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"OLEFIN METATHESIS" REACTIONS OF $(\eta^5\text{-}C_5H_5)NiRu_3(\mu\text{-}H)(CO)_9\text{-}(\mu_4\text{-}\eta^2)\text{-}(C{=}CHBu^t)$ AND RELATED COMPLEXES

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Summary

The complex $(\eta^5\text{-}C_5H_5)NiRu_3(\mu\text{-}H)(CO)_9(\mu_4\text{-}\eta^2\text{-}C{=}CHBu^t)$ (**1a**) reacts with olefins to give several organic products, including species derived from the coupling of the vinylidene ligand with an olefin-derived =CRR′ fragment, representing the first example of a (non catalytic) olefin metathesis reaction involving a metal cluster; other complexes structurally or chemically related to the compound **1a** have also been treated with olefins and alkynes.

Introduction

We have synthesized and characterized the heterometallic butterfly derivatives $(\eta^5\text{-}C_5H_5)NiM_3(\mu\text{-}H)(CO)_9(\mu_4\text{-}\eta^2\text{-}C{=}CHR)$ (**1a**: M = Ru, R = Bu^t [1]; **1b**: R = Pr^i [2]; **1c**: M = Os, R = Bu^t [3]), which are intermediates in the alkyne hydrogenation in the presence of clusters [3–5]. The structures of complexes **1**, obtained by "expansion" of $HM_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_2R)$ (complexes **2**) [6] and by other routes [3] may be compared with those of the butterfly iron clusters investigated as "models" for the homogeneous catalysis of the Fischer–Tropsch (FT) reactions [7]. The cluster shapes of **1**, **2** and of these iron clusters are shown in Fig. 1.

In all the above iron clusters, except for $[Fe_4(CO)_{12}C\text{-}C({=}O)(OCH_3)]$ [8], only C_1 ligands were involved. In complexes **1** a C_2 ligand is present; this may be formally considered as derived from the reaction of a carbocationic heterometallic "peripheral" carbide with a methylene (or carbene) unit, and may hence represent a potential step of chain growth in the FT reaction in the presence of heterometallic clusters. Unfortunately we could not obtain the suggested heterometallic carbides, but indirect evidence for the validity of the hypothesis could be the reaction of **1** with ethylenes to give "olefin metathesis" reactions.

We describe below the reactions of **1** with olefins and some alkynes, for which the organic and organometallic products were investigated. The reactivity of other structurally or chemically related ruthenium and iron complexes are also considered. To our knowledge the results provide the first report of the activity of metal clusters in metathesis reactions, although the processes we describe are not catalytic.

