Reaction of 4-Methylpent-2-yne with Dodecacarbonyltriruthenium. The Structure of a Novel Alkyne Dimerization Dehydrogenation Product

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Reaction of $[Ru_3(CO)_{12}]$ with 4-methylpent-2-yne yields, as the major product, an open cluster $[Ru_3(CO)_8(C_{12}H_{18})]$, the result of an unusual type of dimerization and dehydrogenation of an internal alkyne. The crystal structure of $[Ru_3(CO)_8(C_{12}H_{18})]$ has been determined by *X*-ray methods. Crystals are triclinic, space group $P\bar{1}$, with $Z = 2$ in a unit cell of dimensions $a = 9.719(8)$, $b = 13.862(10)$, $c = 9.039(8)$ Å, $\alpha = 103.40(8)$, $\beta = 103.60(7)$, and $\gamma = 87.76(6)°$. The structure has been solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least squares to $R = 0.033$ for 3 701 observed reflections. The complex consists of a bent arrangement of three Ru atoms (with Ru–Ru bonds of 2.661 and 2.645 Å and Ru–Ru–Ru angle of 89.1°) co-ordinated by eight (six terminal and two bridging) carbonyls and by an organic ligand, derived from dimerization and dehydrogenation of 4-methylpent-2-yne. This organic ligand forms two σ bonds with the central Ru atom, giving rise to a metallocyclopentadiene ring in which the terminal Ru atoms are on opposite sides of this ring and are η interacting with its four carbon atoms.

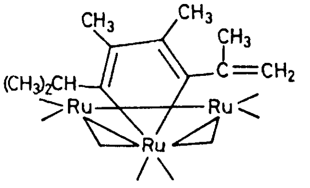
THE compound dodecacarbonyltriruthenium reacts with alkynes to give substituted clusters whose structures are dependent on the nature of the alkyne. Thus, terminal alkynes (HC_2R) give hydrido-clusters $[Ru_3H(CO)_9(C_2R)]$ [1,2] while internal alkynes with hydrogens α to the triple bond (RC_2CH_2R') give the isomeric hydrido-clusters $[Ru_3H(CO)_9(RC_2CHR')]$ [3,4] and $[Ru_3H(CO)_9(RCCHCR')]$.[3,5] In all of these reactions, oxidative addition is the usual reaction mechanism. As part of our programme to evaluate the relative reactivity of different types of C–H bonds α to an internal acetylene, we have studied the reaction of 4-methylpent-2-yne with $[Ru_3(CO)_{12}]$. We report here the results of this study along with the solid-state structure of the major product which represents a novel reaction mechanism in which dimerization of a relatively bulky internal acetylene is coupled with dehydrogenation of the dimerized ligand.

RESULTS AND DISCUSSION

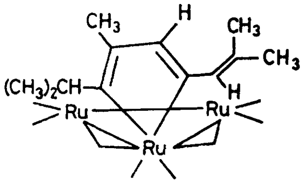
When 4-methylpent-2-yne is treated with $[Ru_3(CO)_{12}]$ in a 10 : 1 or 20 : 1 ratio in refluxing heptane for 30 min, three types of products are formed whose molecular weights have been determined by mass spectroscopic analysis: (1) $[Ru_3(CO)_8(2L - 2H)]$ [L = 4-methylpent-2-yne (C_6H_{10})]; (2) $[Ru_3(CO)_9L]$; and (3) $[Ru_4(CO)_{12}L]$. Three products of type (1) are formed and are separated by preparative thin-layer chromatography (t.l.c.). All three have identical mass spectra and similar i.r. spectra which show two bridging carbonyl stretching frequencies. Two of these products, (1a) and (1b), are formed in sufficient quantities to be investigated by ^1H n.m.r., and (1a) constitutes the major product of the reaction {20% based on $[Ru_3(CO)_{12}]$}.

The ^1H n.m.r. of both (1a) and (1b) show two broadened singlet resonances in the olefinic region (each of relative intensity one), three singlet methyl resonances (each of relative intensity three), and one isopropyl group (a septet of relative intensity one and a doublet of relative intensity six). No hydride resonances are observed for (1a) or (1b).

Based on this evidence, we can suggest several possible structures for the isomers (1a) and (1b). They are apparently closely related to the metallacyclopentadienyl clusters previously reported, $[M_3(CO)_8(alkyne)_2]$ [6] (M = Fe, Ru, or Os), but differ in that an additional degree of unsaturation must be present in the carbon framework of the ligand in order to agree with the formula $[Ru_3(CO)_8(C_{12}H_{18})]$. Two structures which accord with the ^1H n.m.r. data are (1) and (1′) where the isomers (1a) and (1b) may differ in the orientation of dimerization. We then undertook an *X*-ray crystallographic investigation of the major product (1a) in order to decide between these two possibilities.



