\eta^1:\eta^2:\eta^1\text{-}C_2Me_2)_2$ was initially based on a comparison of the IR spectrum with that of the known compound $Ru_6C(CO)_{13}(\mu_3\text{-}\eta^1:\eta^2:\eta^1\text{-}C_2Ph_2)_2$.[10] The IR spectrum showed a similar profile of bands to that of the known cluster. Confirmation of this formulation was supplied by mass and ^1H NMR spectroscopy. The mass spectrum of **4** exhibits a parent peak at m/z 1090 (calcd 1090) followed by peaks corresponding to the sequential loss of 13 carbonyl ligands. The ^1H NMR spectrum contains one singlet at δ 2.98, indicating equivalence of the two alkyne ligands.

Molecular Structures of 3, 5, and 6. The structures of clusters **3** and **6** are closely related and will therefore be discussed together. Cluster **3** was crystallized from a solution of dichloromethane−hexane by slow evaporation at −25 °C, and single crystals of **6** were grown from dichloromethane at −10 °C. The molecular structures of **3** and **6** are shown in Figures 1 and 2, respectively. Relevant bond parameters are listed in

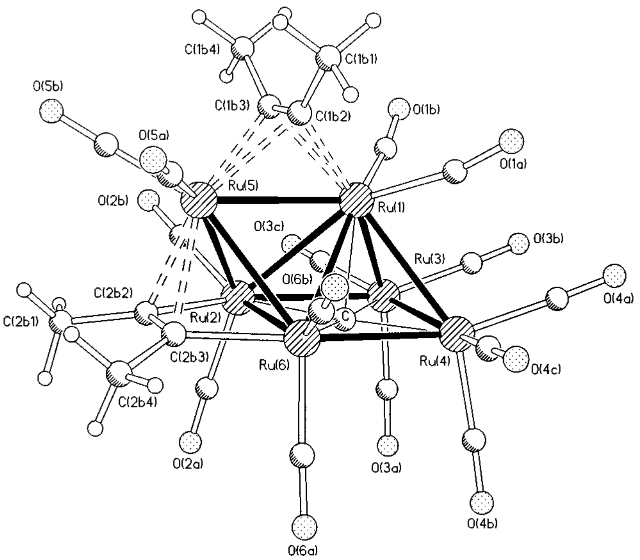


Figure 1. The molecular structure of $\mathrm{Ru_6C(CO)_{14}}(\mu\text{-}\eta^2{:}\eta^2\text{-}\mathrm{C_2Me_2})(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}\mathrm{C_2Me_2})$, **3**, in the solid state.

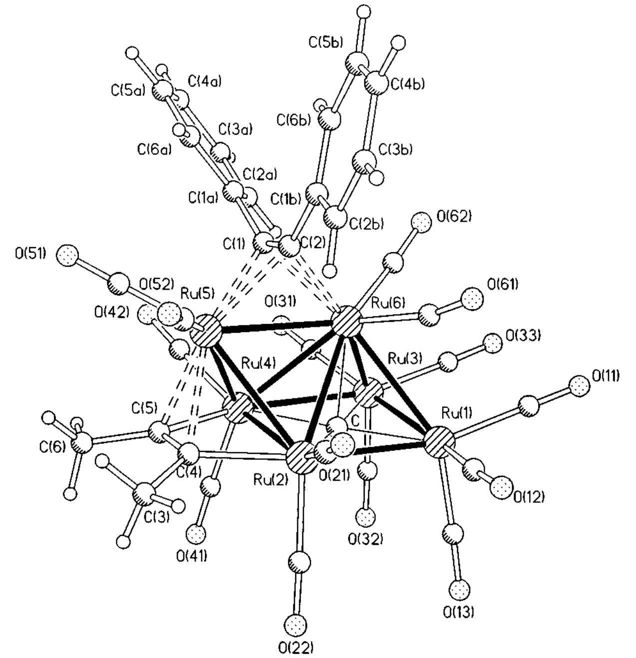


Figure 2. The molecular structure of $\mathrm{Ru_6C(CO)_{14}}(\mu\text{-}\eta^2{:}\eta^2\text{-}\mathrm{C_2Ph_2})(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}\mathrm{C_2Me_2})$, **6**, in the solid state.