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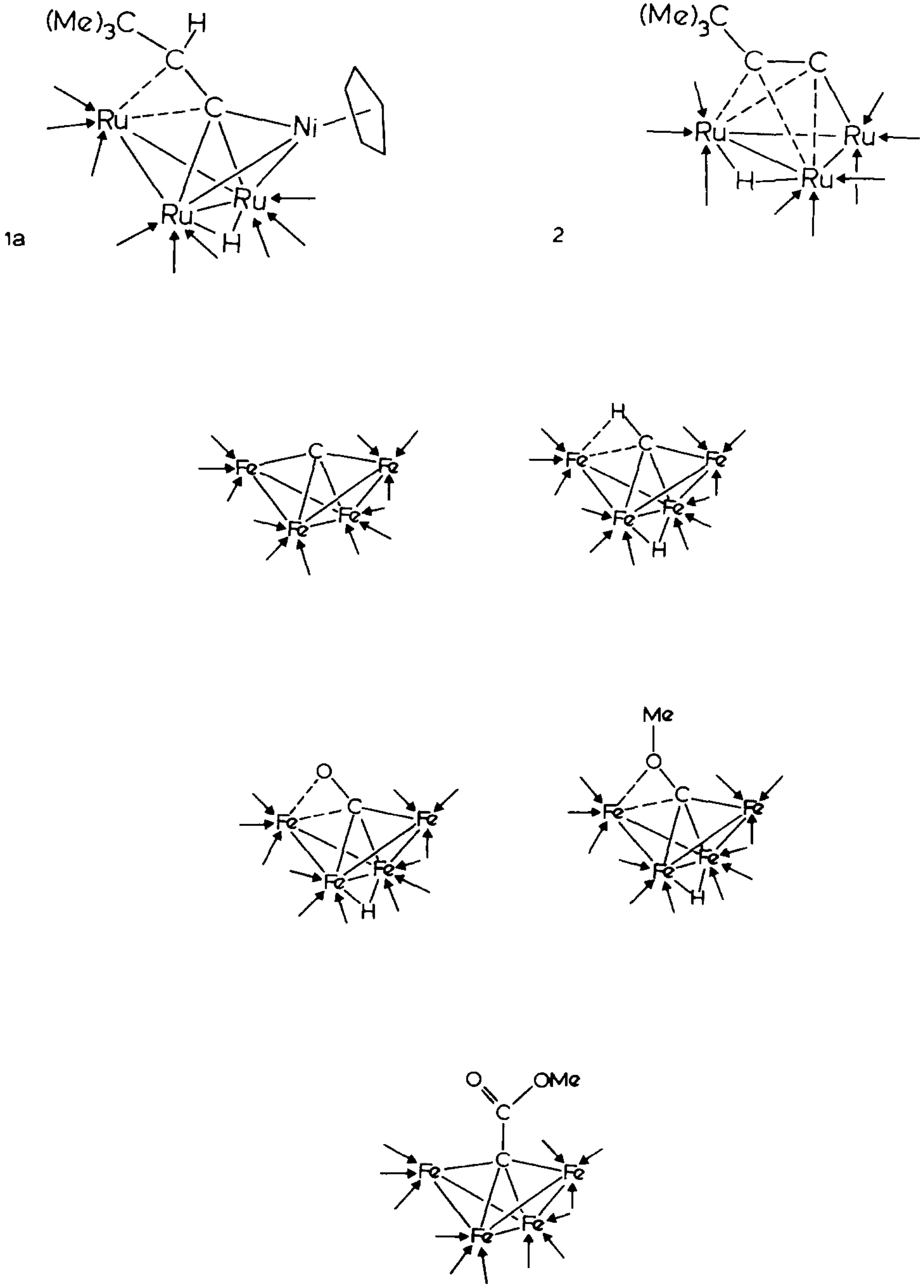

Fig. 1. Schematic structures of complexes **1a**, **2** and of some iron derivatives relevant to homogeneous FT catalysis.

Experimental

Complexes **1** and **2** were made and crystallized as previously reported [1–3,6]. The hydrocarbon solvents were distilled over sodium and kept on molecular sieves. The olefins (and acetylenes) were commercial products used without further purification; ultra-pure grade ethylene was purchased by SIAD, C_2D_4 from Merck, Sharp & Dohme; the other alkenes and the alkynes were from Fluka. The purity of the compounds was checked by ^1H NMR spectroscopy. Dry nitrogen was bubbled into the solvents before the metathesis runs.

The organic products from the reaction solution * were analyzed with a Carlo Erba 4200 F.I.D. gas-liquid chromatograph fitted with capillary columns and coupled with a Kratos MS-50 mass spectrometer **. A Carlo Erba 4200 F.I.D. gas-liquid chromatograph was also used with 2.5 m × 6 mm Chromosorb 105 (60–80 mesh) columns, N_2 flow 10 ml in 6 sec.; T 70 °C for 5 min, then 9 °C/min up to 200 °C.

The organometallic products were separated by TLC and identified by IR (Perkin–Elmer 580B instrument) and ^1H NMR (JEOL C60 HL instrument) spectroscopy; the identification of some products was confirmed by mass spectrometry (Hitachi–Perkin–Elmer RMU 6H single focusing instrument, with a direct inlet system and operating at 70 eV).