(1)



(1′)

Solid-state Structure of (1a).—The structure of complex (1a) is shown in the Figure. Bond distances and angles not involving hydrogen atoms are given in Table 1. The complex consists of an open, bent arrangement of three Ru atoms, co-ordinated by eight carbonyls and, through σ and η bonds, by an organic ligand derived from the head-to-tail dimerization of 4-methylpent-2-yne with elimination of one molecule of H_2. The two Ru–Ru bonds are nearly equal in length: Ru(1)–Ru(2) = 2.661(1) and Ru(1)–Ru(3) = 2.645(2) Å and form an angle of 89.1(1)°. Open arrangements of three Ru atoms in complexes substituted with alkynes have already been found in $[Ru_3(CO)_8(HC_2Bu^t)_3]$ [7] and $[Ru_3(CO)_8(C_{16}H_{22})]$.[8] In the former, both the metal–metal bonds (2.669 and 2.661 Å) and the angle (88.8°) are very close to those of

(1a), while in the latter the metal–metal bonds (2.731 and 2.838 Å) are longer and the angle (118.1°) is larger than in (1a). The shorter metal–metal bonds in $[Ru_3(CO)_8(HC_2Bu^t)_3]$ and (1a) compared with those of $[Ru_3(CO)_8(C_{16}H_{22})]$ can be attributed to the presence of two bridging CO groups.

Six carbonyls, two on each Ru atom, are terminal (the Ru–C–O angles being very close to 180°) and the remainder asymmetrically bridge the terminal and central Ru atoms [Ru(2)–C(3) = 1.990, Ru(1)–C(3) = 2.153; Ru(3)–C(8) = 1.992, Ru(1)–C(8) = 2.148 Å] with the carbon atoms closer to the terminal metal atoms.

The bonding of the organic moiety to the metal atoms in (1a) is also very similar to that found in $[Ru_3(CO)_8(HC_2Bu^t)_3]$. The central Ru(1) atom forms two rather long σ bonds with the C(9) and C(12) carbon atoms of the organic ligand [Ru(1)–C(9) = 2.154 and Ru(1)–C(12) = 2.206 Å] giving rise to a metallacyclopentadiene ring. The terminal ruthenium atoms Ru(2) and Ru(3) are η^2 bonded to the carbon atoms of this ring [Ru–C bonds are in the range 2.228—2.340 Å] and lie on opposite sides, each at a distance of 1.86 Å, from the midpoint of the carbon–carbon double bonds. The double bonds are

TABLE 1

Bond distances (Å) and angles (°) (not involving hydrogen atoms) with estimated standard deviations in parentheses

(*a*) In the co-ordination sphere of the ruthenium atoms

Ru(1)–Ru(2)	2.661(1)	Ru(2)–C(9)	2.299(7)
Ru(1)–Ru(3)	2.645(2)	Ru(2)–C(10)	2.340(7)
Ru(1)–C(1)	1.906(8)	Ru(2)–C(11)	2.316(7)
Ru(1)–C(2)	1.916(8)	Ru(2)–C(12)	2.228(8)
Ru(1)–C(3)	2.153(8)	Ru(3)–C(6)	1.861(9)
Ru(1)–C(8)	2.148(8)	Ru(3)–C(7)	1.880(9)
Ru(1)–C(9)	2.154(7)	Ru(3)–C(8)	1.992(7)
Ru(1)–C(12)	2.206(8)	Ru(3)–C(9)	2.301(7)
Ru(2)–C(3)	1.990(7)	Ru(3)–C(10)	2.329(7)
Ru(2)–C(4)	1.866(8)	Ru(3)–C(11)	2.321(8)
Ru(2)–C(5)	1.867(9)	Ru(3)–C(12)	2.249(7)

