Inorganica Chimica Acta, 85 (1984) 161–168

An Inspection into the Class of Bis(alkyne)-undecacarbonyl-*quadro*-tetraruthenium Complexes. Crystal Structure and Dynamic Behaviour of $Ru_4(CO)_{11}(\mu_4, \eta^2\text{-}MeC_2Ph)_2$

SILVIO AIME, GIUSEPPE NICOLA, DOMENICO OSELLA

Istituto di Chimica Generale ed Inorganica, Università di Torino, Corso M. d'Azeglio 48, 10125 Turin, Italy

ANNA MARIA MANOTTI LANFREDI and ANTONIO TIRIPICCHIO

Istituto di Chimica Generale ed Inorganica, Università di Parma, Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Via M. d'Azeglio 85, 43100 Parma, Italy

Received September 20, 1983

The reactions of the butterfly complex $Ru_4(CO)_{12}(MeC_2Ph)$ with several alkynes give the quasi-*planar derivatives $Ru_4(CO)_{11}(MeC_2Ph)(Alkyne)$ in almost quantitative yields.*

The structure of $Ru_4(CO)_{11}(MeC_2Ph)_2$ has been determined by X-ray methods. Crystals are monoclinic, space group C2/c, *with $Z = 4$ in a unit cell of dimensions* a *22.383(16),* b *9.048(8),* c *18.268(12) Å, $\beta = 127.25(4)°$. The structure has been solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least-squares to* R = *0.034 for 1420 observed reflections. The complex, having an imposed C_2 symmetry, presents a tetranuclear metal cluster in which the Ru atoms are in a tetrahedrally-distorted square arrangement. Ten carbonyls are terminal and one symmetrically bridges an edge of the cluster. Each of the two alkyne ligands is σ-bonded to two Ru atoms on the opposite vertices of the cluster and π-bonded to the other two. The organometallic cluster has a Ru_4C_4 core in which the metal and carbon atoms occupy the vertices of a triangulated dodecahedron.*

Introduction

The study of reactions between transition metal carbonyl clusters and unsaturated hydrocarbons is still receiving widespread interest and a number of novel molecular geometries have been recently reported [1]. However, in order to get more insight into the basic paths of these reactions, particular attention has to be devoted to single mechanistic steps.

In the reactions between $Ru_3(CO)_{12}$ and alkynes it has been shown that three major reaction schemes can be found:

i) terminal alkynes ($HC{\equiv}CR$) give the μ_3-alkynyl complex $HRu_3(CO)_9(C_2R)$ (I) [2];

ii) internal alkynes bearing a methylene group adjacent to the triple bond ($RC{\equiv}C{-}CH_2R'$) give the μ_3-allenyl complex $HRu_3(CO)_9$ ($RC{=}C{=}CHR'$) (II) which isomerises thermally into the μ_3-allyl complex $HRu_3(CO)_9(RC{\doteq}CH{\doteq}CR')$ (III) [3, 4];

iii) internal alkynes ($RC{\equiv}CR'$) without a $-CH_2-$ group α to the triple bond give, *via* the condensation of metallic fragments on the alkyne moiety, the butterfly complex $Ru_4(CO)_{12}(RC_2R')$ (IV) [5].

It has also been shown that these compounds further react with alkyne to form complexes containing a ruthena-cyclopentadiene system [3].

Compounds I to III are formed by oxidative addition with cleavage of C–H bonds. Following the cluster-surface analogy [6], they can be envisaged as a model for dissociative chemisorption of alkynes over a flat site of a metallic surface. On the other hand complex IV can be viewed as model for non-dissociative chemisorption over a step or a kink site of a metallic surface.

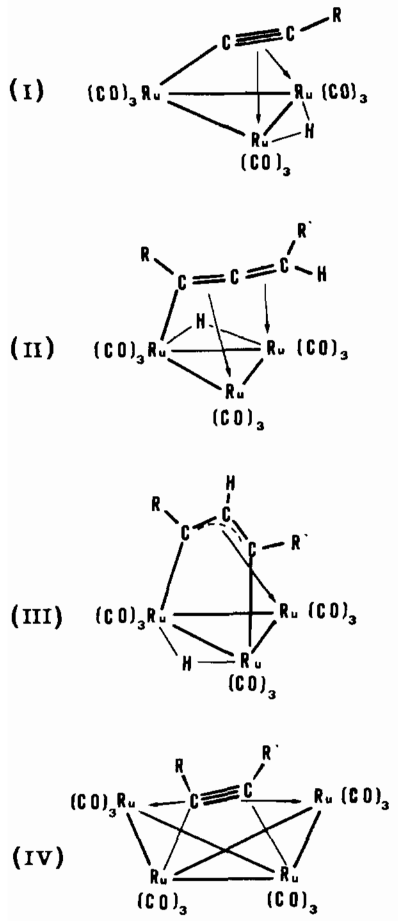
Some different reaction paths have been found when functionalized alkynes are used: $HC{\equiv}C{-}(CH_2)_n{-}OH$ [7], $XC{\equiv}CPh$ (X = Cl, Br) [8], $MeC{\equiv}C{-}CH_2{-}NMe_2$ [9] give rise to the expected products, as depicted in (i) and (ii), *via* the activation of C–H and C–X bonds, but acetylenic

0020-1693/84/$3.00

TABLE I. Spectroscopic Data of Complexes Va–Vd.

