Metal Clusters as Models of Intermediates in Organic Syntheses. Reactions of the Terminal Dialkynes $NR(CMe_2C{\equiv}CH)_2$ (R = H or Me) with $[Ru_3(CO)_{12}]$ *

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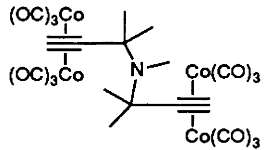
The compound $NMe(CMe_2C{\equiv}CH)_2$ **1** reacts with $[Ru_3(CO)_{12}]$ giving a trinuclear cluster and a dinuclear ruthenacyclopentadiene derivative. Under the same conditions, $NH(CMe_2C{\equiv}CH)_2$ **2** gives only the dinuclear ruthenacyclopentadiene derivative. The crystal structure of the trinuclear cluster $[Ru_3(CO)_8(HC\overline{CCMe_2NMeCMe_2C}CHCCCMe_2)]$ has been determined by X-ray diffraction: triclinic, space group $P\bar{1}$, with $a = 15.607(8)$, $b = 15.912(7)$, $c = 11.674(5)$ Å, $\alpha = 104.88(2)$, $\beta = 90.01(3)$, $\gamma = 103.53(2)°$ and $Z = 4$. Two independent, but practically identical, molecules are present in the crystals. In the structure a six-carbon-atom chain, formed by partial cyclization of one molecule of ligand **1** and coupling with a $CC{=}CMe_2$ fragment, interacts with all three ruthenium atoms. The cluster represents a rare example of a derivative characterized by a six-carbon-atom chain co-ordinated to three metals; this interaction and its role in the synthesis of organic products is discussed.

Dipropargylamines $NMe(CMe_2C{\equiv}CH)_2$ **1** and $NH(CMe_2C{\equiv}CH)_2$ **2** (propargyl = prop-2-ynyl) react with $[Co_2(CO)_8]$ forming cobaltacycles which incorporate alkynes $RC{\equiv}CH$ or nitriles $RC{\equiv}N$ to give condensed aromatic or heterocyclic products.[1] Two complexes have recently been isolated and characterized: in $[\{Co_2(CO)_6\}_2\{(HC{\equiv}CCMe_2)_2NMe\}]$ **3** each terminal acetylenic carbon–carbon bond interacts with one $Co_2(CO)_6$ unit through two π bonds,[1] while in $[Co_2(CO)_5\{(HC{\equiv}CCMe_2)_2NMe\}]$ **4** a cobaltacyclopentadiene ring co-ordinated to the other Co atom is present.[2] Evidence has been gained for the intermediacy of these species in catalytic reactions leading to cyclic compounds.[1,2]



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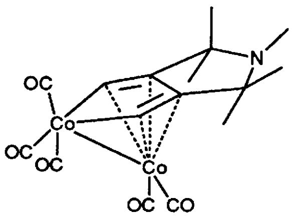

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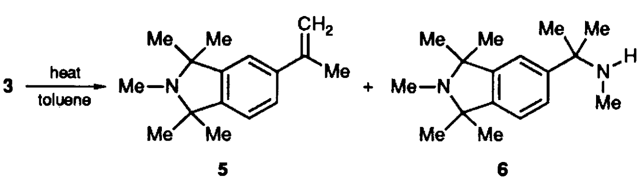

Scheme 1

Thermal decomposition of complex **3** (toluene, 100 °C, 2.5 h) gave, among other products, **5** and **6** in about 1:1 molar ratio (52% with respect to the theoretical yield) as in Scheme 1. Under similar conditions, in benzonitrile, complex **3** gave products **5** and **6** (each *ca.* 14% yield) along with pyridine derivatives and carbonylated products.[1] Formation of organic molecules **5** and **6**, requiring cleavage of the carbon–nitrogen bond of **1**, apparently occurred under the action of a cobalt centre. The fragments obtained as a consequence of this process presumably react with a cobaltacyclopentadiene intermediate leading to the organic derivatives shown. Isolation of the relevant cobalt-co-ordinated intermediates proved to be very difficult, however. We have therefore investigated the reactions of the propargylamines **1** and **2** with $[Ru_3(CO)_{12}]$ which should give more stable and more easily isolable complexes.

Reports on carbon–nitrogen bond cleavage of $NMe_2(CH_2C{\equiv}CH)$ by $[Ru_3(CO)_{12}]$ or $[Os_3(CO)_{12}]$ have appeared.[3] Such bond cleavage has also been reported in the reaction of NEt_2H with $[Os_3(CO)_{10}(MeCN)_2]$[4] and in that of NEt_3 or $NEtPr^i_2$ with $[Ru_3(CO)_{12}]$,[5] the latter in the presence of catalytic amounts of iron complexes.