Ru(2)–Ru(1)–Ru(3)	89.1(1)	C(4)–Ru(2)–C(9)	105.4(3)
Ru(2)–Ru(1)–C(1)	120.4(2)	C(4)–Ru(2)–C(10)	103.8(3)
Ru(2)–Ru(1)–C(2)	120.6(3)	C(4)–Ru(2)–C(11)	127.9(3)
Ru(2)–Ru(1)–C(3)	47.4(2)	C(4)–Ru(2)–C(12)	164.7(3)
Ru(2)–Ru(1)–C(8)	136.7(2)	C(5)–Ru(2)–C(9)	167.5(3)
Ru(2)–Ru(1)–C(9)	55.9(2)	C(5)–Ru(2)–C(10)	135.5(3)
Ru(2)–Ru(1)–C(12)	53.5(2)	C(5)–Ru(2)–C(11)	104.6(3)
Ru(3)–Ru(1)–C(1)	122.7(3)	C(5)–Ru(2)–C(12)	98.6(3)
Ru(3)–Ru(1)–C(2)	115.6(3)	C(9)–Ru(2)–C(10)	36.0(2)
Ru(3)–Ru(1)–C(3)	136.4(2)	C(9)–Ru(2)–C(11)	63.6(3)
Ru(3)–Ru(1)–C(8)	47.7(2)	C(9)–Ru(2)–C(12)	69.5(3)
Ru(3)–Ru(1)–C(9)	56.2(2)	C(10)–Ru(2)–C(11)	36.6(3)
Ru(3)–Ru(1)–C(12)	54.3(2)	C(10)–Ru(2)–C(12)	63.2(3)
C(1)–Ru(1)–C(2)	91.6(4)	C(11)–Ru(2)–C(12)	36.8(3)
C(1)–Ru(1)–C(3)	85.3(3)	Ru(1)–Ru(3)–C(6)	122.8(3)
C(1)–Ru(1)–C(8)	87.5(3)	Ru(1)–Ru(3)–C(7)	135.5(3)
C(1)–Ru(1)–C(9)	98.8(3)	Ru(1)–Ru(3)–C(8)	53.0(2)
C(1)–Ru(1)–C(12)	171.3(3)	Ru(1)–Ru(3)–C(9)	51.1(2)
C(2)–Ru(1)–C(3)	94.0(3)	Ru(1)–Ru(3)–C(10)	78.1(2)
C(2)–Ru(1)–C(8)	87.9(3)	Ru(1)–Ru(3)–C(11)	79.5(2)
C(2)–Ru(1)–C(9)	169.3(3)	Ru(1)–Ru(3)–C(12)	52.8(2)
C(2)–Ru(1)–C(12)	97.1(3)	C(6)–Ru(3)–C(7)	86.1(5)
C(3)–Ru(1)–C(8)	172.7(3)	C(6)–Ru(3)–C(8)	94.4(4)
C(3)–Ru(1)–C(9)	89.5(3)	C(6)–Ru(3)–C(9)	166.1(4)
C(3)–Ru(1)–C(12)	92.7(3)	C(6)–Ru(3)–C(10)	136.0(4)
C(8)–Ru(1)–C(9)	89.9(3)	C(6)–Ru(3)–C(11)	104.2(4)
C(8)–Ru(1)–C(12)	94.1(3)	C(6)–Ru(3)–C(12)	97.2(4)
C(9)–Ru(1)–C(12)	72.6(3)	C(7)–Ru(3)–C(8)	96.1(4)
Ru(1)–Ru(2)–C(3)	52.8(2)	C(7)–Ru(3)–C(9)	106.7(4)
Ru(1)–Ru(2)–C(4)	135.7(3)	C(7)–Ru(3)–C(10)	105.3(3)
Ru(1)–Ru(2)–C(5)	125.4(3)	C(7)–Ru(3)–C(11)	129.4(4)
Ru(1)–Ru(2)–C(9)	50.8(2)	C(7)–Ru(3)–C(12)	166.0(3)
Ru(1)–Ru(2)–C(10)	77.5(2)	C(8)–Ru(3)–C(9)	89.8(3)
Ru(1)–Ru(2)–C(11)	79.2(2)	C(8)–Ru(3)–C(10)	125.4(3)
Ru(1)–Ru(2)–C(12)	52.7(2)	C(8)–Ru(3)–C(11)	131.2(3)
C(3)–Ru(2)–C(4)	97.9(3)	C(8)–Ru(3)–C(12)	97.3(3)
C(3)–Ru(2)–C(5)	95.8(3)	C(9)–Ru(3)–C(10)	36.1(2)
C(3)–Ru(2)–C(9)	89.7(3)	C(9)–Ru(3)–C(11)	63.5(3)
C(3)–Ru(2)–C(10)	125.0(3)	C(9)–Ru(3)–C(12)	69.1(3)
C(3)–Ru(2)–C(11)	130.6(3)	C(10)–Ru(3)–C(11)	36.6(3)
C(3)–Ru(2)–C(12)	96.6(3)	C(10)–Ru(3)–C(12)	63.1(3)
C(4)–Ru(2)–C(5)	85.1(4)	C(11)–Ru(3)–C(12)	36.6(3)

TABLE 1 (*continued*)

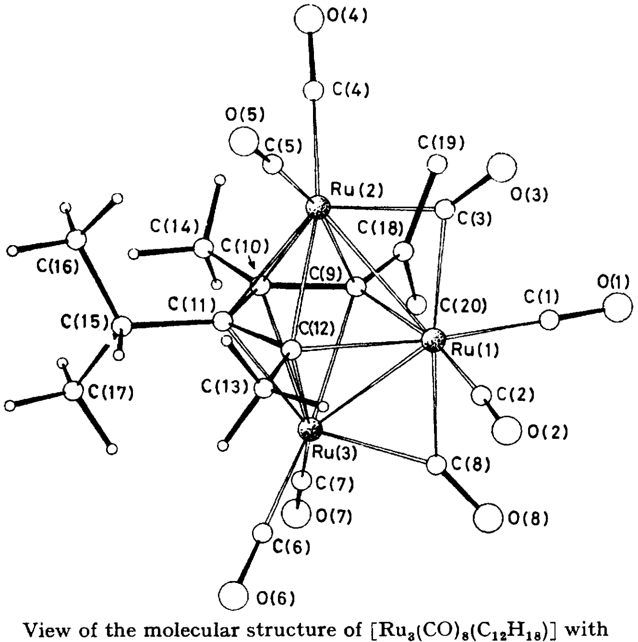
(*b*) In the carbonyl groups

O(1)–C(1)	1.12(1)	O(5)–C(5)	1.14(1)
O(2)–C(2)	1.12(1)	O(6)–C(6)	1.15(1)
O(3)–C(3)	1.16(1)	O(7)–C(7)	1.14(1)
O(4)–C(4)	1.14(1)	O(8)–C(8)	1.14(1)