Olefin metathesis in the presence of 1 and 2

The reactions of **1a** and **2** in the presence of olefins were performed in glass vials, sealed under vacuum (50 ml of 1 mM solution of the complex and a 10 to 1 excess of liquid olefins; for the gaseous olefins see Table 1). The vials were then kept in a thermostattic oven at 80–120 °C for several hours.

The reactions of C_2D_4 were carried out in rubber-septum glass vials, with sampling of either the gas phase and/or the solution: in order to minimize the loss of gas, the reaction temperatures used were in the range 60–70 °C.

Details of the reaction conditions and the organic and organometallic products detected are shown in Table 1 (see below).

Other reactions. Reactions of 1a with alkynes and alkenes

Treatment of **1a** with excess HC_2Bu^t in refluxing heptane for 6 h leads to an oily mixture of several products not separable on the TLC plates. The IR spectra indicate the absence of any signal due to bridging carbonyls. The same happens when **1a** is treated under closely comparable conditions with $H_2C{=}CHBu^t$.

Treatment of **1a** with excess C_2Ph_2 in refluxing heptane for 90 min gives some unchanged **1a** and not less than six bands on the TLC plates; one of these yields an oily mixture of at least two products, showing strong IR absorptions at 1870 and 1835 cm^{-1}. These values differ from the signals at 1878 and 1859 cm^{-1} due to $Ru_3(CO)_8(HC_2Bu^t)_3$ [9], and are presumably due to an open triruthenium cluster of the same structure, but containing both the alkynes in the metalla-cyclic ring.

On the other hand, treatment of $Ru_4(CO)_{12}(C_2Ph_2)$ [10] with HC_2Bu^t in comparable conditions resulted in several fractions on the TLC plates; one of them yielded material showing IR signals at 1882 and 1861 cm^{-1}, and hence probably containing $Ru_3(CO)_8(C_2Ph_2)_2$ [11].

Reaction of $HRu_3(CO)_9$ (EtCCHCMe) [12] (complex 3) with trans-stilbene

Treatment of **3** in sealed vials with an excess of *trans*-stilbene under vacuum for 3

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* The gas phase was analyzed only when C_2D_4 was used.

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h at 120 °C leads to several oligomerization products and, in addition to unreacted, hydrogenated, and dehydrogenated stilbene, to small amounts of PhCH=CHEt, PhCH=CHMe. The TLC plates showed the presence of organometallic products different from the parent complex; none of these seemed to contain carbonyl bridges. The parent ruthenium complex has been shown, however, to react with alkynes to give metallacyclic tri- and bi-metallic derivatives [13,22].

Synthesis, thermal decomposition and reactions with alkynes and alkenes, of some ruthenium and iron metallacyclopentadienic complexes

Unless otherwise specified, these reactions were performed under the same conditions as described for those of **1a** and **2**.

*Reactions of $Ru_3(CO)_8(C_2Ph_2)_2$ (complex **4a**)*

(i) With HC_2Bu^t. After 15 h at 120 °C, the main organic products observed were: t-butylalkyne, alkyne oligomerization products (2–4 units); t-butylalkyne oligomerization-dehydrogenation products (2–4 units); cluster decomposition products, C_2Ph_2 and $(C_2Ph_2)_2$ and, finally, "metathesis products", HC≡CPh, H_2C=CHPh (and their dimers), $Bu^tC{\equiv}CBu^t$, $[(HC_2Bu^t)(C_2Ph_2)]$.

(ii) With $H_2C{=}CHBu^t$. After 15 h at 120 °C only products of dehydrogenation to t-butylalkyne, dimerization of the alkene, and formation of stilbene (hydrogenation of C_2Ph_2) were observed and no metathesis products could be detected. Some of the cluster was recovered unaltered.