Propargyl fragments can easily form metal complexes and these are expected to undergo various reactions, including isomerization. A propargyl-to-allenyl ligand rearrangement requiring a hybridization change of the propargyl carbon ($sp^3 \longrightarrow sp^2$) has been reported to occur under the influence of a trinuclear ruthenium cluster, leading to new homo- and hetero-nuclear metal complexes.[6]

Results and Discussion

From the reaction of an excess of compound **1** with

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

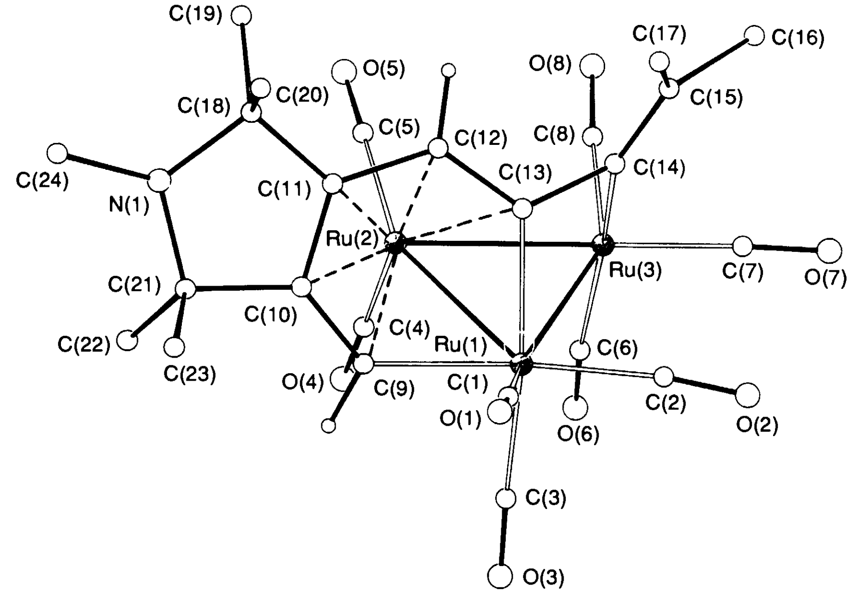
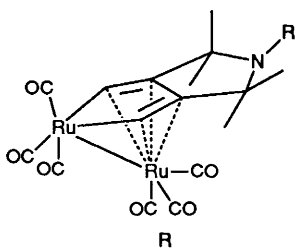


Fig. 1 View of the structure of one of the two independent molecules of $[\mathrm{Ru_3(CO)_8(HC\overline{CCMe_2NMeCMe_2C}CHCCCMe_2)}]$ **7** with the atomic numbering scheme. The two independent molecules have been numbered equivalently. When necessary atoms are distinguished by C(*nn*1) and C(*nn*2), *etc.*



R
8a Me
8b H

$[\mathrm{Ru_3(CO)_{12}}]$ in refluxing toluene for short time a dark brown solution was obtained. By preparative TLC on $\mathrm{SiO_2}$ the following products were obtained: a trinuclear complex $[\mathrm{Ru_3(CO)_8(HC\overline{CCMe_2NMeCMe_2C}HCCCMe_2)}]$ **7** (15% yield), a dinuclear complex $[\mathrm{Ru_2(CO)_6\{(HC{\equiv}CCMe_2)_2NMe\}}]$ **8a** (15% yield) and trace amounts of a yellow substance.*

From the reaction of ligand **2** with $[\mathrm{Ru_3(CO)_{12}}]$ under comparable conditions a red-brown solution was obtained; preparative TLC on silica showed the presence only of the dinuclear complex $[\mathrm{Ru_2(CO)_6\{(HC{\equiv}CCMe_2)_2NH\}}]$ **8b** (15% yield). No trinuclear complexes, homologues of **7**, could be obtained, probably because secondary amines give more complex reactions, leading to intractable materials.

The identification of the very similar derivatives **8a**, **8b** was based on elemental analysis, IR, ^{1}H and ^{13}C NMR spectroscopy and for **8a** on the mass spectrum. Analytical and spectroscopic data for the complexes are in accord with a formula $[\mathrm{Ru_2(CO)_6(ligand)}]$, where the ligand **1** or **2** forms a ruthenacyclopentadiene ring. From the IR data the presence of semibridging CO can be excluded. The proposed 'sawhorse' structure[9] is shown (left).

The structure of complex **7** has been determined by X-ray diffraction methods. This complex is formed by partial cyclization of one molecule of ligand **1** and coupling with a $\mathrm{CC{=}CMe_2}$ fragment to give a six-carbon-atom chain interacting with all three ruthenium atoms. To our knowledge **7** is the first example of a ruthenium cluster showing this metal–ligand interaction.

Crystal Structure of Complex **7**.—In the crystals two crystallographically independent, but practically identical, molecules are present. A view of one of them is shown in Fig. 1 together with the atomic numbering system. Selected bond distances and angles in the two independent molecules are given in Table 1. The structure consists of an isosceles triangle of ruthenium atoms, the Ru(1)–Ru(2) side being the shortest, 2.754(2) [2.763(2)] against 2.814(3) and 2.818(3) Å [2.802(2) and 2.816(2) Å] (the values in square brackets refer to the second molecule). Three terminal carbonyls are bound to atoms Ru(1) and Ru(3) and two to Ru(2). All three metals interact through a complex bonding system with an organic ligand presumably derived from the coupling of one cyclized molecule of dialkyne **1** with a $\mathrm{CC{=}CMe_2}$ fragment (necessarily from another alkyne molecule). The cyclized ligand **1** forms a σ bond with Ru(1) through the terminal C(9) atom [Ru(1)–C(9) 2.07(2) Å [2.08(2) Å]; the C(13) and C(14) atoms of the $\mathrm{CCCMe_2}$ fragment, coupled with the ligand **1**, are also involved in σ bonds with Ru(1) and Ru(3) respectively [Ru(1)–C(13) 2.09(2) [2.02(2)] and Ru(3)–C(14) 2.04(2) Å [2.10(2) Å]. The $\mathrm{CC{=}CMe_2}$ fragment can be considered a substituted vinyl group with the double bond localized on the C(14)–C(15) bond, 1.36(3) Å [1.34(3) Å] and with the C(13), Ru(3), C(14), C(15), C(16) and C(17) moiety roughly planar.