Tables 2 and 3 for clusters **3** and **6**, respectively. In **3** and **6**, the octahedral metal core of the parent molecule **1** has undergone a transformation to a square-based pyramid of Ru-atoms with the sixth Ru-atom capping a triangular face. This type of metal polyhedron has been observed previously on a number of occassions.[10,11] The Ru−Ru bonds range from 2.8168(9) to 2.8829(10) Å, mean 2.850 Å, in **3** and from 2.8074(9) to 2.9030(8) Å, mean 2.857 Å, in **6**. In both clusters, the two alkyne ligands occupy analogous positions and bond to the cluster in the same modes. One of the alkyne ligands adopts the familiar μ_3-η^1:η^2:η^1 face-capping bonding mode comparable to that observed in **2** and a phenylacetylene analogue of **2** previously reported.[12] The C−C−C bonds angles of the μ_3-η^1:η^2:η^1 ligand average 125° in both **3** and **6**. Elongation of the C−C multiple bond is also observed, with a value of 1.368(12) Å in **3** and 1.363(8) Å in **6**. A second alkyne, dimethylacetylene in **3** and diphenylacetylene in **6**, occupies a μ-η^2:η^2 bridging position spanning the Ru−Ru edge involving the apical Ru-atom of the square-based pyramid and the capping Ru-atom. The alkyne forms π interactions with each of these metals; this bonding mode has been observed before.[13] The C−C−C bond angles average 141° in **3** and 140° in **6**. The length of the C−C multiple bond is 1.306(12) Å in **3** and 1.305(8) Å in **4**. A comparison of the parameters of the edge-bridging alkynes with the face-capping alkynes clearly shows that the modifications to the edge-bridging alkyne are less pronounced. This suggests that the alkyne in the μ-η^2:η^2 bonding mode is a two-electron donor unlike the μ_3-η^1:η^2:η^1 bonded alkyne which is formally a four-electron donor. It has been noted before that μ-η^2:η^2 alkynes can contribute two or four electrons to cluster bonding, although in contrast to the situation observed here, when they donate two electrons, the alkyne lies parallel to the metal−metal bond. If the μ-η^2:η^2 alkyne

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $\mathrm{Ru_6C(CO)_{15}}(\mu_3\eta^2{:}\eta^2\text{-}\mathrm{C_2Me_2})(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}\mathrm{C_2Me_2})$, 3

Ru(1)−Ru(2)	2.8610(9)	mean Ru−C$_{\text{(carbonyl)}}$	1.91
Ru(1)−Ru(3)	2.8441(9)	mean C−O	1.14
Ru(1)−Ru(4)	2.8368(10)	Ru(1)−C(1B2)	2.168(8)
Ru(1)−Ru(5)	2.8784(10)	Ru(1)−C(1B3)	2.171(9)
Ru(1)−Ru(6)	2.8761(10)	Ru(5)−C(1B2)	2.186(8)
Ru(2)−Ru(3)	2.8820(10)	Ru(5)−C(1B3)	2.210(8)
Ru(2)−Ru(5)	2.8168(9)	C(1B1)−C(1B2)	1.498(12)
Ru(2)−Ru(6)	2.8302(9)	C(1B2)−C(1B3)	1.306(12)
Ru(3)−Ru(4)	2.8173(10)	C(1B3)−C(1B4)	1.492(12)
Ru(4)−Ru(6)	2.8829(10)	Ru(5)−C(2B2)	2.230(8)
Ru(5)−Ru(6)	2.8301(10)	Ru(5)−C(2B3)	2.249(9)
Ru(1)−C	2.084(8)	Ru(2)−C(2B2)	2.081(9)
Ru(2)−C	2.002(8)	Ru(6)−C(2B3)	2.090(9)
Ru(3)−C	2.017(8)	C(2B1)−C(2B2)	1.521(12)
Ru(4)−C	2.022(8)	C(2B2)−C(2B3)	1.368(12)
Ru(6)−C	2.033(8)	C(2B3)−C(2B4)	1.515(12)