Compound	IR[a] νCO, cm^{-1}	^{1}H NMR[b], δ/ppm	MS, m/z
$Ru_4(CO)_{11}(MeC_2Ph)$Va	2083s, 2053vs, 2036vs, 2024vs 2014s, 1980s, 1833m(br)	7.00–6.50 (10,m) 1.70(6,s)	948[c]
$Ru_4(CO)_{11}(MeC_2Ph)(EtC_2Et)$Vb	2081m, 2049s, 2035vs, 2021vs, 2010s, 1980s, 1836m(br)	7.10–6.30 (5,m) 1.94(4,q), 1.71(3,s), 0.92(6,t)	914[c]
$Ru_4(CO)_{11}(MeC_2Ph)(HC_2Bu^t)$Vc	2084m, 2079m, 2052s, 2045s, 2036vs, 2022s, 2014s, 1992m, 1982m, 1840m(br)	7.15–6.55 (5,m) 5.92(1,s), 1.82(3,s), 1.3(9,s)	914[c]
$Ru_4(CO)_{11}(MeC_2Ph)(HC_2H)$Vd	2090m, 2060s, 2040vs, 2027vs, 1988s, 1844m(br)	7.20–6.45(5,m) 5.20(2,s), 1.80(3,s)	858[c]

[a] n-Hexane. [b] $CDCl_3$. [c] Followed by loss of 11 CO groups and then by complicated fragmentation of organic moiety to give ultimately the $Ru_4C_4^+$ ion.



Scheme 1. Diagrammatic representation of the structures of complexes I–IV.

diols [10] and $HC{\equiv}C{-}CH_2{-}NMe_2$ [11] showed an easy cleavage of a σ C–C and C–N bond respectively.

Experimental

Physical Measurements

Infrared spectra were recorded on a Perkin-Elmer 580 B instrument using 0.5 mm NaCl cells. ^{1}H NMR spectra were obtained on a Jeol 60 HL spectrophotometer; VT ^{13}C NMR spectra of Va were measured on a 20% ^{13}CO-enriched sample in the presence of ~0.03 *M* $Cr(acac)_3$ using a Jeol PS-100-FT spectrophotometer. Mass spectra were recorded on a Hitachi Perkin-Elmer AMU-6 spectrometer (at 70 eV).

Spectroscopic data of the compounds V are reported in Table I.

Reaction of MeC_2Ph with $Ru_3(CO)_{12}$

A solution of $Ru_3(CO)_{12}$ (0.6 g) and the alkyne (0.15 ml) in n-hexane (250 ml) was heated at the reflux under N_2 for 3 h. Chromatography (t.l.c., SiO_2, eluent: light petroleum–diethyl ether 10:1) of the mixture after removal of the solvent gave, among other well known bi- and tri-nuclear derivatives [13], IVa and Va in 15% and 5% yields respectively.

Reaction of MeC_2Ph with $H_2Ru_4(CO)_{13}$

$H_2Ru_4(CO)_{13}$ was synthesized according to the recent high yield method reported by Shore *et al.* [14]. $H_2Ru_4(CO)_{13}$ (0.5 g) and the alkyne (0.15 ml) in n-heptane (200 ml) were refluxed under N_2 for 2 h. Similar work-up gave IVa (35%), Va (trace) and little amounts of $Ru_3(CO)_{12}$ and $Ru_3(CO)_8(MeC_2Ph)_2$, readily identified by IR and MS spectroscopy.

Reaction of $Ru_4(CO)_{12}(MeC_2Ph)$ (IVa) with Alkynes

In a typical run 100 mg of IVa was reacted with the appropriate alkyne (in 1:1.5 molar ratio) for 1 h in n-hexane at the reflux. The formation of type V compounds was almost quantitative.