The C(9)–C(13) atoms of the organic chain form a six-atom ring with Ru(1), through the two Ru(1)–C(9) and Ru(1)–C(13) σ bonds. This ring is characterized by a strictly planar C(9)–C(12) moiety with C(13) and Ru(1) deviating from the mean plane through them by 0.23(2) [0.27(2)] and 0.459(3) [0.492(2)] Å respectively. The five-atom heterocyclic ring, having the C(10)–C(11) bond in common with the six-atom ruthenacycle, shows an 'envelope' conformation with the C(10), C(11), C(18),

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* This yellow substance was examined by mass and ^{1}H NMR spectroscopy. The mass spectrum exhibits the isotopic pattern $\mathrm{Ru_3}$, *m*/*z* (P^+) 749, loss of 10 CO (the corresponding doubly charged ions are also observed in high intensity), followed a fragment of 30 mass units and complex fragmentation of the organic moiety. The ^{1}H NMR spectrum, though not diagnostically conclusive, however exhibits a distinguishable (even though weak) signal at δ −17.56. The substance is probably a mixture. At least two products might be present: $[\mathrm{Ru_3(CO)_{10}}(\mu_3,\eta^2\text{-}\|\text{-}\mathrm{HC{\equiv}CR})]$ **9** (as the major component; R = $\mathrm{CMe_2NMeCMe_2C{\equiv}CH}$), which accounts for the mass spectrum and $[\mathrm{Ru_3}(\mu\text{-H})(\mathrm{CO})_9(\mu_3,\eta^2\text{-}\perp\text{-}\mathrm{C{\equiv}CR})]$ **10**, which may derive from **9** by oxidative addition of the alkyne. Both compounds are commonly produced when unfunctionalized alkynes are treated with ruthenium or osmium carbonyls.[7,8]

Table 1 Selected bond distances (Å) and angles (°) in the two independent molecules of complex **7**