C(1B1)−C(1B2)−C(1B3)	140.6(8)	C(2B1)−C(2B2)−C(2B3)	124.3(8)
C(1B2)−C(1B3)−C(1B4)	142.2(8)	C(2B2)−C(2B3)−C(2B4)	125.3(8)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $\mathrm{Ru_6C(CO)_{14}}(\mu\text{-}\eta^2{:}\eta^2\text{-}\mathrm{C_2Ph_2})(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}\mathrm{C_2Me_2})$, 6

Ru(1)−Ru(2)	2.9030(8)	mean Ru−C$_{\text{(carbonyl)}}$	1.90
Ru(1)−Ru(3)	2.8255(10)	mean C−O	1.13
Ru(1)−Ru(6)	2.8474(7)	Ru(5)−C(1)	2.222(6)
Ru(2)−Ru(4)	2.8082(10)	Ru(5)−C(2)	2.170(6)
Ru(2)−Ru(5)	2.8789(8)	Ru(6)−C(1)	2.145(5)
Ru(2)−Ru(6)	2.8793(7)	Ru(6)−C(2)	2.182(5)
Ru(3)−Ru(4)	2.8797(8)	C(1A)−C(1)	1.486(7)
Ru(3)−Ru(6)	2.8529(8)	C(1)−C(2)	1.305(8)
Ru(4)−Ru(5)	2.8074(9)	C(2)−C(1B)	1.472(7)
Ru(4)−Ru(6)	2.8868(7)	Ru(2)−C(4)	2.086(6)
Ru(5)−Ru(6)	2.8632(7)	Ru(4)−C(5)	2.099(6)
Ru(1)−C	2.010(5)	Ru(5)−C(4)	2.241(6)
Ru(2)−C	2.024(5)	Ru(5)−C(5)	2.245(5)
Ru(3)−C	2.038(5)	C(3)−C(4)	1.512(8)
Ru(4)−C	2.004(5)	C(4)−C(5)	1.363(8)
Ru(6)−C	2.095(5)	C(5)−C(6)	1.505(9)

C(1A)−C(1)−C(2)	140.4(5)	C(3)−C(4)−C(5)	124.1(6)
C(1)−C(2)−C(1B)	138.9(5)	C(4)−C(5)−C(6)	125.1(6)

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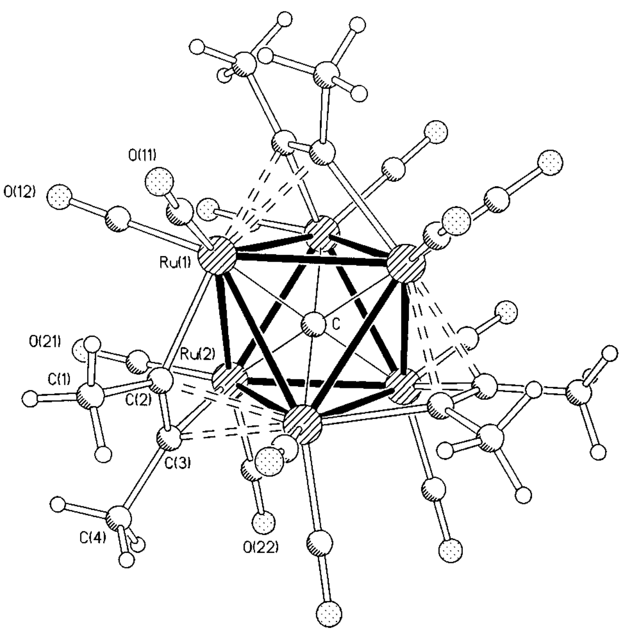