Synthesis and reactions of $Fe_3(CO)_8(C_2Et_2)_2$ and $Fe_3(CO)_8(C_2Et_2)(C_2Ph_2)$

*Complexes **4b**, **4c**.* Complex **4b** was made by established methods [14]; **4c** was prepared by treating $Fe_3(CO)_9(C_2Et_2)$ with an excess of C_2Ph_2 in refluxing heptane, under N_2, for 40 min; several complexes were formed including about 30% of the dark-green **4c** (mass spectrometry; IR ν(CO) (heptane solution) 2059s, 2020s(sh), 2014vs, 1998s, 1974s, 1885m-s, 1855m-s cm^{-1}).

Treatment of **4b** with HC_2Bu^t gives many organic products derived from the oligomerization and co-oligomerization of the two ligands, sometimes with hydrogenation or dehydrogenation; however, comparison with the products obtained by simple thermal decompositon of **4b** shows the presence of small amounts of metathesis products, such as $EtHC{=}CHBu^t$; treatment with C_2Ph_2 gives some EtC_2Ph and H(Et)C=CHPh. Thermal decomposition of **4c** gives considerable amounts of EtC_2Ph and (Et)HC=CHPh, together with oligo- and co-oligomerization products.

Synthesis and reactions of $Fe_2(CO)_6(C_2Ph_2)_2$ and $Fe_2(CO)_6(C_2Ph_2)(C_2Et_2)$

*Complexes **5a**, **5b**.* Complex **5a** was obtained by established methods [11]; **5b** was obtained together with **4c** and identified by mass spectrometry and IR (ν(CO), heptane solution, 2062m, 2025vs, 1991vs(b) cm^{-1}). No metathesis products could be identified among the many organic derivatives obtained upon treatment of **5a** with HC_2Bu^t and C_2Ph_2 or with the corresponding alkenes (compared with the thermal decomposition products of **5a**). In contrast thermal treatment of **5b** gives good amounts of EtC_2Ph and (Et)HC=CHPh together with other products.

Results and discussion

*"Metathesis" reactions in the presence of **1a** and **2***

The results of these reactions are reported in Table 1.

The reactions of **1a** with ethylenes (t-butyl-ethylene, 3-hexene, 4-octene, ethylene and C_2D_4) afford complex mixtures of organic products, including oligomerization products (with or without dehydrogenation), products derived from C–C bond cleavage and hydrogenolysis, and "metathesis" products (coupling of $=CHBu^t$ with $=CRR'$). Only cyclohexene gives no metathesis products, and this behaviour is that generally observed in the "true" metathesis reactions. Products deriving from the coupling of the whole vinylidene $C=CHBu^t$ of **1a** with ethylenes are absent, or formed only in trace amounts; small amounts of products obtained from the coupling of the vinylidene with $=CRR'$ (in particular CH_2) to give "allyls" are also observed.

The "metathesis" character of the reactions described (and the role of **1a**) are also indicated by the absence of metathesis products upon simple thermal decomposition of **1a** in the presence or absence of metal powder. Metal powder alone was also found to be ineffective.

As further evidence, C_2D_4 gives deuterated metathesis products, as shown by the appearance in the GLC/MS system, of compounds with parent ions 2 *m/e* heavier than those observed for ethylene; in the gas phase, products (difficult to separate) derived from H/D exchange, are also formed.

The reactivity of complex **2** has also been investigated because in the mass spectrometer [1–2] and in the presence of hydrogen [5], complex **1a** readily gives **2**. Indeed, in the presence of **2** olefin metathesis also occurs (see below).

These results are not in conflict with the recent report by Schrock of the difficulties found in the metathesis of terminal alkynes [15]; the cluster-bound ligands giving metathesis are a vinylidene (**1a**) and an acetylide (**2**). When HC_2Bu^t reacts with **4** the main organic products were those derived from oligomerization with or without dehydrogenation.