TABLE II. Fractional Atomic Coordinates ($\times 10^4$) with E.s.d.'s in Parentheses for the Non Hydrogen Atoms.

	x/a	*y/b*	*z/c*
Ru1	768(1)	−1544(1)	3100(1)
Ru2	665(1)	1495(1)	3374(1)
O1	1170(5)	−3734(9)	2192(7)
O2	924(5)	−4110(9)	4266(6)
O3	2360(4)	−677(11)	4664(6)
O4	1033(5)	2665(11)	5152(6)
O5	2051(5)	3074(10)	3926(6)
O6	0	4427(11)	2500
C1	1052(6)	−2868(13)	2551(8)
C2	863(5)	−3171(11)	3816(8)
C3	1745(6)	−908(12)	4073(8)
C4	878(6)	2258(12)	4460(7)
C5	1535(6)	2456(13)	3719(7)
C6	0	3154(14)	2500
C7	−70(5)	−543(11)	1592(6)
C8	487(5)	488(10)	2186(6)
C9	980(5)	1065(10)	1942(7)
C10	898(6)	2522(12)	1623(8)
C11	1359(7)	3052(13)	1404(8)
C12	1908(7)	2175(15)	1483(9)
C13	2008(7)	707(17)	1822(9)
C14	1561(6)	189(12)	2075(8)
C15	−172(6)	−1003(12)	715(7)

Crystallographic Data Collection of $Ru_4(CO)_{11}(MeC_2Ph)_2$ (Va)

Deep-orange, air-stable crystals of Va were obtained by cooling at 0 °C a solution of Va in a n-heptane-chloroform 2:1 mixture.

A flattened crystal of dimensions *ca.* 0.07 × 0.20 × 0.23 mm was selected and used for the data collection. The cell parameters were obtained from a least-squares refinement of the θ values of 30 reflections accurately measured on a Siemens AED single crystal diffractometer. The crystal data are as follows: $C_{29}H_{16}O_{11}Ru_4$, $M = 944.72$, monoclinic, $a = 22.383(16)$, $b = 9.048(8)$, $c = 18.268(12)$ Å, $\beta = 127.25(4)°$; $V = 2945(4)$ Å^3, $Z = 4$, $D_{\text{calcd}} = 2.131$ g cm^{-3}, $F(000) = 1816$, $\mu(\text{MoK}\alpha) = 20.35$ cm^{-1}, space group *C2/c* from systematic absences and structure determination.

A complete set of intensity data was collected, with θ in the range 3–25°, on the same diffractometer using the Nb-filtered MoKα radiation and the $\theta/2\theta$ scan technique. Of a total of 2331 independent reflections, 1420 having $I \geqslant 2\sigma(I)$ were considered observed and used in the analysis. One reflection was re-measured after 40 reflections as a check on crystal and instrument stability; no significant change in the measured intensity of this reflection was observed during the data collection.

The structure amplitudes were obtained after the usual Lorentz and polarization reduction and the absolute scale was established by Wilson's method. No correction for absorption effects was applied in view of the low absorbance of the sample.

The structure was solved by the heavy-atom method starting from a three-dimensional Patterson map. The positions of all non-hydrogen atoms were revealed by the subsequent Fourier synthesis phased on the contributions of the Ru atoms. The refinement was carried out by least-squares full-matrix cycles using the SHELX system of computer programs [15] with first isotropic and then anisotropic thermal parameters for all non-hydrogen atoms. A difference Fourier map did not clearly reveal the positions of all the hydrogen atoms, so they were placed in their geometrically-calculated positions and included in the final structure factor calculations. The function minimized in the least-squares calculations was $\Sigma w|\Delta F|^2$; unit weights were used in the first cycles of refinement, the weight calculated as $w = 0.2675/[\sigma^2(F_o) + 0.00525F_o^2]$ was chosen in the final cycles. The atomic scattering factors (corrected for anomalous dispersion of Ru) were taken from the International Tables [16]. The final R and R_w values were 0.034 and 0.037 respectively (observed reflections only).

The atomic fractional coordinates for the non-hydrogen atoms and hydrogen atoms are given in Tables II and III respectively. Lists of thermal parameters and of the observed and calculated structure factors are available on request from the authors.

TABLE III. Calculated Coordinates ($\times 10^4$) for the Hydrogen Atoms.

	x/a	*y/b*	*z/c*
H10	477	3235	1547
H11	1288	4177	1166
H12	2248	2597	1292
H13	2424	−6	1885
H14	1665	−897	2376
H151	−622	−1798	341
H152	342	−1492	896
H153	−307	−43	289

Calculations were performed on the CYBER 7600 computer of the Centro di Calcolo Universitario dell' Italia Nord-Orientale, Bologna, with financial support from the University of Parma.