Figure 3. The molecular structure of $Ru_6C(CO)_{12}(\mu_3\text{-}\eta^1\text{:}\eta^2\text{:}\eta^1\text{-}C_2Me_2)_3$, **5**, in the solid state.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $Ru_6C(CO)_{12}(\mu_3\text{-}\eta^1\text{:}\eta^2\text{:}\eta^1\text{-}C_2Me_2)_3$, 5

Ru(1)−Ru(2)′	2.9257(6)	Ru(1)−C(2)′	2.284(5)
Ru(1)−Ru(1)′	2.9361(7)	Ru(1)−C(3)′	2.340(5)
Ru(1)−Ru(2)	2.9479(6)	Ru(2)−C(3)	2.032(5)
Ru(2)−Ru(2)′	2.8732(7)	Ru(1)′−C(2)′	2.041(5)
Ru(1)′−Ru(1)‴	2.9009(8)	Ru(2)′−C(2)′	2.351(5)
Ru(1)′−Ru(2)‴	2.9130(6)	Ru(2)′−C(3)′	2.294(6)
Ru(1)′−Ru(2)′	2.9138(6)	Ru(2)′−C(3)‴	2.142(6)
Ru(2)′−Ru(2)‴	2.9416(7)	C(1)−C(2)	1.520(7)
Ru(1)−C	2.111(5)	C(2)−C(3)	1.374(7)
Ru(2)−C	2.020(5)	C(3)−C(4)	1.499(7)
mean Ru−C(carbonyl)	1.88	C(1)′−C(2)′	1.495(8)
mean C−O	1.16	C(2)′−C(3)′	1.380(8)
Ru(1)−C(2)	2.144(5)	C(3)′−C(4)′	1.513(8)
C(1)−C(2)−C(3)	121.4(5)	C(2)−C(3)−C(4)	125.1(5)
C(1)′−C(2)′−C(3)′	125.9(5)	C(2)′−C(3)′−C(4)′	121.3(5)

is taken as a two-electron donor, the total electron count for **3** and **6** is 86, the electron count predicted for a capped square pyramid. In the closely related cluster $Ru_5PtC(CO)_{13}(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_2Ph_2)(\mu_3\text{-}\eta^1\text{:}\eta^2\text{:}\eta^1\text{-}C_2Ph_2)$, the electron count is 88.[10] The excess electrons in this cluster have been accounted for as close examination of the metal core shows that two bonds are considerably longer than the others. This lengthening has been attributed to a weakening of the M−M bonds due to the presence of excess electrons. A similar effect is not observed in **3** or **6**. The carbonyl ligands all adopt terminal positions with Ru−C−O angles averaging 175° in both **3** and **6**.

Single crystals of **5** suitable for X-ray diffraction were grown from a solution of dichloromethane−hexane by slow evaporation at −25 °C. The crystal of **5** contains two independent molecules, and the structure of one of these is illustrated in Figure 3. Relevant bond parameters are listed in Table 4. The structure of **5** exhibits a 3-fold crystallographic symmetry. The ruthenium cage comprises a regular octahedron encapsulating a carbide atom. The Ru−Ru bond lengths are in the range 2.8732(7)−2.9479(6) Å, mean 2.919 Å. The three alkyne ligands all bond to the cluster in the $\mu_3\text{-}\eta^1\text{:}\eta^2\text{:}\eta^1$ mode, occupying three alternate faces of the octahedron. The C−C−C bond angles for the three alkynes are of a similar magnitude to those observed in other $\mu_3\text{-}\eta^1\text{:}\eta^2\text{:}\eta^1$ ligands, the values being 121.4(5)° and 125.1(5)°. The C−C multiple bond for the ligands also exhibits a lengthening typical for the face-capping bonding mode, *viz.* 1.374(7) Å. All of the carbonyl ligands are terminally bound, with slight deviations from linearity with Ru−C−O angles averaging 178°. It should be noted that this cluster has a total electron count of 88, if the three alkyne ligands act as four-electron donors. This does appear to be the case from both the spectroscopy and the structural determination as all three alkynes are equivalent. The value of the mean Ru−Ru distance is longer than that usually observed for neutral hexaruthenium−carbido clusters, and it is possible that the excess electrons in **5** have caused a slight weakening of the bonds.