	Molecule 1	Molecule 2		Molecule 1	Molecule 2
Ru(1)–Ru(2)	2.754(2)	2.763(2)	C(1)–O(1)	1.12(3)	1.10(2)
Ru(1)–Ru(3)	2.818(3)	2.802(2)	C(2)–O(2)	1.15(2)	1.16(3)
Ru(2)–Ru(3)	2.814(3)	2.816(2)	C(3)–O(3)	1.10(3)	1.15(3)
Ru(1)–C(1)	1.93(2)	1.89(2)	C(4)–O(4)	1.16(3)	1.09(2)
Ru(1)–C(2)	1.91(2)	1.93(2)	C(5)–O(5)	1.10(3)	1.14(2)
Ru(1)–C(3)	1.97(2)	1.94(2)	C(6)–O(6)	1.12(3)	1.12(3)
Ru(1)–C(9)	2.07(2)	2.08(2)	C(7)–O(7)	1.13(3)	1.17(3)
Ru(1)–C(13)	2.09(2)	2.02(2)	C(8)–O(8)	1.18(3)	1.18(2)
Ru(2)–C(4)	1.86(2)	1.89(2)	C(9)–C(10)	1.37(2)	1.38(2)
Ru(2)–C(5)	1.92(2)	1.86(2)	C(10)–C(11)	1.44(3)	1.45(3)
Ru(2)–C(9)	2.18(2)	2.17(2)	C(11)–C(12)	1.46(3)	1.38(3)
Ru(2)–C(10)	2.33(2)	2.30(2)	C(12)–C(13)	1.39(3)	1.47(2)
Ru(2)–C(11)	2.35(2)	2.35(2)	C(13)–C(14)	1.46(3)	1.42(3)
Ru(2)–C(12)	2.29(2)	2.28(2)	C(14)–C(15)	1.36(3)	1.34(3)
Ru(2)–C(13)	2.41(2)	2.42(2)	C(10)–C(21)	1.54(3)	1.52(3)
Ru(3)–C(6)	1.96(2)	1.96(2)	N(1)–C(21)	1.46(2)	1.47(2)
Ru(3)–C(7)	1.89(2)	1.85(2)	N(1)–C(18)	1.50(3)	1.45(3)
Ru(3)–C(8)	1.83(2)	1.83(2)	C(11)–C(18)	1.46(2)	1.53(2)
Ru(3)–C(14)	2.04(2)	2.10(2)			
Ru(2)–Ru(1)–Ru(3)	60.6(1)	60.8(1)	C(7)–Ru(3)–C(8)	92.6(9)	93.6(9)
Ru(1)–Ru(2)–Ru(3)	60.8(1)	60.3(1)	C(7)–Ru(3)–C(14)	89.1(8)	90.0(8)
Ru(1)–Ru(3)–Ru(2)	58.6(1)	58.9(1)	C(8)–Ru(3)–C(14)	95.4(9)	95.7(8)
Ru(2)–Ru(1)–C(3)	105.5(7)	105.6(6)	Ru(1)–C(9)–C(10)	129.9(14)	129.0(13)
Ru(2)–Ru(1)–C(9)	51.3(5)	51.0(5)	C(9)–C(10)–C(11)	123.0(16)	122.3(15)
Ru(2)–Ru(1)–C(13)	57.6(5)	58.3(5)	C(9)–C(10)–C(21)	130.8(16)	129.5(16)
Ru(3)–Ru(1)–C(2)	71.9(6)	71.2(6)	C(11)–C(10)–C(21)	106.2(15)	108.2(15)
Ru(3)–Ru(1)–C(3)	106.5(6)	104.8(6)	C(10)–C(11)–C(12)	123.2(16)	124.5(16)
Ru(3)–Ru(1)–C(9)	111.5(5)	111.3(5)	C(10)–C(11)–C(18)	113.9(16)	110.3(14)
Ru(3)–Ru(1)–C(13)	60.0(5)	59.1(5)	C(12)–C(11)–C(18)	123.0(17)	124.9(16)
C(1)–Ru(1)–C(2)	92.3(9)	92.6(9)	C(11)–C(12)–C(13)	128.0(18)	126.8(17)
C(1)–Ru(1)–C(3)	98.6(9)	97.7(9)	C(12)–C(13)–C(14)	119.5(17)	113.1(15)
C(1)–Ru(1)–C(9)	85.1(8)	84.9(8)	Ru(1)–C(13)–C(12)	124.6(14)	125.1(13)
C(1)–Ru(1)–C(13)	98.2(8)	100.9(8)	Ru(1)–C(13)–C(14)	112.9(13)	119.3(13)
C(2)–Ru(1)–C(3)	92.7(8)	92.0(8)	C(13)–C(14)–C(15)	126.6(17)	132.1(17)
C(2)–Ru(1)–C(13)	94.3(8)	92.2(8)	Ru(3)–C(14)–C(15)	142.0(15)	140.5(14)
C(3)–Ru(1)–C(9)	85.2(8)	87.4(7)	Ru(3)–C(14)–C(13)	91.1(12)	87.2(11)
C(9)–Ru(1)–C(13)	88.5(7)	89.1(7)	N(1)–C(21)–C(10)	102.6(15)	102.4(14)
Ru(1)–Ru(2)–C(4)	100.9(7)	99.4(6)	C(18)–N(1)–C(21)	112.1(15)	114.3(15)
Ru(3)–Ru(2)–C(4)	93.6(6)	95.5(6)	C(18)–N(1)–C(24)	119.0(15)	118.8(15)
Ru(3)–Ru(2)–C(5)	95.6(7)	96.9(6)	C(21)–N(1)–C(24)	116.2(16)	117.2(15)
C(4)–Ru(2)–C(5)	87.9(10)	88.0(9)	N(1)–C(18)–C(11)	100.6(15)	101.4(14)
Ru(1)–Ru(3)–C(6)	91.1(7)	91.5(6)	Ru(1)–C(1)–O(1)	176.0(18)	175.5(20)
Ru(1)–Ru(3)–C(7)	115.3(7)	113.7(7)	Ru(1)–C(2)–O(2)	170.6(17)	169.8(16)
Ru(1)–Ru(3)–C(14)	73.7(5)	73.5(5)	Ru(1)–C(3)–O(3)	176.0(21)	173.5(18)
Ru(2)–Ru(3)–C(6)	89.7(7)	89.5(6)	Ru(2)–C(4)–O(4)	179.7(20)	177.1(18)
Ru(2)–Ru(3)–C(8)	92.3(7)	92.7(7)	Ru(2)–C(5)–O(5)	177.0(21)	178.0(18)
Ru(2)–Ru(3)–C(14)	83.7(5)	83.2(5)	Ru(3)–C(6)–O(6)	173.0(19)	174.9(18)
C(6)–Ru(3)–C(7)	96.2(9)	95.8(9)	Ru(3)–C(7)–O(7)	177.6(20)	179.1(18)
C(6)–Ru(3)–C(8)	98.7(10)	97.7(9)	Ru(3)–C(8)–O(8)	176.1(20)	178.1(18)

C(21) moiety strictly planar and the N atom deviating by 0.31(2) [0.26(2)] Å from the mean plane through them. The plane containing the four-atom moiety is tilted only by 2(1) [3(1)]° with respect to the C(9)–C(12) plane so that all carbon atoms of the dialkyne **1** lie in the same plane with the Ru(1) and N atoms deviating on opposite sides from it.