Results and Discussion

The thermal reaction of $Ru_3(CO)_{12}$ and MeC≡CPh has already been widely investigated and most of the products fully characterized [5]. No hydridic compound corresponding to an oxidative addition

TABLE IV. Bond Distances (Å) and Angles (°).

i) *In the coordination sphere of the ruthenium atoms*			
Ru(1)–Ru(2)	2.829(3)	Ru(1)–C(7^i)	2.155(13)
Ru(1)–Ru(1^i)	2.739(5)	Ru(2)–C(4)	1.869(11)
Ru(2)–Ru(2^i)	2.748(4)	Ru(2)–C(5)	1.860(14)
Ru(1)–C(1)	1.902(14)	Ru(2)–C(6)	2.035(10)
Ru(1)–C(2)	1.894(11)	Ru(2)–C(8)	2.157(10)
Ru(1)–C(3)	1.889(13)	Ru(2)–C(7^i)	2.297(12)
Ru(1)–C(7)	2.382(9)	Ru(2)–C(8^i)	2.309(12)
Ru(1)–C(8)	2.301(9)		
Ru(2)–Ru(1)–Ru(1^i)	86.8(1)	C(8)–Ru(1)–C(7^i)	86.0(4)
Ru(1)–Ru(2)–Ru(2^i)	86.6(1)	Ru(1)–Ru(2)–C(4)	123.4(3)
Ru(1^i)–Ru(1)–C(1)	103.7(4)	Ru(1)–Ru(2)–C(5)	109.5(4)
Ru(1^i)–Ru(1)–C(2)	96.6(4)	Ru(1)–Ru(2)–C(6)	132.6(2)
Ru(1^i)–Ru(1)–C(3)	158.5(4)	Ru(1)–Ru(2)–C(8)	52.9(2)
Ru(1^i)–Ru(1)–C(7)	49.2(3)	Ru(1)–Ru(2)–C(7^i)	48.3(3)
Ru(1^i)–Ru(1)–C(8)	76.1(3)	Ru(1)–Ru(2)–C(8^i)	74.2(3)
Ru(1^i)–Ru(1)–C(7^i)	56.8(3)	Ru(2^i)–Ru(2)–C(4)	129.4(4)
Ru(2)–Ru(1)–C(1)	142.6(4)	Ru(2^i)–Ru(2)–C(5)	124.7(3)
Ru(2)–Ru(1)–C(2)	128.4(4)	Ru(2^i)–Ru(2)–C(6)	47.5(3)
Ru(2)–Ru(1)–C(3)	73.1(4)	Ru(2^i)–Ru(2)–C(8)	54.6(3)
Ru(2)–Ru(1)–C(7)	75.1(2)	Ru(2^i)–Ru(2)–C(7^i)	78.1(2)
Ru(2)–Ru(1)–C(8)	48.4(2)	Ru(2^i)–Ru(2)–C(8^i)	49.6(2)
Ru(2)–Ru(1)–C(7^i)	52.8(3)	C(4)–Ru(2)–C(5)	85.7(6)
C(1)–Ru(1)–C(2)	86.6(5)	C(4)–Ru(2)–C(6)	99.0(4)
C(1)–Ru(1)–C(3)	97.0(6)	C(4)–Ru(2)–C(8)	175.5(5)
C(1)–Ru(1)–C(7)	84.9(5)	C(4)–Ru(2)–C(7^i)	92.7(5)
C(1)–Ru(1)–C(8)	98.8(5)	C(4)–Ru(2)–C(8^i)	96.6(5)
C(1)–Ru(1)–C(7^i)	158.3(5)	C(5)–Ru(2)–C(6)	92.3(4)
C(2)–Ru(1)–C(3)	90.3(5)	C(5)–Ru(2)–C(8)	93.2(5)
C(2)–Ru(1)–C(7)	140.8(5)	C(5)–Ru(2)–C(7^i)	150.6(5)
C(2)–Ru(1)–C(8)	171.7(6)	C(5)–Ru(2)–C(8^i)	173.7(4)
C(2)–Ru(1)–C(7^i)	86.7(5)	C(6)–Ru(2)–C(8)	85.4(3)
C(3)–Ru(1)–C(7)	128.7(5)	C(6)–Ru(1)–C(7^i)	116.9(3)
C(3)–Ru(1)–C(8)	95.3(4)	C(6)–Ru(2)–C(8^i)	81.6(3)
C(3)–Ru(1)–C(7^i)	103.6(5)	C(8)–Ru(2)–C(7^i)	86.1(4)
C(7)–Ru(1)–C(8)	34.8(4)	C(8)–Ru(2)–C(8^i)	84.9(4)
C(7)–Ru(1)–C(7^i)	87.4(4)	C(7^i)–Ru(2)–C(8^i)	35.4(4)
ii) *In the carbonyl groups*			
O(1)–C(1)	1.15(2)	O(4)–C(4)	1.15(1)
O(2)–C(2)	1.13(1)	O(5)–C(5)	1.12(2)
O(3)–C(3)	1.14(2)	O(6)–C(6)	1.15(2)
Ru(1)–C(1)–O(1)	174(1)	Ru(2)–C(5)–O(5)	178(1)
Ru(1)–C(2)–O(2)	178(1)	Ru(2)–C(6)–Ru(2^i)	84.9(5)
Ru(1)–C(3)–O(3)	173(1)	Ru(2)–C(6)–O(6)	137.5(3)
Ru(2)–C(4)–O(4)	176(1)		
iii) *In the organic ligand*			
C(7)–C(8)	1.40(1)	C(12)–C(13)	1.42(2)
C(8)–C(9)	1.51(2)	C(13)–C(14)	1.41(2)
C(9)–C(10)	1.41(1)	C(9)–C(14)	1.41(2)
C(10)–C(11)	1.40(2)	C(7)–C(15)	1.53(2)
C(11)–C(12)	1.39(2)		
Ru(1)–C(7)–Ru(1^i)	74.1(3)	Ru(2)–C(8)–Ru(2^i)	75.9(4)
Ru(1)–C(7)–Ru(2^i)	109.7(4)	Ru(2)–C(8)–C(7)	126.6(9)