Ru(1)–C(1)–O(1)	179.0(7)	Ru(2)–C(5)–O(6)	177.5(8)
Ru(1)–C(2)–O(2)	177.4(8)	Ru(3)–C(6)–O(6)	176.4(9)
Ru(1)–C(3)–O(3)	135.8(5)	Ru(3)–C(7)–O(7)	178.3(9)
Ru(2)–C(3)–O(3)	144.3(6)	Ru(3)–C(8)–O(8)	143.8(7)
Ru(1)–C(3)–Ru(2)	79.8(3)	Ru(1)–C(8)–C(8)	136.8(7)
Ru(2)–C(4)–O(4)	178.0(8)	Ru(1)–C(8)–Ru(3)	79.3(3)

C(9)–C(10)	1.43(1)	C(12)–C(13)	1.55(1)
C(10)–C(11)	1.46(1)	C(15)–C(16)	1.50(1)
C(11)–C(12)	1.44(1)	C(15)–C(17)	1.49(1)
C(9)–C(18)	1.51(1)	C(18)–C(19)	1.43(1)
C(10)–C(14)	1.54(1)	C(18)–C(20)	1.40(1)
C(11)–C(15)	1.55(1)		

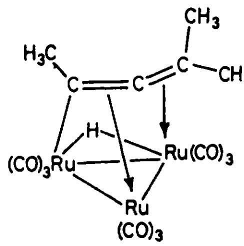
Ru(1)–C(9)–C(18)	119.5(5)	Ru(1)–C(12)–C(13)	120.5(5)
Ru(1)–C(9)–C(10)	120.9(5)	Ru(1)–C(12)–C(11)	120.5(5)
Ru(1)–C(9)–Ru(2)	73.3(2)	Ru(1)–C(12)–Ru(2)	73.8(3)
Ru(1)–C(9)–Ru(3)	72.8(2)	Ru(1)–C(12)–Ru(3)	72.8(2)
Ru(2)–C(9)–Ru(3)	108.0(3)	Ru(2)–C(12)–Ru(3)	112.5(3)
Ru(2)–C(9)–C(10)	73.6(4)	Ru(2)–C(12)–C(11)	75.0(4)
Ru(3)–C(9)–C(10)	73.0(4)	Ru(3)–C(12)–C(11)	74.5(4)
C(10)–C(9)–C(18)	119.6(6)	C(11)–C(12)–C(13)	119.0(7)
C(9)–C(10)–C(11)	114.3(6)	C(11)–C(15)–C(16)	115.5(8)
C(9)–C(10)–C(14)	122.2(6)	C(11)–C(15)–C(17)	114.1(9)
C(11)–C(10)–C(14)	123.5(6)	C(16)–C(15)–C(17)	115.9(9)
C(10)–C(11)–C(12)	111.7(6)	C(9)–C(18)–C(19)	119.4(7)
C(10)–C(11)–C(15)	123.9(7)	C(9)–C(18)–C(20)	120.5(8)
C(12)–C(11)–C(15)	124.4(7)	C(19)–C(18)–C(20)	120.1(9)



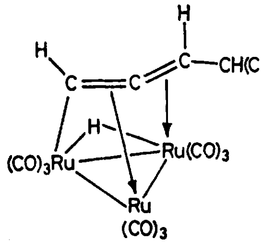
View of the molecular structure of $[Ru_3(CO)_8(C_{12}H_{18})]$ with the atomic numbering scheme delocalized over the three C–C bonds of the ring as shown by the distances C(9)–C(10), C(10)–C(11), and C(11)–C(12) of 1.43, 1.46, and 1.44 Å respectively. The heterocycle is perfectly planar, Ru(1), C(9), C(10), C(11), and C(12) being insignificantly displaced from the mean plane passing through them. In addition, the C(13), C(14), C(15), and C(18) atoms are also coplanar with the ring, their displacements from the plane being only 0.01, 0.01, 0.02, and 0.03 Å.

The structures of (1b) and (1c) undoubtedly differ from (1a) only in the relative orientation of the two dimerized alkynes but we cannot decide which isomers of (1a) they are on the basis of the ^{1}H n.m.r. of (1b) alone.