From the above experimental evidence, two important points emerge: (a) Complexes **1a** and **2** form (among others) carbene fragments and (with greater difficulty) release the vinylidene or acetylide; (b) The generation of carbene fragments may provide potential uses for **1a** and **2**. It is noteworthy that Ru and Ni are generally ineffective in metathesis.

Some comments on the reactivity of complexes 3, 4, 5

Olefin and acetylene metathesis mechanisms involving one metal centre have been proposed for olefins [16] and for alkynes [17,18]; in this latter case, carbyne complexes are reported as catalysts. The above mechanisms, together with those suggested for reactions involving two metal centres [19] are schematically represented in Scheme 1.

For metathesis on clusters, metallacyclobutadiene, metalloallyl or (less probably) metallacyclopentadiene intermediates would be expected. We could not find any evidence for the presence of metallacyclobutadiene derivatives in the reactions studied.

Allylic intermediates would be more probable; indeed, structures **1** may decompose into **2** which, in the presence of H_2 (formed upon partial dehydrogenation of

(Continued on p. 126)

TABLE 1

ORGANIC AND ORGANOMETALLIC PRODUCTS FROM THE REACTIONS OF **1a** AND **2** WITH OLEFINS

Reaction conditions: (A) heptane, 15 h, 120 °C; (B) heptane, 24 h, 100 °C; (C) toluene, 24 h, 100 °C, 1 atm C_2H_4; (D) toluene, 24 h, 70 °C, 0.6 atm C_2D_4.

Reactant	Reaction conditions	Organic products [a]										Organometallic products
		C_4	C_5	C_6	C_7	C_8	C_{11}	C_{10}	C_{11}	C_{12}	C_{12}	
Complex **1a**												
–	(A)				C_7H_{14}				$C_{11}H_{16}$ [b]	$C_{12}H_{16}$ [c]		Complex **2** $Ru_3(CO)_8(HC_2Bu^t)_3$
NiRu powder	(A)		C_5H_6 [d]		C_7H_{14}					$C_{12}H_{16}$		
NiRu powder $H_2C{=}CHBu^t$	(A)		C_5H_6 [d]	C_6H_{12} [e]	C_7H_{14}	C_8H_{16}			$C_{11}H_{16}$ [b]	$C_{12}H_{16}$ $C_{12}H_{24}$	$C_{18}H_{36}$ [e]	
3-Hexene	(B)	C_4H_8	C_5H_{10} C_5H_8 C_5H_6	C_6H_{10} C_6H_{12} [e]	C_7H_{12} C_7H_{14} C_7H_{10}	C_8H_{16} C_8H_{18}		$C_{10}H_{20}$		$C_{12}H_{16}$		Complex **2**
Cyclohexene	(B)			C_6H_{12} [e,f] C_6H_{14}							$C_{15}H_{24}$	Complex **1** Complex **2**