Mechanistic Inferences. The use of trimethylamine *N*-oxide (Me_3NO) as an oxidative decarbonylation reagent to stoichiometrically remove carbonyl ligands from transition metal carbonyl complexes and clusters has been well-documented.[14] In the general reaction described in this paper, 2 equiv of Me_3NO are used to displace two CO ligands, as CO_2, formally leaving two vacant coordination sites on the metal cluster. Since the reaction is carried out in the presence of but-2-yne, the coordinatively unsaturated cluster undergoes reaction with the alkyne in order to regain coordinative saturation.

What is surprising is the polyhedral rearrangement which takes place on substitution of the second alkyne moiety, irrespective of whether but-2-yne or diphenylacetylene is used. The metal framework undergoes transformation from an octahedron to a monocapped square-based pyramid. While the hexaosmium octahedral cluster $[Os_6(CO)_{18}]^{2-}$ readily undergoes reversible rearrangement to a bicapped tetrahedron $Os_6(CO)_{18}$, upon oxidation and reduction,[15] the carbide atom in $Ru_6C(CO)_{17}$ is usually considered to confer stability to the cluster unit and polyhedral rearrangements are rare.[16] Relatively minor modifications to the Ru_6C core have been observed; for example, $Ru_6C(CO)_{15}(\eta\text{-}C_4Ph_4)$[17] and $Ru_6C(CO)_{15}(\mu\text{-dppf})$[18] are prepared from **1** under ambient conditions. In the former cluster, one Ru−Ru edge has opened, and in the latter, two edges have opened, both to distances beyond that which is generally considered to constitute a Ru−Ru bond. However, their frameworks can still be viewed as *pseudo*octahedral in which the sterically demanding ligands bring about the observed distortion.

The mechanism by which the octahedron converts to a monocapped square pyramid has not been established. While it is conceivable that it may involve a dissociative mechanism in which one Ru-atom undergoes complete cleavage from the rest of the cluster followed by recombination in the alternative position, circumstantial

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(16) J. S. Bradley comments in his review on carbido clusters (*Advs. Organomet. Chem.* **1983**, *22*, 1) that from his observations, it would appear that carbide atoms confer stability to clusters. This is a feature we would tend to agree with from our reactivity studies of carbido clusters over the years.

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evidence would indicate this process is quite unlikely. The preparation of the a square-based pyramidal cluster $Ru_5C(CO)_{15}$ from $Ru_6C(CO)_{17}$ requires forcing conditions (70 atm of CO at elevated temperatures for several hours).[19] It is possible that the transformation takes place according to a more "fluid" process in which the cohesive energy is kept to a minimum by stepwise M−M bond cleavage. Synthesis of **6** demonstrates that the initial alkyne remains in the face-capping position, with the incoming alkyne adopting the μ-η^2:η^2 bonding site.

It has also been noted that the polyhedral rearrangement is reversible (**3** → **4**). This adds further complications to the system as one must question why the monocapped square-based pyramidal complex should exist in the first place. Clearly, the reactions involving Me_3NO are more complicated than the related reaction involving photochemical activation techniques. The photolysis of $Ru_6C(CO)_{15}(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_2Ph_2)$ with diphenylacetylene affords the bis(diphenylacetylene) complexes analogous to **4** in which the octahedral Ru_6C core remains intact; no compound similar **3** or **6** is observed.[10] This does not appear to be a consequence of the alkyne used as it has been found that rearrangement of the cluster skeleton takes place when diphenylacetylene reacts with $Ru_6C(CO)_{15}(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_2Ph_2)$ using chemical activation.[20]