The distances involving atoms C(9)–C(13) with Ru(2), in the range 2.18(2)–2.41(2) Å [2.17(2)–2.42(2) Å], are consistent with a complex η-bonding interaction. The bonding between atoms C(9)–C(13) and Ru(2) could be considered as formed by an 'allylic' interaction between the C(9)–C(11) system and Ru(2) and a π interaction between the C(12)–C(13) bond and Ru(2). In this way the organic ligand with a donation of five electrons through these interactions, together with that of three electrons through the σ bonds, should behave as an eight-electron donor, as expected. The C(9)–C(10), C(10)–C(11), C(11)–C(12) and C(12)–C(13) bond lengths, in the range 1.37(2)–1.46(3) Å [1.38(2)–1.47(2) Å], are in agreement with this hypothesis. It is to be noted that no semibridging carbonyl is present between Ru(2) and Ru(3), even if Ru(2) should formally be richer of electrons (19) and Ru(3) poorer (17).

Six-atom metallacycles, formed from organic ligands derived by oligomerization of alkynes or alkenes, are rather rare. A partially comparable organic moiety interacting with a triangular cluster has been reported for $[Fe_3(CO)_8(HC_2Me)_3]$.[10] This complex however, was obtained in the reaction of $HC{\equiv}CMe$ with $[Fe_3(CO)_{12}]$ and the organic ligand was formed by trimerization of $HC{\equiv}CMe$ so that it may be considered as a model for the cyclotrimerization of alkynes on several metal centres. The eight-electron donation of this organic ligand is achieved through a π bond between the C(13)–C(14) double bond and Fe(3), two σ bonds with Fe(1) and a η^4 interaction between the C(9)–C(12) system, on which there are two delocalized double bonds, and Fe(1) (for a comparison a similar atom numbering in this complex has been taken to that of complex **7**). In the iron complex, even if the metal atoms are 18-electron precise, a semibridging CO has been observed.

In addition (as suggested by a referee), the six-membered ring

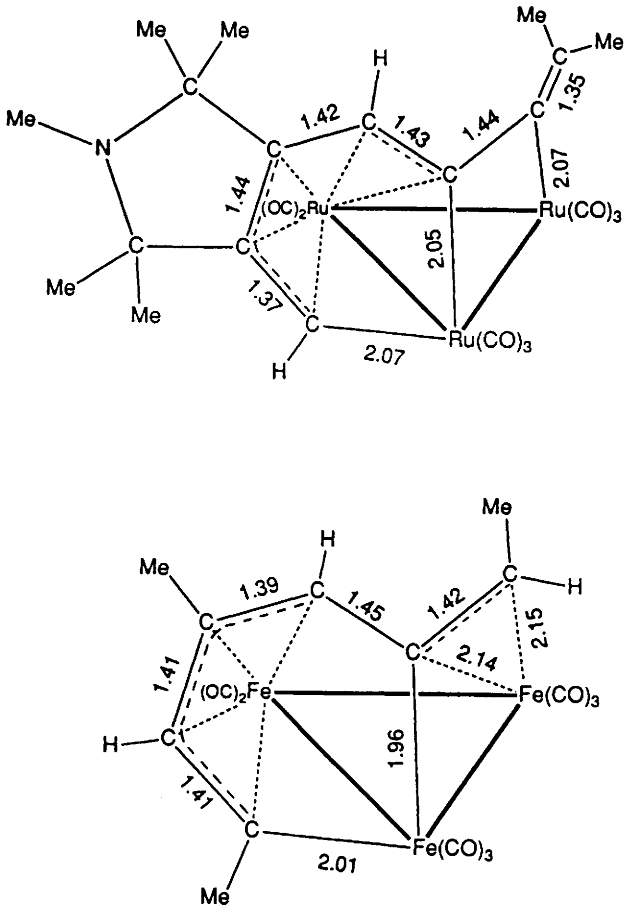


Fig. 2 Comparison of the bonding of the organic moieties to the metal triangle in complex **7** (average bond lengths in Å for the two independent molecules) and in $[Fe_3(CO)_8(HC_2Me)_3]$

composed of Ru(1) and C(9)–C(13), even if not planar as a whole, could be regarded as a metallabenzene co-ordinated to Ru(2); since $Ru(CO)_3$ is isolobal with CH^+, the whole complex could be regarded as an analogue of a doubly metallated dimethylstyrene.

A comparison of the bonding systems in the ruthenium and iron clusters is shown in Fig. 2.

Some Mechanistic Hypotheses.—We have no direct evidence supporting the mechanism of formation of complex **7**; however, we can consider the fact that terminal alkynes have a strong tendency to form trinuclear complexes such as **9** and **10** (see footnote to page 2586) from reactions with $[Ru_3(CO)_{12}]$.[7,8,11]

Thus, a tempting hypothesis could be that shown in Scheme 2 involving complexes **9** and **10** as precursors. Transfer and loss of hydrogen are required to give complex **7**. Carbon–nitrogen bond cleavage[3–5] would give unsaturated trinuclear clusters containing a monoallenyl ligand;[6] addition of a second molecule of alkyne would give complex **7**. Other possibilities cannot be excluded, in particular the intermediacy of binuclear ruthenium cyclopentadiene complexes **8** interacting with alkyne fragments co-ordinated to metal centres. Similar mechanisms may be at work with complex **3**; one of the terminal $Co_2(CO)_6$ units of this complex could interact with the nitrogen atom leading to C–N bond cleavage and leaving different propargyl fragments on each $Co_2(CO)_6$ unit. Another molecule of the original diacetylene ligand must also form a metallacycle of type **4** which reacts with either of the propargyl fragments and eventually liberates compounds **5** and **6**.