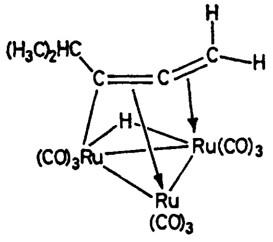
The relative abundance of product (2), $[Ru_3(CO)_9L]$, is increased when the reaction is performed under milder conditions {60 °C, 3 : 1, L : $[Ru_3(CO)_{12}]$} or when the reaction is stopped after a few minutes. The ^{1}H n.m.r. spectrum of this product shows three hydride resonances of non-integral relative intensities at δ −18.31, −20.04, and −20.55 (in the relative intensity ratio 0.2 : 1 : 0.2), indicating the presence of three compounds of general formula $[Ru_3H(CO)_9(L - H)]$. These compounds are all undoubtedly isomeric since the mass spectrum shows only one parent ion at a molecular mass corresponding to $[Ru_3H(CO)_9(L - H)]$. These compounds (which cannot be separated by t.l.c.) are probably analogues of the ‘ allenic ’ and ‘ allylic ’ complexes formed when $[Ru_3(CO)_{12}]$ is treated with pent-2-yne [see structures (2a)—(2d)].



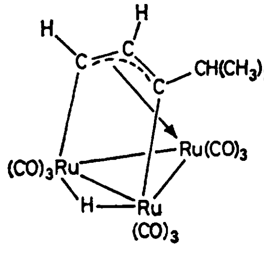
(2a)



(2b)



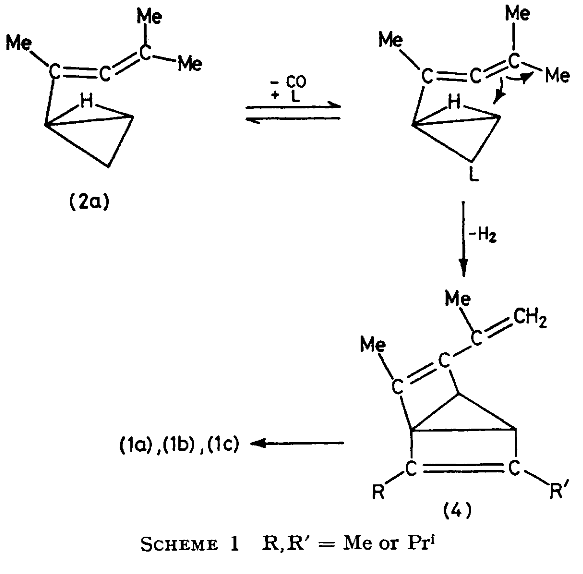
(2c)



(2d)

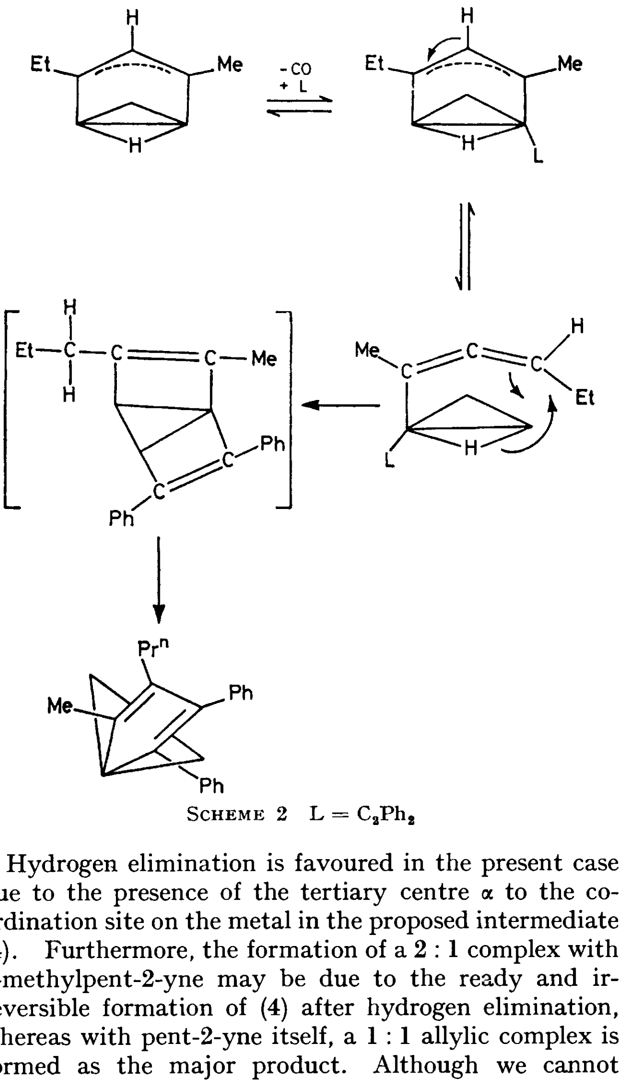
Structure (2d) is the only ‘ allylic ’ compound which can be formed from 4-methylpent-2-yne and would be expected to show resonances in the olefinic regions δ 7.0—7.3 and 8.0—8.5 in a 1 : 1 ratio based on analogy with previously reported complexes of this type.[3,5,9] Indeed, two broadened singlets are observed at δ 8.18 and 7.26 which integrate in a 1 : 1 ratio with the hydride resonance at δ −18.31. We have previously shown that the ‘ allenic ’ isomers of type (2a)—(2c) are direct precursors to the ‘ allylic ’ isomers of type (2d).[3] In this particular case only (2b) and (2c) can undergo this rearrangement. When the reaction of 4-methylpent-2-yne with $[Ru_3(CO)_{12}]$ is performed at lower temperatures (60 °C), only two resonances in the hydride region are observed at δ −20.04 and −20.55 which we associate with two of the three possible ‘ allenic ’ isomers (2a)—(2c). We have found that in general ‘ allenic ’ hydride resonances are found at higher field than the ‘ allylic ’ ones, as is observed in this case.[3,9,10] The two ‘ allenic ’ hydride resonances are in approximately 5 : 1 ratio indicating that formation of one of the allenic isomers is favoured. Two singlet methyl resonances at δ 2.54 and 2.04 integrate in a 1 : 3 and 1 : 6 ratio with the more intense hydride resonance at δ −20.04 demonstrating that the major allenic isomer has structure (2a). The methyl group resonance at δ 2.04 is broad at room temperature but sharpens as the temperature is raised to 65 °C. At −35 °C the broadened methyl resonance at δ 2.04 is resolved into two resonances at δ 2.23 and 1.91 (relative intensity 1 : 1). Thus, an exchange process which averages the two magnetically inequivalent methyl groups on the terminal allenic carbon in (2a) is operative. This process could involve motion of either the organic ligand or the bridging hydride in (2a). We are currently investigating this novel exchange process more fully and the results of these studies will be reported separately. Although we cannot definitely assign the structure of the minor ‘ allenic ’ isomer to either (2b) or (2c), (2c) seems to be the more likely of the two since its formation involves a recognized pattern of oxidative addition of one C–H bond with no other rearrangement of the organic ligand.[3]