4-Octene	(B)		$\mathrm{C_5H_6}$ [d]	$\mathrm{C_6H_{10}}$ $\mathrm{C_6H_{12}}$	$\mathrm{C_7H_{14}}$	$\mathit{C_8H_{16}}$ [g]	$\mathit{C_9H_{18}}$	$\mathit{C_{10}H_{20}}$	$\mathrm{C_{11}H_{18}}$	$\mathrm{C_{12}H_{22}}$	$\mathrm{C_{16}H_{24}}$	Complex **1** Complex **2**
Ethylene	(C)	$\mathrm{C_4H_8}$ $\mathrm{C_4H_{10}}$	$\mathrm{C_5H_6}$ [d] $\mathrm{C_5H_{10}}$	$\mathit{C_6H_8}$ $\mathit{C_6H_{10}}$				$\mathit{C_{10}H_{20}}$				not investigated
$\mathrm{C_2D_4}$ (0.6 atm)	(D)	$\mathrm{C_4H_8}$		$\mathit{C_6H_8D_2}$ [h] $\mathit{C_6H_{10}D_2}$ $\mathrm{C_6H_{10}}$ $\mathrm{C_6H_{12}}$	$\mathrm{C_7H_{12}}$	$\mathit{C_8H_{16}}$ $\mathrm{C_8H_{18}}$		$\mathit{C_{10}H_{20}}$				not investigated
Complex **2**												
3-Hexene	(A)	$\mathrm{C_4H_8}$	$\mathrm{C_5H_6}$ [d]	$\mathrm{C_6H_{12}}$	$\mathrm{C_7H_{12}}$	$\mathit{C_8H_{16}}$ $\mathit{C_8H_{18}}$		$\mathit{C_{10}H_{20}}$				Complex **2** $\mathrm{H_3Ru_3(CO)_9CCH_2Bu^t}$
Ethylene	(C)	$\mathrm{C_4H_8}$ $\mathrm{C_4H_{10}}$		$\mathit{C_6H_8}$ $\mathrm{C_6H_{12}}$	$\mathrm{C_7H_{12}}$	$\mathrm{C_8H_{10}}$		$\mathit{C_{10}H_{20}}$				Complex **2**
$\mathrm{C_2D_4}$	(D)	$\mathrm{C_4H_8}$		$\mathit{C_6H_8D_2}$ $\mathit{C_6H_{10}D_2}$ $\mathrm{C_6H_{10}}$	$\mathrm{C_7H_{12}}$ $\mathrm{C_7H_{14}}$	$\mathit{C_8H_{18}}$ $\mathit{C_8H_{16}}$		$\mathrm{C_{10}H_{20}}$				Complex **2**

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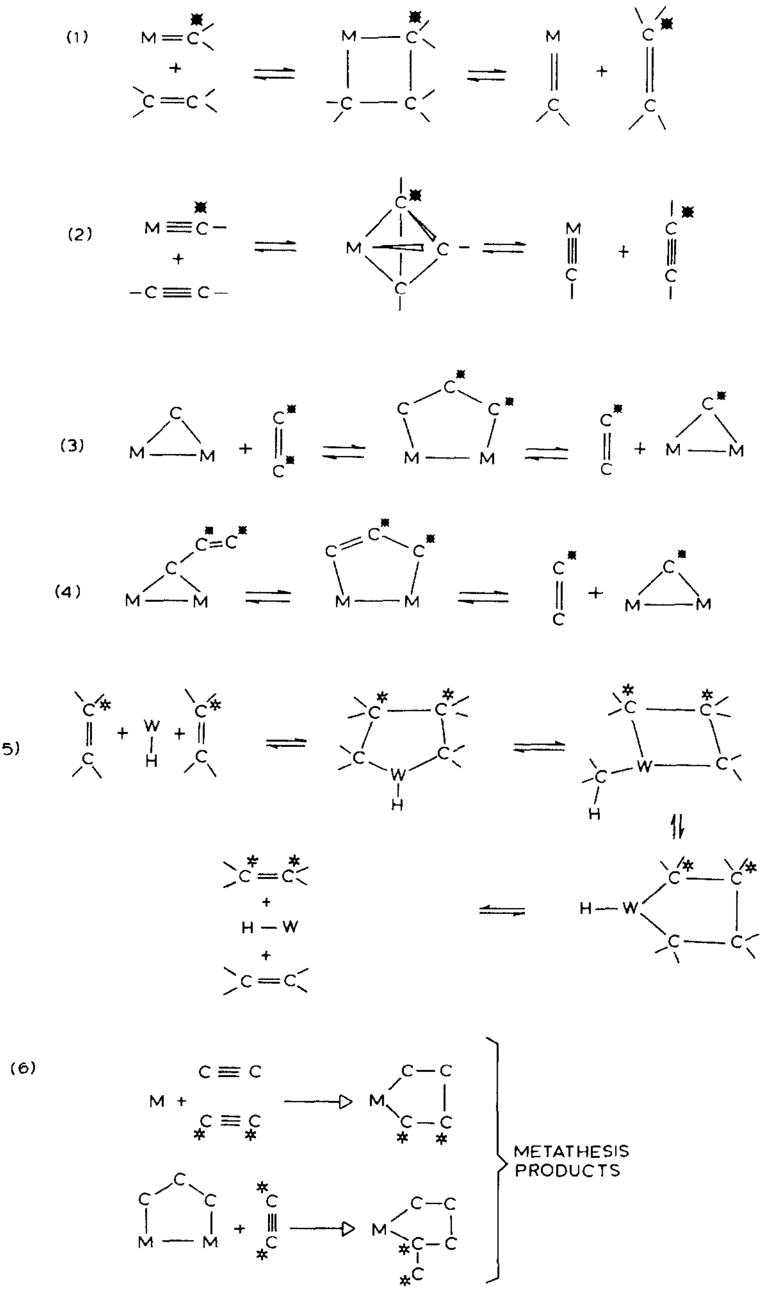
[a] Solvent not included. The products typical of "metathesis" are in italic type. Products C_{10} not mentioned if not necessary. [b] Coupling (Cp)–t-butyl-vinyl. [c] Coupling t-butylvinyl–t-butylvinyl. [d] Cyclopentadiene. [e] 3-Hexane. [f] Two peaks at the GLC/MS; t-butylethylene and cyclohexene. [g] Two peaks at the GLC/MS; *cis*- and *trans*-$\mathrm{Bu^tHC{=}CHBu^t}$. [h] Other partly deuterated species (H/D exchange) in small amount are detected; not reported here.