The presumably low stability of the intermediate species originated in the reactions with $[Co_2(CO)_8]$ leads directly to products **5** and **6**. With ruthenium only organometallic products have been isolated which can be regarded as models of intermediates in the synthesis of the organic molecules **5** and **6**.

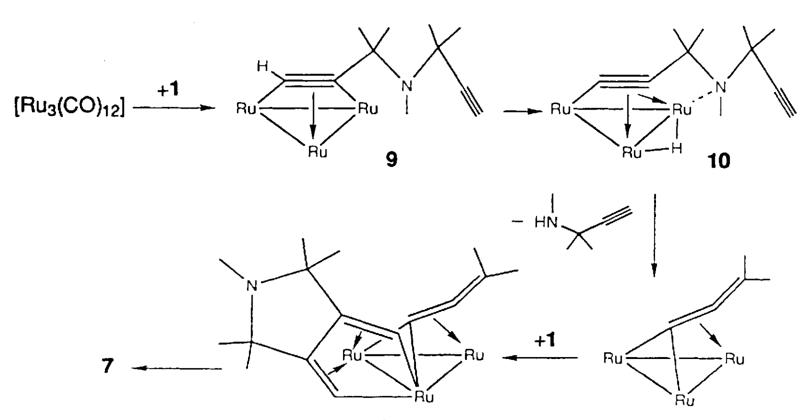
Di- and tri-ruthenium complexes are generally too stable to release organic moieties under the conditions adopted here; however, by refluxing complex **7** in chlorobenzene for 6 h a small amount of product **5** was obtained. Formation of **5** from **7** would require reorientation of the $C(14)–C(15)Me_2$ fragment, C–C bond formation between C(9) and C(14) and a hydrogen shift from the methyl group to the C(14) carbon; examples of hydrogen transfer in reactions of metal carbonyls with alkynes have been reported.[12]

Experimental

General Procedures and Materials.—*Analysis of the products.* The compound $[Ru_3(CO)_{12}]$ was obtained from Strem Chemicals; ligands **1** and **2** were prepared following established procedures.[13] All the reactions were performed in three-necked flasks equipped with gas inlet, reflux condenser and mercury check valve, using solvents distilled over sodium and under an atmosphere of dry nitrogen. Kieselgel PF (Merck) was used for TLC purifications [eluent light petroleum (b.p. 40–70 °C)–diethyl ether (1:1)].

Elemental analyses were performed with a F & M C,H,N analyser and with a Perkin Elmer AAS device. Infrared spectra were recorded on a Perkin Elmer 580 instrument, ^1H and ^{13}C NMR spectra on a JEOL JNM GX 270 FT and on a Bruker CPX 200. Shifts are reported relative to external $SiMe_4$. The mass spectrum of complex **8a** was registered with a Kratos MS-50 instrument [electron-impact (EI), 70 eV (*ca.* 1.12×10^{-17} J)].

Preparations.—*Complexes* **7** *and* **8a**. The reaction of $[Ru_3(CO)_{12}]$ (0.5 g, 0.78 mmol) with compound **1** (0.26 g, 1.6 mmol) in refluxing toluene (50 cm^3) for about 4 min, under nitrogen, yielded a dark brown solution which contained trace amounts of unreacted $[Ru_3(CO)_{12}]$. After filtration the solvent



Scheme 2

Table 2 Fractional atomic coordinates (× 10^4) with estimated standard deviations in parentheses for the non-hydrogen atoms of complex 7