Since structure (2a) is the major product initially formed on reaction of one molecule of 4-methylpent-2-yne with $[Ru_3(CO)_{12}]$ it seems likely that it reacts with a second molecule of alkyne to give the major product (1a) (Scheme 1).



SCHEME 1 R,R′ = Me or Pr^i

Dissociation of one molecule of CO is followed by co-ordination of a second alkyne molecule and this intermediate rearranges with elimination of a molecule of H_2 to give structure (4) which is analogous to the violet isomer of $[Fe_3(CO)_8(alkyne)_2]$ previously isolated in the case of iron.[6a] This molecule then undergoes a thermal rearrangement to (1a) as is observed for the iron analogue. A similar reaction is observed for the reaction of the allylic complexes $[Ru_3H(CO)_9(CH_3CH_2CCHCCH_3)]$ with diphenylacetylene, the only difference being that in this case the proposed allenic intermediate undergoes metal-to-ligand hydrogen transfer rather than H_2 elimination (Scheme 2).[3]



SCHEME 2 L = C_2Ph_2

Hydrogen elimination is favoured in the present case due to the presence of the tertiary centre α to the co-ordination site on the metal in the proposed intermediate (4). Furthermore, the formation of a 2 : 1 complex with 4-methylpent-2-yne may be due to the ready and irreversible formation of (4) after hydrogen elimination, whereas with pent-2-yne itself, a 1 : 1 allylic complex is formed as the major product. Although we cannot determine whether alkyne coupling takes place before or after H_2 elimination, the reaction scheme suggested here relates more directly to the observed rearrangement of analogous compounds.[3,6a] Thus, it appears that the isopropyl C–H bond is more reactive than the methyl C–H bond in 4-methylpent-2-yne as evidenced by the formation of (2a) as the major 1 : 1 adduct with $[Ru_3(CO)_{12}]$.

We also suggest that formation of the 2 : 1 complex, (1a), as the major product under these reaction conditions is a consequence of the presence of a tertiary centre on the intermediate formed after co-ordination of a second molecule of alkyne, which results in a ready dehydrogenation and dimerization process. Although both of these processes have been observed independently in the reaction of $[Ru_3(CO)_{12}]$ with alkenes and alkynes, this represents the first example where both processes are coupled in a single reaction. We are continuing our studies on substituted internal alkynes in the hope of verifying the mechanistic suggestions made here.

Finally, on the basis of the n.m.r. and i.r. data, (3) is suggested to be isostructural with $[Ru_4(CO)_{12}(PhC{\equiv}CPh)]$ [11] and $[Ru_4(CO)_{12}(C_6H_8)]$ [12] where the metal atoms are in a 'butterfly' arrangement capped by the alkyne.

EXPERIMENTAL

Materials.—The compound $[Ru_3(CO)_{12}]$ was obtained by literature methods; [13] 4-methylpent-2-yne was purchased from Farchan. The solvents were reagent grade and were dried over molecular sieves before use; all reactions were carried out under nitrogen.