SCHEME 1. Proposed mechanisms for olefin and acetylene metathesis on one or two metal centres. Eq. 1, ref. 16; eq. 2 ref. 18: eq. 3, 4 ref. 19; eq. 5 ref. 24; eq. 6 alternative possibilities considered in this work.



the ligands) may afford $H_3Ru_3(CO)_9CCH_2Bu^t$ [20]. Keister has recently shown that complexes $H_3Ru_3(CO)_9CR$ can react reversibly with alkynes and H_2 to give the $HRu_3(CO)_9(RCCR'CR'')$ "allylic" clusters [21].

We found some allylic products formed by the coupling of the vinylidene ligand on **1** with CRR′ olefin fragments (see above). Moreover, complex **3** gives metathesis products in the presence of *trans*-stilbene.

With reference to the presence of metallacyclopentadiene intermediates, it should be remembered that complexes such as **3** have been shown to react further with alkenes and alkynes [13,22] to give metallacyclopentadienic tri- and bi-nuclear derivatives. Thus, the formation of metathesis products via metallacyclopentadienes cannot be completely ruled out, especially when one considers that we observed small amounts of ruthenium homologues of complexes **4** and **5** in the reaction mixtures of **1** and **2**, and that complex **4a** undergoes olefin metathesis.

A metallacyclopentane intermediate has been suggested by Grubbs [23] and by Rudler [24] for tungsten-catalyzed olefin metathesis reactions (see Scheme 1). Surprisingly, however, the well known derivatives **4** and **5** [14,22] had not yet been tested as possible intermediates in metathesis reactions. We observed that upon simple thermal treatment complexes **4** and **5**, with rings formed by two different alkynes, give metathesis products in stoichiometric amounts *. Our results also show that, in the reactions of complexes **4** and **5** with alkynes and alkenes, metathesis products are formed only in the case of alkynes.

Although the presence of several decomposition and side products prevents firm conclusions about the reaction mechanisms, the results suggest that the "allylic" route is more probable for olefin metathesis and the metallacyclopentadiene route for the alkyne metathesis on clusters.

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* All the reactions reported are stoichiometric, so that the overall yields of organic products, and in particular of metathesis products are dependent on the amount of metal-bound ligands, and hence on the concentration of the complex in solution.

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