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ru(11)	4 452(1)	3 731(1)	1 750(1)	Ru(12)	7 353(1)	1 871(1)	7 471(1)
Ru(21)	2 883(1)	2 454(1)	1 096(1)	Ru(22)	8 687(1)	3 387(1)	7 601(1)
Ru(31)	3 843(1)	2 570(1)	3 194(1)	Ru(32)	8 594(1)	2 507(1)	9 421(1)
O(11)	5 780(11)	4 360(10)	53(14)	O(12)	6 509(14)	510(10)	5 248(14)
O(21)	5 939(11)	4 179(10)	3 676(14)	O(22)	6 956(9)	426(9)	8 839(12)
O(31)	3 981(11)	5 510(10)	2 919(13)	O(32)	5 776(9)	2 638(10)	8 424(14)
O(41)	1 604(9)	3 457(11)	2 395(12)	O(42)	7 815(8)	4 803(8)	8 872(12)
O(51)	1 534(10)	753(11)	1 115(17)	O(52)	10 424(8)	4 701(9)	8 490(11)
O(61)	2 812(11)	3 838(11)	4 707(13)	O(62)	7 522(10)	3 760(11)	10 866(12)
O(71)	5 121(11)	2 750(11)	5 236(13)	O(72)	8 396(10)	1 291(9)	11 060(11)
O(81)	2 729(11)	840(10)	3 513(13)	O(82)	10 384(9)	3 595(10)	10 516(12)
N(11)	2 464(10)	1 902(11)	−2 316(13)	N(12)	9 141(10)	3 553(11)	4 400(13)
C(11)	5 295(14)	4 160(12)	701(18)	C(12)	6 793(14)	998(13)	6 092(19)
C(21)	5 351(12)	3 942(12)	2 976(17)	C(22)	7 159(11)	1 019(13)	8 413(16)
C(31)	4 119(15)	4 860(14)	2 486(17)	C(32)	6 328(12)	2 304(12)	8 044(16)
C(41)	2 093(14)	3 070(14)	1 897(17)	C(42)	8 114(13)	4 269(12)	8 407(16)
C(51)	2 040(14)	1 359(16)	1 095(20)	C(52)	9 758(14)	4 211(13)	8 142(17)
C(61)	3 177(16)	3 397(15)	4 098(18)	C(62)	7 881(12)	3 293(13)	10 300(18)
C(71)	4 635(14)	2 663(14)	4 472(17)	C(72)	8 470(13)	1 766(13)	10 434(17)
C(81)	3 144(16)	1 520(13)	3 360(18)	C(82)	9 675(15)	3 177(13)	10 101(16)
C(91)	3 518(11)	3 581(12)	409(15)	C(92)	7 518(12)	2 753(10)	6 398(14)
C(101)	3 262(11)	2 907(11)	−617(15)	C(102)	8 174(11)	2 925(10)	5 641(14)
C(111)	3 434(12)	2 036(12)	−786(16)	C(112)	8 992(11)	2 649(10)	5 681(15)
C(121)	3 920(11)	1 798(13)	98(15)	C(122)	9 219(12)	2 235(11)	6 504(14)
C(131)	4 400(10)	2 363(12)	1 127(16)	C(132)	8 625(11)	1 808(11)	7 274(14)
C(141)	4 652(11)	1 981(12)	2 047(17)	C(142)	9 079(11)	1 569(11)	8 149(15)
C(151)	5 181(13)	1 399(12)	1 933(17)	C(152)	9 619(12)	1 016(13)	8 068(18)
C(161)	5 264(14)	921(14)	2 891(17)	C(162)	10 162(14)	1 000(14)	9 146(17)
C(171)	5 781(13)	1 242(13)	948(17)	C(172)	9 699(14)	348(13)	6 951(17)
C(181)	3 063(13)	1 406(12)	−1 916(15)	C(182)	9 605(11)	2 972(12)	4 782(14)
C(191)	2 542(12)	474(12)	−1 913(16)	C(192)	10 533(11)	3 489(12)	5 279(15)
C(201)	3 823(12)	1 303(13)	−2 796(17)	C(202)	9 624(13)	2 087(12)	3 794(17)
C(211)	2 718(12)	2 864(12)	−1 736(16)	C(212)	8 209(11)	3 411(12)	4 676(14)
C(221)	1 889(12)	3 191(12)	−1 437(16)	C(222)	7 965(11)	4 315(11)	5 090(14)
C(231)	3 324(13)	3 465(13)	−2 408(17)	C(232)	7 524(13)	2 801(13)	3 621(16)
C(241)	2 155(13)	1 648(14)	−3 569(16)	C(242)	9 367(12)	3 799(12)	3 334(15)

was removed under vacuum. The residue was taken up in CH_2Cl_2 and eluted on silica gel TLC plates using light petroleum–hexane (1 : 1) as eluent. Two reddish derivatives, **7** and **8a** (in maximum yields of about 15% each), were obtained together with trace amounts of a yellow substance (see footnote to p. 2586).

Complex **7** (Found: C, 37.3; H, 3.3; N, 1.7; Ru, 40.0. Calc. for $C_{24}H_{23}NO_8Ru_3$: C, 38.1; H, 3.05; N, 1.85; Ru, 40.1%): IR (ν_{CO}, heptane solution) 2082vs, 2050vs(br), 2020vs, 2008vs, 1985(sh) and 1958m cm^{-1}; NMR ($CDCl_3$) ^1H, δ 9.53 (s, CH), 4.38 (s, CH), 2.47 (s, NMe), 2.16 (s), 2.15 (s, =CMe_2), 1.55 (s, Me), 1.48 (s, 2Me) and 1.39 (s, Me); ^{13}C, δ 202.6, 198.9, 195.8, 192.1 (8 CO), 168.8 (1 CH), 165.9, 164.2, 139.6, 130.6, 113.6 (5 quaternary C), 70.3 (1 CH), 64.7 (2 quaternary C), 31.4, 29.4, 26.7, 26.5, 25.4, 24.7 and 23.9 (7 Me).