Spectra.—Infrared spectra were recorded on a Beckman IR-12 spectrophotometer. Proton n.m.r. spectra were determined on a JEOL 60 HL and mass spectra on a Hitachi RMU 6H mass spectrometer using an ionizing energy of 70 eV.*

Reaction of 4-*Methylpent*-2-*yne with* $[Ru_3(CO)_{12}]$.—Dodecacarbonyltriruthenium (0.400 g, 0.62 mmol) and 4-methylpent-2-yne (0.6—1.2 cm³, 6—12 mmol) were refluxed in heptane (300 cm³) for 30 min. The cooled solution was filtered, concentrated under reduced pressure, and separated by t.l.c. (absorbent Kieselgel PF Merck, eluant light petroleum and 10% diethyl ether).

The following derivatives were eluted: $[Ru_3(CO)_8(C_{12}H_{18})]$ (1a), yellow-orange crystals (20%) (Found: C, 35.05; H, 2.50; Ru, 44.1. Calc. for $C_{20}H_{18}O_8Ru_3$: C, 34.85; H, 2.65; Ru, 44.0%). [*M*, 692, mass spectrum: *m/e* 692 followed by loss of eight carbonyl groups; i.r., (cm^{-1}, CCl_4) ν(CO): 2 068ms, 2 023vs, 2 008s, 1 977s, 1 880ms, 1 860ms; ^1H n.m.r. (δ, $CDCl_3$): CH_2, 4.58 (1, br s), 4.04 (1, br s); CH, 3.45 (1, septet); CH_3, 2.94 (3, s), 2.03 (6, d), 1.58 (3, s), 1.38 (3, s).]

$[Ru_3(CO)_8(C_{12}H_{18})]$ (1b), yellow-orange crystals (7%) [*M*, 692, mass spectrum: *m/e* 692 followed by loss of eight carbonyl groups; i.r. (cm^{-1}, CCl_4) ν(CO): 2 070ms, 2 021vs, 2 010s, 1 977s, 1 882ms, 1 862ms; ^1H n.m.r. (δ, $CDCl_3$): CH_2, 4.72 (1, br s), 4.13 (1, br s); CH, 1.94 (1, septet); CH_3, 3.34 (3, s), 3.17 (3, s), 1.53 (3, s), 0.64 (6, d).]

$[Ru_3(CO)_8(C_{12}H_{18})]$ (1c), yellow-orange crystals (1%) [*M*, 692, mass spectrum: *m/e* 692 followed by loss of eight carbonyl groups; i.r. (cm^{-1}, CCl_4) ν(CO): 2 068ms, 2 023vs, 2 007s, 1 976s, 1 878ms, 1 857ms.

$[Ru_3(CO)_9(C_6H_{10})]$ (2), pale yellow powder (10%) (Found: C, 28.4; H, 1.45; Ru, 47.5. Calc. for $C_{15}H_{10}O_9Ru_3$: C, 28.25; H, 1.60; Ru, 47.55%). [*M*, 640, mass spectrum: *m/e* 640 followed by loss of nine carbonyl groups.]

$[Ru_4(CO)_{12}(C_6H_{10})]$ (3), red-violet crystals (2%) (Found: C, 26.4; H, 1.15; Ru, 49.25. Calc. for $C_{18}H_{10}O_{12}Ru_4$: C, 26.3; H, 1.25; Ru, 49.15%). [*M*, 826, mass spectrum:

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* Throughout this paper: 1 eV ≈ 1.60 × 10^{-19} J.

m/*e* 826 followed by loss of twelve carbonyl groups; i.r., (cm^{-1}, CCl_4) ν(CO): 2 094m, 2 062vs, 2 041vs, 2 035vs, 2 013ms, 1 999m.]

Complex (1a) was crystallized from heptane at −5 °C.

X-*Ray Data Collection*.—An irregular yellow-orange crystal of complex (1a) with dimensions *ca.* 0.12 × 0.18 × 0.30 mm was used for data collection. The unit-cell dimensions were determined first from rotation and Weissenberg photographs and then refined by least squares using 15 high-angle reflections accurately measured on a Siemens AED single-crystal diffractometer.

Crystal data. $C_{20}H_{18}O_8Ru_3$, $M = 689.57$, Triclinic, $a = 9.719(8)$, $b = 13.862(10)$, $c = 9.039(8)$ Å, $\alpha = 103.40(8)$, $\beta = 103.60(7)$, $\gamma = 87.76(6)°$, $U = 1\,151(2)$ Å^3, $Z = 2$, $D_c = 1.989$ g cm^{-3}, Mo-K_α radiation ($\lambda = 0.710\,69$ Å), μ(Mo-K_α) = 19.48 cm^{-1}, space group $P\bar{1}$ from structure determination.