(continued on facing page)

TABLE IV. *(continued)*

Ru(1)–C(7)–C(8)	69.4(5)	Ru(2)–C(8)–C(9)	115.3(6)
Ru(1)–C(7)–C(15)	128.4(8)	$Ru(2^i)$–C(8)–C(7)	71.8(7)
$Ru(1^i)$–C(7)–$Ru(2^i)$	78.8(4)	$Ru(2^i)$–C(8)–C(9)	123.5(6)
$Ru(1^i)$–C(7)–C(8)	121.6(8)	C(7)–C(8)–C(9)	118(1)
$Ru(1^i)$–C(7)–C(15)	119.1(8)	C(8)–C(9)–C(10)	121(1)
$Ru(2^i)$–C(7)–C(8)	72.8(6)	C(8)–C(9)–C(14)	121(1)
$Ru(2^i)$–C(7)–C(15)	121.6(7)	C(10)–C(9)–C(14)	118(1)
C(8)–C(7)–C(15)	119(1)	C(9)–C(10)–C(11)	120(1)
Ru(1)–C(8)–Ru(2)	78.7(3)	C(10)–C(11)–C(12)	122(1)
Ru(1)–C(8)–$Ru(2^i)$	112.2(5)	C(11)–C(12)–C(13)	118(2)
Ru(1)–C(8)–C(7)	75.8(6)	C(12)–C(13)–C(14)	120(2)
Ru(1)–C(8)–C(9)	124.2(7)	C(13)–C(14)–C(9)	121(1)

$^{i}-x, y, \frac{1}{2}-z$.

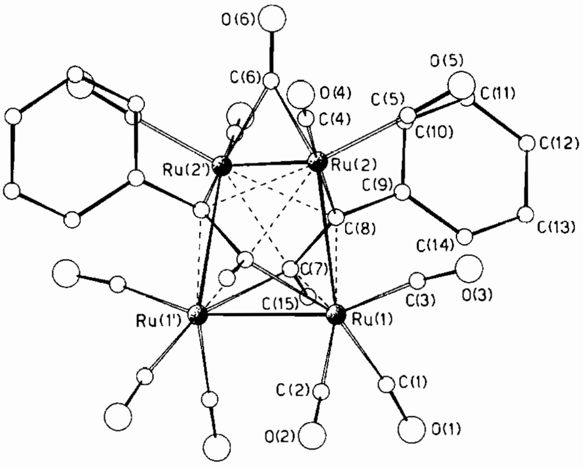


Fig. 1. View of the molecular shape of the complex $Ru_4(CO)_{11}(MeC_2Ph)_2$ with the atomic numbering scheme.

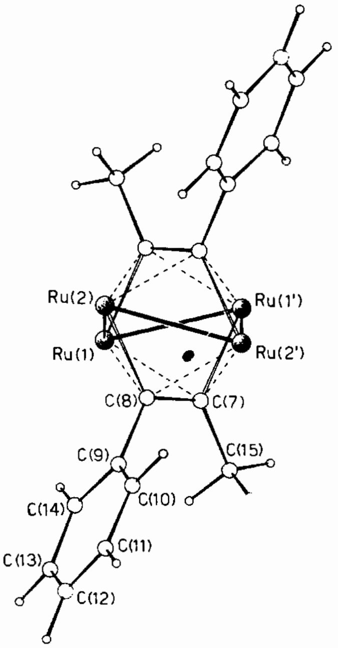


Fig. 2. View of the bonding of the alkyne ligands to the metal cluster with the dodecahedrally Ru_4C_4 core.

of the ligand to the triruthenium cluster has been observed, but two tetrametallic derivatives of formula $Ru_4(CO)_{12}(MeC_2Ph)$ (IVa) and $Ru_4(CO)_{11}(MeC_2Ph)_2$ (Va) have been obtained. Only IVa has been completely characterized as a μ_4-η^2 butterfly compound [12], whereas the structure of Va has remained undetermined.