Table 5. Crystal Data and Structure Refinement Details for 3, 5, and 6

	3	5	6
formula	$C_{23}H_{12}O_{14}Ru_6$	$C_{25}H_{18}O_{12}Ru_6$	$C_{25}H_{16}O_{14}Ru_6$
M_w	1118.76	1116.81	1242.88
temperature (K)	150.0(2)	150.0(2)	223(2)
cryst syst	monoclinic	trigonal	monoclinic
space group	$P2_1/n$	$R3$	$P2_1/c$
a (Å)	9.6953(8)	16.7383(11)	17.494(2)
b (Å)	19.206(2)	16.7383(11)	12.336(2)
c (Å)	16.140(2)	37.505(3)	17.479(2)
α (deg)	90	90	90
β (deg)	93.393(9)	90	98.73(3)
γ (deg)	90	120	90
U (Å^3)	3000.1(5)	9100(1)	3728.4(9)
Z	4	12	4
D_{calcd} (g cm^{-3})	2.477	2.466	2.214
μ (mm^{-1})	3.009	2.971	2.434
T_{min}/T_{max}	0.104/0.129	0.686/0.605	DIFABS: 0.716/1.147
cryst size (mm)	0.50 × 0.50 × 0.40	0.35 × 0.15 × 0.15	0.47 × 0.31 × 0.23
θ range (deg)	2.5−22.5	2.59−22.53	2.79−24.99
no. reflns coll	3912	2652	13 267
no. independent reflns	3912	2652	6538
no. used	3891	2646	6518
R(int)			10.88
R_1 [$I > 2\sigma(I)$] (%)	3.45	2.42	4.84
wR^a (%)	9.73	6.40	12.63
S	1.241	1.068	1.090
params refined	388	259	479
$\Delta\rho_{max}$ (e Å^{-3})	1.225	0.508	1.932
$\Delta\rho_{min}$ (e Å^{-3})	−0.930	-0.530	−1.775

[a] wR based on F for **1** and F^2 for **5** and **6**. [b] 2886 used for the refinement.

Experimental Section

All reactions were carried out using freshly distilled solvents under an atmosphere of nitrogen. Subsequent purification of products was carried out by thin layer chromatography (TLC) on silca-coated plates using standard laboratory grade solvents, without precautions taken to exclude air. Infrared spectra were recorded on a Perkin-Elmer 1710 Fourier-transform instrument. Mass spectra were obtained by positive fast atom bombardment on a Kratos MS50TC. ^1H NMR spectra were recorded using a Bruker WM200 spectrometer. The cluster $Ru_6C(CO)_{17}$ was prepared according to a literature method.[21] Trimethylamine N−oxide (Me_3NO), but-2-yne (C_2Me_2), and diphenylacetylene (C_2Ph_2) were purchased from Aldrich Chemical Co. Me_3NO was dried and then sublimed prior to use.

Reaction of $Ru_6C(CO)_{17}$ with C_2Me_2 and Me_3NO (2 equiv)—Synthesis of $Ru_6C(CO)_{15}(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_2Me_2)$ (2) and $Ru_6C(CO)_{14}(\mu\text{-}\eta^2{:}\eta^2\text{-}C_2Me_2)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_2Me_2)$ (3). The cluster $Ru_6C(CO)_{17}$ (**1**, 120 mg, 0.109 mmol) was dissolved in CH_2Cl_2 (60 mL), and the red solution was cooled to −78 °C. An excess amount of C_2Me_2 (1 mL) was added, followed by the dropwise addition of Me_3NO (17 mg, 0.219 mmol) in CH_2Cl_2 (5 mL) over a 5 min period. The solution was allowed to warm to room temperature over 30 min. This was accompanied by a change in color to dark brown. The solvent was removed *in vacuo*, and the products were isolated by TLC using CH_2Cl_2−hexane (1:4 v/v) as the eluent. In order of elution, two products were extracted and characterized as $Ru_6C(CO)_{15}(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_2Me_2)$ (**2**, 37%, brown) and $Ru_6C(CO)_{14}(\mu\text{-}\eta^2{:}\eta^2\text{-}C_2Me_2)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_2Me_2)$ (**3**, 12%, brown).