Complex **8a** (Found: C, 38.5; H, 3.1; N, 2.5; Ru, 35.6. Calc. for $C_{17}H_{17}NO_6Ru_2$: C, 38.3; H, 3.2; N, 2.65; Ru, 37.9%): IR (ν_{CO}, heptane solution) 2080vs, 2060s, 2041vs, 2029vs, 2012vs, 1992vs and 1952vs cm^{-1}; NMR ($CDCl_3$): ^1H, δ 6.50 (s, 2 CH), 2.33 (s, NMe), 1.33 (s) and 1.20 (s, 4 Me); ^{13}C, δ 197.8, 195.7, 192.3 (6 CO), 149.4 (2 quaternary C), 128.9 (2 CH), 60.1 (2 quaternary C), 30.3 (2 Me), 27.0 (NMe) and 24.4 (2 Me); mass spectrum: isotopic pattern Ru_2, *m*/*z* 535 (P^+), loss of six CO (the corresponding doubly charged ions are observed, albeit in low intensity) followed by two 30 mass unit fragments and complex fragmentation of the organic moiety.

Complex **8b**. The compound $[Ru_3(CO)_{12}]$ (0.5 g, 0.78 mmol) was treated with **2** (0.24 g, 1.6 mmol) in refluxing toluene (50 cm^3) for 4–10 min under nitrogen. The resulting dark red solution was filtered and concentrated under vacuum. The residue was taken up in CH_2Cl_2 and eluted with light petroleum–hexane (1 : 1) on silica gel TLC plates. The following products were found: unreacted $[Ru_3(CO)_{12}]$ (15%), two yellow derivatives (traces not characterized), the red complex **8b** (15%) and large amounts of unidentified products. Complex **8b** (Found: C, 37.2; H, 3.1; N, 2.5; Ru, 38.6. Calc. for $C_{16}H_{15}NO_6Ru_2$: C, 37.0; H, 2.9; N, 2.7; Ru, 38.9%): IR (ν_{CO}, heptane solution) 2081s, 2048vs, 2013vs, 1998vs, 1984s and 1958m(br) cm^{-1}; NMR ($CDCl_3$): ^1H, δ 6.24 (2 CH), 2.38 (NH), 1.58 (2 Me) and 1.32 (2 Me); ^{13}C, δ 198.5 (2 CO), 195.2 (1 CO), 194.2 (3 CO), 154.7 (s, 2 quaternary C), 125.6 (2 CH), 50.0 (s, 2 quaternary C), 33.4 (2 Me) and 31.9 (2 Me).

Thermal Decomposition of Complex 7.—In a sealed tube, complex **7** (72 mg, 0.095 mmol) in chlorobenzene (6 cm^3) was heated at 120 °C for 6 h under nitrogen. The solvent was distilled under vacuum and the residue separated by TLC on silica gel using hexane–ethyl acetate (8 : 2) as eluent; 6 mg (0.026 mmol, 26% yield) of **5** were obtained.

Crystal Structure Determination of Complex 7.—Crystals of complex **7** were obtained by cooling heptane–$CHCl_3$ or –toluene solutions under N_2; after some days deep red crystals were collected. A crystal of approximate dimensions 0.20 × 0.23 × 0.30 mm was used for the X-ray analysis.

Crystal data. $C_{24}H_{23}NO_8Ru_3$, $M = 756.66$, triclinic, space group $P\bar{1}$, $a = 15.607(8)$, $b = 15.912(7)$, $c = 11.674(5)$ Å, $\alpha = 104.88(2)$, $\beta = 90.01(3)$, $\gamma = 103.53(2)°$, $U = 2719(2)$ Å^3 (by least-squares refinement from the θ values of 30 accurately measured reflections with θ in the range 10.3–15.3°, $\lambda = 0.710\ 73$ Å), $Z = 4$, $D_c = 1.849$ g cm^{-3}, $F(000) = 1480$, μ(Mo-Kα) = 16.59 cm^{-1}.

Data were collected at room temperature on a Philips PW 1100 single-crystal diffractometer using graphite-monochromated Mo-Kα radiation and the θ–2θ scan mode. All reflections with θ in the range 3–23° were measured; of 7825 independent reflections, 2950 having $I > 2\sigma(I)$ were considered observed and used in the analysis. The individual profiles were analysed according to Lehmann and Larsen.[14] The intensity of one standard reflection was measured after 50 reflections as a general check on crystal and instrument stability. No significant change in the measured intensities was observed during the data collection. No corrections for absorption effects were applied.

The structure was solved by Patterson and Fourier methods, and refined by blocked-matrix least squares first with isotropic and then with anisotropic thermal parameters in the last cycles for all the non-hydrogen atoms, except for the carbon atoms of the methyl groups. The hydrogen atoms were placed at their calculated positions (C–H 1.08 Å) and refined 'riding' on the corresponding carbon atoms. A weighting scheme $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$ was used in the last cycles of refinement; at convergence K and g were 0.657 and 0.001 respectively. Final R and R' values were 0.0443 and 0.0470. The SHELX 76 and SHELXS 86 systems of computer programs were used.[15] Atomic scattering factors, corrected for anomalous dispersion, were taken from ref. 16. Final atomic coordinates for the non-hydrogen atoms are given in Table 2. All calculations were carried out on the CRAY X-MP/48 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Bologna and on the GOULD POWERNODE 6040 of the Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Parma.

Additional data available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters, and remaining bond lengths and angles.

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