A total of 4 979 independent reflections (with θ in the range 3—27°) were collected on the same diffractometer using niobium-filtered Mo-K_α radiation and the θ—2θ scan technique; 3 701 of these, for which $I > 2\sigma(I)$, were employed in the analysis, the remaining 1 278 were considered unobserved. The structure amplitudes were obtained after the usual Lorentz and polarization reduction and the absolute scale was established first by Wilson's method and then by least-squares refinement. No correction for absorption was applied because of the low value of μR.

Structure Determination and Refinement.—The structure was solved by Patterson and Fourier methods localizing first the Ru atoms from the Patterson synthesis and then the remaining non-hydrogen atoms from the successive Fourier maps.

The refinement was carried out by means of full-matrix least squares using the SHELX system of computer programs [14] with first isotropic and then anisotropic thermal parameters for all the non-hydrogen atoms. An inspection of the bond distances in the organic ligand reveals that in the isopropenyl substituent the two C–C distances are equal and the values of 1.43 and 1.40 Å, for C(18)–C(19) and C(18)–C(20) respectively, are intermediate between those expected for a single and a double bond. This result can be explained by assuming that the isopropenyl group is disordered and distributed in two positions of equivalent occupancy. All the hydrogen atoms, except for those belonging to the disordered isopropenyl group, were introduced in their geometrically calculated positions in the final structure-factor calculations with isotropic thermal parameters. These values were obtained from the average of the thermal parameters of the atoms to which the hydrogens were attached. The final conventional R was 0.033 for the observed reflections. The atomic scattering factors used, corrected for the anomalous dispersion of Ru, were taken from ref. 15. The function minimized in the least-squares calculations was $\Sigma w|\Delta F|^2$; unit weights were chosen at each stage of the refinement after analysing the variation of $|\Delta F|$ with respect to $|F_o|$. Final atomic co-ordinates for non-hydrogen atoms and for hydrogen atoms are given in Tables 2 and 3 respectively. Observed and calculated structure factors and thermal parameters are listed in Supplementary Publication No. SUP 23115 (13 pp.).*

TABLE 2

Fractional atomic co-ordinates (× 10^4) for the non-hydrogen atoms with estimated standard deviations in parentheses

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Ru(1)	3 725(1)	2 894(1)	4 967(1)
Ru(2)	3 523(1)	3 278(1)	2 173(1)
Ru(3)	1 421(1)	1 761(1)	3 781(1)
O(1)	6 478(6)	2 154(5)	6 675(7)
O(2)	3 546(8)	4 551(5)	7 774(7)
O(3)	6 133(6)	4 147(4)	4 590(6)
O(4)	5 309(8)	2 955(6)	−190(8)
O(5)	2 990(8)	5 291(5)	1 464(9)
O(6)	−1 267(7)	2 275(7)	4 870(10)
O(7)	670(9)	−385(5)	3 465(9)
O(8)	2 791(7)	1 734(5)	7 100(7)
C(1)	5 455(8)	2 432(6)	6 055(9)
C(2)	3 645(9)	3 945(6)	6 742(9)
C(3)	5 053(8)	3 723(5)	4 090(8)
C(4)	4 647(8)	3 065(6)	717(9)
C(5)	3 213(9)	4 525(6)	1 712(9)
C(6)	−254(9)	2 047(8)	4 443(11)
C(7)	970(10)	422(7)	3 572(11)
C(8)	2 638(8)	1 964(6)	5 938(8)
C(9)	3 407(7)	1 777(5)	2 814(8)
C(10)	2 205(7)	1 802(5)	1 551(8)
C(11)	1 277(7)	2 643(6)	1 860(8)
C(12)	1 781(8)	3 266(5)	3 390(8)
C(13)	932(9)	4 196(7)	3 922(10)
C(14)	1 952(9)	1 018(6)	−7(9)
C(15)	−80(9)	2 833(8)	680(11)
C(16)	152(12)	3 141(10)	−727(12)
C(17)	−1 241(10)	2 087(12)	378(16)
C(18)	4 461(8)	954(5)	2 636(8)
C(19)	5 727(11)	1 125(8)	2 190(16)
C(20)	4 218(13)	37(8)	2 943(15)

TABLE 3

Calculated fractional co-ordinates (× 10^4) for the hydrogen atoms except for those belonging to the disordered isopropenyl group

Atom	*x*/*a*	*y*/*b*	*z*/*c*
H(131)	1 453	4 579	5 093
H(132)	−125	3 975	3 909
H(133)	875	4 684	3 136
H(141)	990	1 182	−782
H(142)	1 856	292	210
H(143)	2 833	1 030	−541
H(15)	−492	3 504	1 288
H(161)	1 011	3 678	−372
H(162)	−802	3 467	−1 280
H(163)	414	2 500	−1 544
H(171)	−1 312	1 921	1 468
H(172)	−1 017	1 417	−408
H(173)	−2 233	2 384	−144

All calculations were performed on the CYBER 76 computer of the Centro di Calcolo Elettronico Interuniversitario dell' Italia Nord-Orientale, Casalecchio, Bologna, with final support from the University of Parma.

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

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