Reaction of $Ru_6C(CO)_{15}(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_2Me_2)$ (2) with C_2Me_2 and Me_3NO (2 equiv)—Synthesis of $Ru_6C(CO)_{14}(\mu\text{-}\eta^2{:}\eta^2\text{-}C_2Me_2)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_2Me_2)$ (3) and $Ru_6C(CO)_{12}(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_2Me_2)_3$ (5). The cluster $Ru_6C(CO)_{15}(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_2Me_2)$ (**2**, 90 mg, 0.081 mmol) and an excess amount of C_2Me_2 (1 mL) were dissolved in CH_2Cl_2 (30 mL) and cooled to −78 °C. Me_3NO (13 mg, 0.161 mmol) in CH_2Cl_2 (5 mL) was added dropwise to the solution over a period of 5 min. The solution was allowed to warm to room temperature over 30 min, during which time the color became dark brown. The solvent was removed *in vacuo*, and the products were isolated by TLC using CH_2Cl_2−hexane (3:7 v/v) as the eluent. In the order of elution, two products were extracted and characterized as $Ru_6C(CO)_{14}(\mu\text{-}\eta^2{:}\eta^2\text{-}C_2Me_2)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_2Me_2)$ (**3**, 35%, brown) and $Ru_6C(CO)_{12}(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_2Me_2)_3$ (**5**, 7%, brown).

Reaction of $Ru_6C(CO)_{14}(\mu\text{-}\eta^2{:}\eta^2\text{-}C_2Me_2)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_2Me_2)$ (3) with C_2Me_2 and Me_3NO (2 equiv)—Synthesis of $Ru_6C(CO)_{12}(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_2Me_2)_3$ (5). The cluster $Ru_6C(CO)_{14}(\mu\text{-}\eta^2{:}\eta^2\text{-}C_2Me_2)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_2Me_2)$ (**3**, 70 mg, 0.063 mmol) was dissolved in CH_2Cl_2 (40 mL), and the solution was cooled to −78 °C. An excess amount of C_2Me_2 (1 mL) was added. Me_3NO (10 mg, 0.125 mmol) in CH_2Cl_2 (5 mL) was added dropwise to the solution over a period of 5 min. The solution was allowed to warm to room temperature over 30 min. The solvent was removed *in vacuo*, and the products were isolated by TLC using CH_2Cl_2−hexane (3:7 v/v) as the eluent. One major product was extracted and characterized as $Ru_6C(CO)_{12}(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_2Me_2)_3$ (**5**, 39%, brown).

Reaction of $Ru_6C(CO)_{15}(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_2Me_2)$ (2) with C_2Ph_2 and Me_3NO (2 equiv)—Synthesis of $Ru_6C(CO)_{14}(\mu\text{-}\eta^2{:}\eta^2\text{-}C_2Ph_2)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_2Me_2)$ (6). The cluster $Ru_6C(CO)_{15}(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_2Me_2)$ (**2**, 100 mg, 0.092 mmol) was dissolved in CH_2Cl_2 (50 mL), and the resulting red solution was cooled to −78 °C. An excess amount of C_2Ph_2 (100 mg) was added, followed by the dropwise addition of Me_3NO (14 mg, 0.184 mmol) in CH_2Cl_2 (5 mL) over a 5 min period. The solution was allowed to warm to room temperature over 30 min. This was accompanied by a change in color from red to dark brown. The solvent was removed *in vacuo*, and the compounds were isolated by TLC using CH_2Cl_2−hexane (3:7 v/v) as the eluent. In the order of elution, two bands were extracted and char-

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acterized as the starting material $Ru_6C(CO)_{15}(\mu_3\text{-}\eta^1:\eta^2:\eta^1\text{-}C_2Me_2)$ (**2**, 15%, red) and the new compound $Ru_6C(CO)_{14}(\mu\text{-}\eta^2:\eta^2\text{-}C_2Ph_2)(\mu_3\text{-}\eta^1:\eta^2:\eta^1\text{-}C_2Me_2)$ (**6**, 33%, brown).