In order to get a better understanding of the transformation leading to the formation of Va we have examined the reaction of IVa with different alkynes:

$$\underset{(IVa)}{Ru_4(CO)_{12}(MeC_2Ph)} + \text{Alkyne} \longrightarrow$$

$$\underset{(V)}{Ru_4(CO)_{11}(MeC_2Ph)(\text{Alkyne})} \qquad (1)$$

$$\text{Alkyne} = \left\{\begin{array}{ll} MeC_2Ph & Va \\ EtC_2Et & Vb \\ HC_2Bu^t & Vc \\ HC_2H & Vd \end{array}\right.$$

Neither TLC work-up nor V.T.N.M.R. investigations lead to the observation of isomeric forms for any complex V whatever substituted alkyne were used: this observation ruled out the structure previously suggested for these molecules [5]. Furthermore the weak absorption in the μ_2-bridging CO region and the equivalence on the N.M.R. time scale of the two alkyne molecules in Va, as well the high field shift of the acetylenic hydrogens in Vc and Vd, suggest a marked change in the metallic frame.

A X-ray analysis of Va was undertaken to assess the molecular structure for these compounds.

The structure of the complex $Ru_4(CO)_{11}(MeC_2Ph)_2$ is represented in Fig. 1 with the atomic numbering scheme. Bond distances and angles are given in Table IV.

The complex, having an imposed crystallographic C_2 symmetry, is characterized by a tetranuclear cluster of Ru atoms coordinated by eleven carbonyls and by two σ- and π-bonded alkyne ligands. Ten carbonyls, three on Ru(1) and Ru(1^i), two on Ru(2) and Ru(2^i), are terminal (as shown by the Ru–C–O angles ranging from 173 to 178°) and one symmetrically bridges the Ru(2)–Ru(2^i) edge [Ru(2)–C(6) = 2.035–(10) Å and Ru(2)–C(6)–O(6) = 137.5(3)°] (i denotes the equivalent related by the two-fold axis position $-x, y, \frac{1}{2} - z$).

The cluster presents a slightly tetrahedrally-distorted square arrangement of metal atoms, Ru(1), Ru(2), Ru(2^i) and Ru(1^i) being 0.33, –0.33, 0.33 and –0.33 Å out of the mean plane passing through them. Two opposite edges of the cluster are longer than the other two [Ru(1)–Ru(2) and Ru(1^i)–Ru(2^i) = 2.829(3) Å, Ru(1)–Ru(1^i) and Ru(2)–Ru(2^i) = 2.739(5) and 2.748(4) Å respectively]. Each of the two alkyne ligands, on opposite sides with respect to the cluster, is σ or π bonded to all the four metal atoms. Two σ-bonds [2.155–2.157 Å] are formed between the acetylenic carbons of each ligand and two Ru atoms on opposite vertices of the cluster; two other π bonds (2.297–2.382 Å) are formed between the same carbons and the other two Ru atoms. The acetylenic bonds being the alkyne ligands bonded to the cluster on the diagonals, are almost perpendicular. The bonding of the alkyne ligands to the cluster is represented in Fig. 2.

The substituted cluster has a Ru_4C_4 core in which the metal and the carbon atoms occupy the vertices of a triangular dodecahedron. This dodecahedron can be envisaged as being the result of the fusion of two distorted tetrahedra, the former (C_4 core) elongated, the latter (Ru_4 core) flattened.

The structure of the present complex Va is very similar to that already found for the isoelectronic complex $Fe_4(CO)_{11}(HC_2Et)_2$ obtained in very low yield (<1%) in the reaction between $Fe_3(CO)_{12}$ and HC≡CEt, among a number of products [17]. The clear observation that type-V compounds are formed from butterfly-complexes IV (as shown in eqn. 1) leads us to suggest that compounds of type-IV are also formed in the reactions of iron carbonyls, although no example has yet been reported.

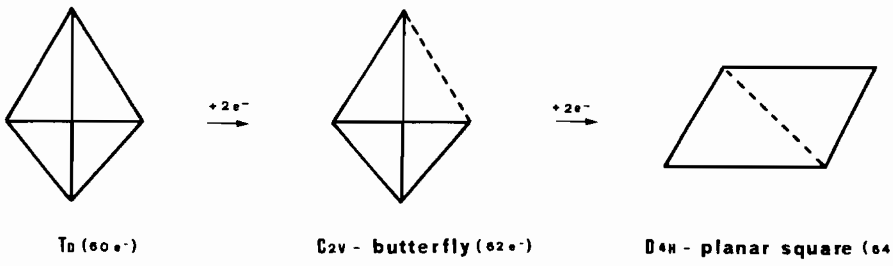
An improved yield of *quasi*-planar type V compounds can be obtained through the following reactions:

$$H_2Ru_4(CO)_{13} + MeC_2Ph \xrightarrow[-H_2,-CO]{} Ru_4(CO)_{12}(MeC_2Ph) + \text{Alkyne} \xrightarrow[-CO]{} Ru_4(CO)_{11}(MeC_2Ph)(\text{Alkyne}) \qquad (2)$$

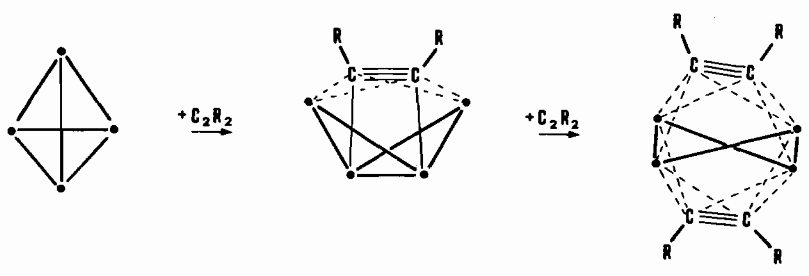
The first stage parallels completely the findings of Geoffroy *et al.* [18] for the reactions of alkynes with the mixed metal cluster $H_2FeRu_3(CO)_{13}$, but the further isolation of type-V compound as depicted in eqn. 2 allows us to draw a complete intrametallic rearrangement process on going from T_d to D_{4h} planar-square tetrametallic clusters.

According to the EAN formalism the number of electrons associated to T_c, C_{2v} and D_{4h} structures would be 60, 62 and 64 respectively, but the alkyne cluster complexes, IV and V, considered in this work both appear to be 2 electrons short if the μ_4–η^2 both appear to be 2 electrons short if the μ_4-η^2 acetylenes are (reasonably) regarded as formal 4e$^-$ donors (Scheme 2).

In a related system, the planar-square $Fe_4(CO)_{11}(PR)_2$, the unsaturated nature of the metallic frame (62e$^-$) has been verified by the easy formation of 1:1 adducts with a variety of Lewis base [19]. In our case neither PPh_3 nor CO gave rise to adducts when reacted with Va at room temperature. A stoichiometric hydrogenation test was also performed with Vd, but no gc-detectable hydrogenation products (ethylene or ethane) were observed at 60 °C after 2 days [Va = 0.025 *M*, P_{H_2} = 760 torr]. It follows



Scheme 2. Relationship between tetrametallic clusters in the EAN formalism.



nido-**trigonal bipyramid** (S = 6, n = 4)

closo-**octahedron** (S = 7, n = 6)

closo-**dodecahedron** (S = 9, n = 8)

Scheme 3. Relationship between tetrametallic clusters in the PSEP theory (S = skeletal electron pairs; n = skeletal atoms).

that, as already found for similar derivatives [20], a description in terms of two centre–two electron bonds results inadequate for clusters containing acetylenic moieties interacting with several metallic atoms. A better approach to the cluster opening process can be obtained on the basis of the Polyhedral Skeleton Electron Pair Theory (PSEPT) developed by Wade and Mingos [21]. Using the concept of isobal analogy between metal carbonyl fragments and main group elements, the further substitution of external CO's with acetylenic moieties corresponds to the insertion of 'CR' units into the growing polyhedra. Thus the following (idealized) structures are predicted (Scheme 3).

The incoming molecule of alkyne causes a flattening of the butterfly framework (IV) and a marked elongation of the hinge Ru–Ru bond: thus the metallic array turns into a *quasi*-square planar system (V). This transformation is clearly related to the work recently reported by Carty and co-workers [22], who showed that the flattening of the Ru_4 butterfly in a series of tetrametallic clusters is related to the ligand donation to the metallic core.

Dynamic Behaviour

The intramolecular CO exchange mechanisms have been widely investigated in the past decade and it has been shown that several processes can occur on the surface of a trimetallic cluster leading to the internuclear exchange of the ligands [23]. Since no example involving planar-square tetrametallic moieties has yet been reported, we thought it worthwhile to explore the dynamic behaviour of this system. The C-13 N.M.R. spectra of a ^{13}CO-enriched (~30%) sample of Va were then recorded at different temperatures. The spectrum at +21 °C shows only a single resonance (at 200.4 ppm), indicating that all the eleven CO ligands are equivalent on the N.M.R. time scale; as the temperature is decreased this resonance broadens, collapses (at –80 °C) and finally splits into two broad resonances, at 203.4 and 194.5 ppm respectively, in the relative intensity ratio of 7:4. Attempts to get spectra at lower temperature were unsuccessful owing to the very limited solubility of this compound in freon/CD_2Cl_2 mixtures at temperatures below –100 °C. The observed behaviour can be accounted for by a rapid 'merry-go-round' process over the edges of the square cluster involving bridging and radial carbonyls coupled, at higher temperatures, with a localized exchange process at each ruthenium centre among radial and axial CO's.