Thermolysis of $Ru_6C(CO)_{14}(\mu\text{-}\eta^2:\eta^2\text{-}C_2Me_2)(\mu_3\text{-}\eta^1:\eta^2:\eta^1\text{-}C_2Me_2)$ (3) in Heptane—Synthesis of $Ru_6C(CO)_{13}(\mu_3\text{-}\eta^1:\eta^2:\eta^1\text{-}C_2Me_2)_2$ (4). The cluster $Ru_6C(CO)_{14}(\mu\text{-}\eta^2:\eta^2\text{-}C_2Me_2)(\mu_3\text{-}\eta^1:\eta^2:\eta^1\text{-}C_2Me_2)$ (**3**, 50 mg, 0.045 mmol) was heated to reflux in heptane (50 mL) for 1 h. The reaction was monitored by IR spectroscopy, which showed a significant change after this time. The solvent was removed *in vacuo*, and the starting material $Ru_6C(CO)_{14}(\mu\text{-}\eta^2:\eta^2\text{-}C_2Me_2)(\mu_3\text{-}\eta^1:\eta^2:\eta^1\text{-}C_2Me_2)$ (**3**, 45%, brown) and the new compound $Ru_6C(CO)_{13}(\mu_3\text{-}\eta^1:\eta^2:\eta^1\text{-}C_2Me_2)_2$ (**4**, 38%, brown) were isolated by TLC using CH_2Cl_2—hexane (3:7 v/v) as the eluent.

Reaction of $Ru_6C(CO)_{14}(\mu\text{-}\eta^2:\eta^2\text{-}C_2Me_2)(\mu_3\text{-}\eta^1:\eta^2:\eta^1\text{-}C_2Me_2)$ (3) with Me_3NO (1 equiv)—Synthesis of $Ru_6C(CO)_{13}(\mu_3\text{-}\eta^1:\eta^2:\eta^1\text{-}C_2Me_2)_2$ (4). The cluster $Ru_6C(CO)_{14}(\mu\text{-}\eta^2:\eta^2\text{-}C_2Me_2)(\mu_3\text{-}\eta^1:\eta^2:\eta^1\text{-}C_2Me_2)$ (**3**, 70 mg, 0.063 mmol) was dissolved in CH_2Cl_2 (40 mL). Me_3NO (5 mg, 0.063 mmol) in CH_2Cl_2 (5 mL) was added dropwise over a 5 min period. The reaction mixture stirred for 20 min. The solvent was removed *in vacuo*, and the compounds were isolated by TLC using CH_2Cl_2—hexane (3:7 v/v) as the eluent. In the order of elution, two bands were extracted and characterized as the starting material $Ru_6C(CO)_{14}(\mu\text{-}\eta^2:\eta^2\text{-}C_2Me_2)(\mu_3\text{-}\eta^1:\eta^2:\eta^1\text{-}C_2Me_2)$ (**3**, 40%, brown) and the new compound $Ru_6C(CO)_{13}(\mu_3\text{-}\eta^1:\eta^2:\eta^1\text{-}C_2Me_2)_2$ (**4** ,33%, brown).

Structural Characterization. Single crystals of **3** and **5** were grown by slow evaporation of a dichloromethane—hexane solution at −25 °C. Compound **6** was crystallized from dichloromethane at −10 °C. X-ray crystal diffraction data was collected on a Stoë Stadi-4 four-circle diffractometer equipped with an Oxford Cryosystems low-temperature device.[22] Following data reduction and application of absorption corrections based on ψ-scan measurements, all structures were solved by direct methods (SIR92 or SHELXS)[23,24] and refined by full-matrix least-squares (against F^2 (SHELXL93)[25]). Hydrogen atoms were placed in calculated positions and treated with a riding model during refinement. Residual absorption errors for **6** were corrected by means of the program DIFABS.[26] All non-H atoms were refined with anisotropic displacement parameters. Refinement data are listed in Table 5.

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Supporting Information Available: Tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and ORTEP diagrams for compounds **3**, **5**, and **6** (30 pages). Ordering information is given on any current masthead page.

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