The high fluxionality of this compound is remarkable and it is likely that the intramolecular CO exchange is accompanied by a cyclic rotation of the alkyne molecules which makes all four ruthenium atoms equivalent on the N.M.R. time scale.

References

1 B. F. G. Johnson and J. Lewis, *Adv. Inorg. Chem. Radiochem., 24,* 225 (1981).
2 (a) E. Sappa, O. Gambino, L. Milone and G. Cetini, *J. Organomet. Chem., 39,* 169 (1972).
(b) M. Catti, G. Gervasio and S. A. Mason, *J. Chem. Soc. Dalton Trans.,* 2260 (1970).
3 S. Aime, L. Milone, D. Osella and M. Valle, *J. Chem. Research,* (S) 77 (1978), (M) 0785–0797 (1978).
4 (a) E. Evans, M. Hursthouse, E. W. Randall, E. Rosenberg, L. Milone and M. Valle, *J. Chem. Soc. Chem. Comm.,* 545 (1972).
(b) G. Gervasio, D. Osella and M. Valle, *Inorg. Chem., 15,* 1221 (1976).
5 B. F. G. Johnson, J. Lewis and K. T. Schorpp, *J. Organomet. Chem., 91,* C13 (1975).
6 E. L. Muetterties, T. N. Rhodin, E. Band, C. F. Brucker and W. R. Pretzer, *Chem. Rev., 79,* 91 (1979).
7 S. Ermer, R. Karpelus, S. Miura, E. Rosenberg, A. Tiripicchio and A. M. Manotti Lanfredi, *J. Organomet. Chem., 187,* 81 (1980).
8 S. Aime, D. Osella, A. J. Deeming, A. M. Manotti Lanfredi and A. Tiripicchio, *J. Organomet. Chem., 224,* C47 (1983).
9 S. Aime, G. Jannon, D. Osella and A. J. Deeming, *J. Organomet. Chem., 114,* C15 (1981).
10 (a) S. Aime, L. Milone and A. J. Deeming, *J. Chem. Soc. Chem. Comm.,* 1168 (1980).
(b) S. Aime, A. Tiripicchio, M. Tiripicchio Camellini and A. J. Deeming, *Inorg. Chem., 20,* 2027 (1981).

11 S. Aime, D. Osella, A. J. Arce, A. J. Deeming, M. B. Hursthouse and A. M. R. Gales, *J. Chem. Soc. Dalton Trans.*, in press.

12 B. F. G. Johnson, J. Lewis, R. E. Reichert, K. T. Schorpp and G. M. Sheldrick, *J. Chem. Soc. Dalton Trans.*, 1417 (1977).

13 O. Gambino, E. Sappa and G. Cetini, *J. Organomet. Chem.*, *44*, 18 (1972).

14 C. C. Nagel and S. G. Shore, *J. Chem. Soc. Chem. Comm.*, 530 (1980).

15 G. M. Sheldrick, System of Computing Programs, University of Cambridge, England, 1976.

16 International Tables for X-Ray Crystallography, Vol. IV, Kynoch Press, Birmingham, England, 1974.

17 E. Sappa, A. Tiripicchio and M. Tiripicchio Camellini, *J. Chem. Soc. Dalton Trans.*, 419 (1978).

18 J. R. Fox, W. L. Gladfelter, G. L. Geoffroy, I. Tavanaiepour, S. Abdel Mequid and V. W. Day, *Inorg. Chem.*, *20*, 3230 (1981).

19 H. Vahrenkamp and D. Woelters, *Organometallics*, *1*, 874 (1982).

20 (a) L. F. Dahl and D. L. Smith, *J. Am. Chem. Soc.*, *84*, 2450 (1962);
(b) J. F. Blount, L. F. Dahl, C. Hoogzand and W. Hubel, *ibid.*, *88*, 292 (1966).

21 (a) K. Wade, *Adv. Inorg. Chem. Radiochem.*, *18*, 1 (1976).
(b) D. M. Mingos, *Nature (London) Phys. Sci.*, *236*, 99 (1972).

22 A. J. Carty, S. A. MacLaughlin, J. Van Wagner and N. J. Taylor, *Organometallics*, *1*, 1013 (1982).

23 F. A. Cotton and R. E. Hanson, in 'Rearrangements in Ground and Excited State', Academic Press, New York, 1980, vol. 2, p. 379.