Journal of Organometallic Chemistry, 91 (1975) C13-C16

Preliminary communication

DERIVATIVES OF THE *closo*-Ru_4C_2 CLUSTER

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(Received March 3rd, 1975)

Summary

The reaction of $Ru_3(CO)_{12}$ with RC≡CR′ yields *closo*-$Ru_4(CO)_{12}$ (RC≡CR′), which reacts with additional alkyne, PhC≡CR″, to yield $Ru_4(CO)_{11}$(RC≡CR′)(PhC≡CR″).

In previous communications [1,2] we reported the production of organometallic compounds based on *closo*-Ru_4C_2 units from the reaction of $H_4Ru_4(CO)_{12}$ and cyclic olefins. Few compounds of this class are known; the only other example, apart from those of ruthenium, being $Co_4(CO)_{10}C_2R_2$ [3], and in the case of $Ru_4(CO)_{11}C_8H_{10}$ [4] it has been shown that the Ru_4C_2 skeleton is essentially the same as that of Co_4C_2 found in $Co_4(CO)_{10}C_2Et_2$ [3]. This paper reports the preparation of several additional compounds based on *closo*-Ru_4C_2 units which are formed in the reaction of $Ru_3(CO)_{12}$ with the alkynes RC≡CR′ (R = Ph, R′ = Ph, Me or Et; R = R′ = CH_3OCH_2).

The cluster compounds Ia—Id are readily prepared by direct reaction of the appropriate alkyne with $Ru_3(CO)_{12}$ in refluxing n-hexane under argon, usually in yields in the region of 5-10%. (Various other, as yet uncharacter-

SCHEME 1. THE REACTION OF $Ru_3(CO)_{12}$ WITH THE ALKYNES RC≡CR′

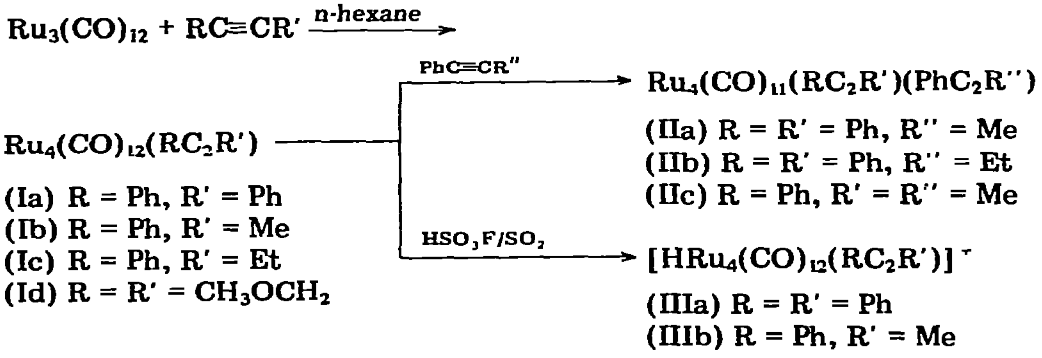

TABLE 1

INFRARED AND MASS SPECTROSCOPIC DATA FOR *closo*-Ru_4C_2 COMPOUNDS

Compound	IR (in n-pentane) (cm^{-1})	M^+ (*m/e*)
Ia	2091m, 2065vs, 2041(sh), 2038vs, 2017m, 2010(sh), 1969m	922
Ib	2091m, 2064vs, 2039(sh), 2034vs, 2013m, 2003(sh), 1968m	860
Ic	2090m, 2062vs, 2040(sh), 2037vs, 2012m, 2003(sh), 1971m	874
Id	2091m, 2063vs, 2037vs, 2012m, 2006(sh), 2003(sh), 1970m	858
$Ru_4(CO)_{12}C_8H_{10}$ [2]	2090m, 2061vs, 2038s, 2035s, 2013w (br), 2003m	
$Ru_4(CO)_{12}C_8H_{12}$ [2]	2088w, 2059s, 2034s, 2010m, 1996m, 1967w (br)	
IIa	2083vs, 2053vs, 2035s, 2024s, 2017(sh), 1978vs	1010
IIb	2083vs, 2054vs, 2038(sh), 2034s, 2024s, 2015(sh), 1978s, 1974(sh)	1024
IIc	2081vs, 2052vs, 2034s, 2024s, 2011s, 1977s	948
$Ru_4(CO)_{11}C_8H_{10}$ [2]	2081m, 2046vs, 2029s, 2019m, 2007w, 1999w, 1990w(br), 1966w(br)	

ised, clusters are also obtained.) Separation of these products is relatively easy and is best carried out by thin layer chromatography on silica. Scheme 1 lists the new compounds prepared and some spectroscopic data are collected in Table 1. All complexes are intensely coloured (brown) as observed with other Ru_4C_2 derivatives [1,2] and not yellow as generally observed for clusters based on the Ru_3 unit [1,2].

The formulation of the compounds as derivatives of *closo*-Ru_4C_2 (Fig.1) is based on mass spectroscopic evidence, supported by the appropriate analytical and infrared spectroscopic data. Thus all complexes exhibit a strong parent ion in their mass spectra (see Table 1) together with ions corresponding to the stepwise loss of the twelve carbonyl groups and fragmentation of the RC≡CR' ligand. An intense peak corresponding to the $Ru_4C_2^+$ ion is also observed; an observation consistent with the presence of a *closo*-Ru_4C_2 unit within the complex. The infrared spectra (Table 1) in the metal carbonyl region (ν(CO)) of complexes Ia-Id are very similar to those of $Ru_4(CO)_{12}C_8H_{10}$ and $Ru_4(CO)_{12}C_8H_{12}$ [2]. They do not resemble those of the trinuclear iron compounds $Fe_3(CO)_9$(RC≡CR') [4]. From their formulae and spectroscopic properties these compounds are obviously similar to those formed from $H_4Ru_4(CO)_{12}$ and cyclic olefins. The formation of Ru_4 clusters from $Ru_3(CO)_{12}$ is perhaps unexpected, particularly in view of previous work with $Fe_3(CO)_{12}$ [5] and $Os_3(CO)_{12}$ [6] which showed that on reaction with acetylenes these carbonyls gave predominantly trinuclear species. In a recent communication Cetini and his coworkers [7] reported the formation of Ru_3 trimers and dimers

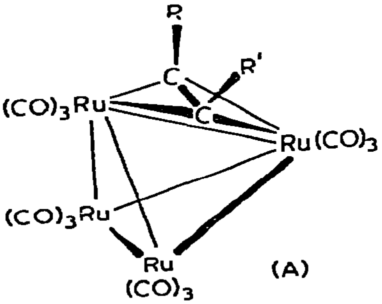

Fig.1. Probable structure of $Ru_4(CO)_{12}(RC_2R')$.

from the reaction of $Ru_3(CO)_{12}$ and diphenylacetylene or tetraphenylcyclopentadienone under conditions similar to those reported here. No mention of tetranuclear Ru_4 derivatives was made.

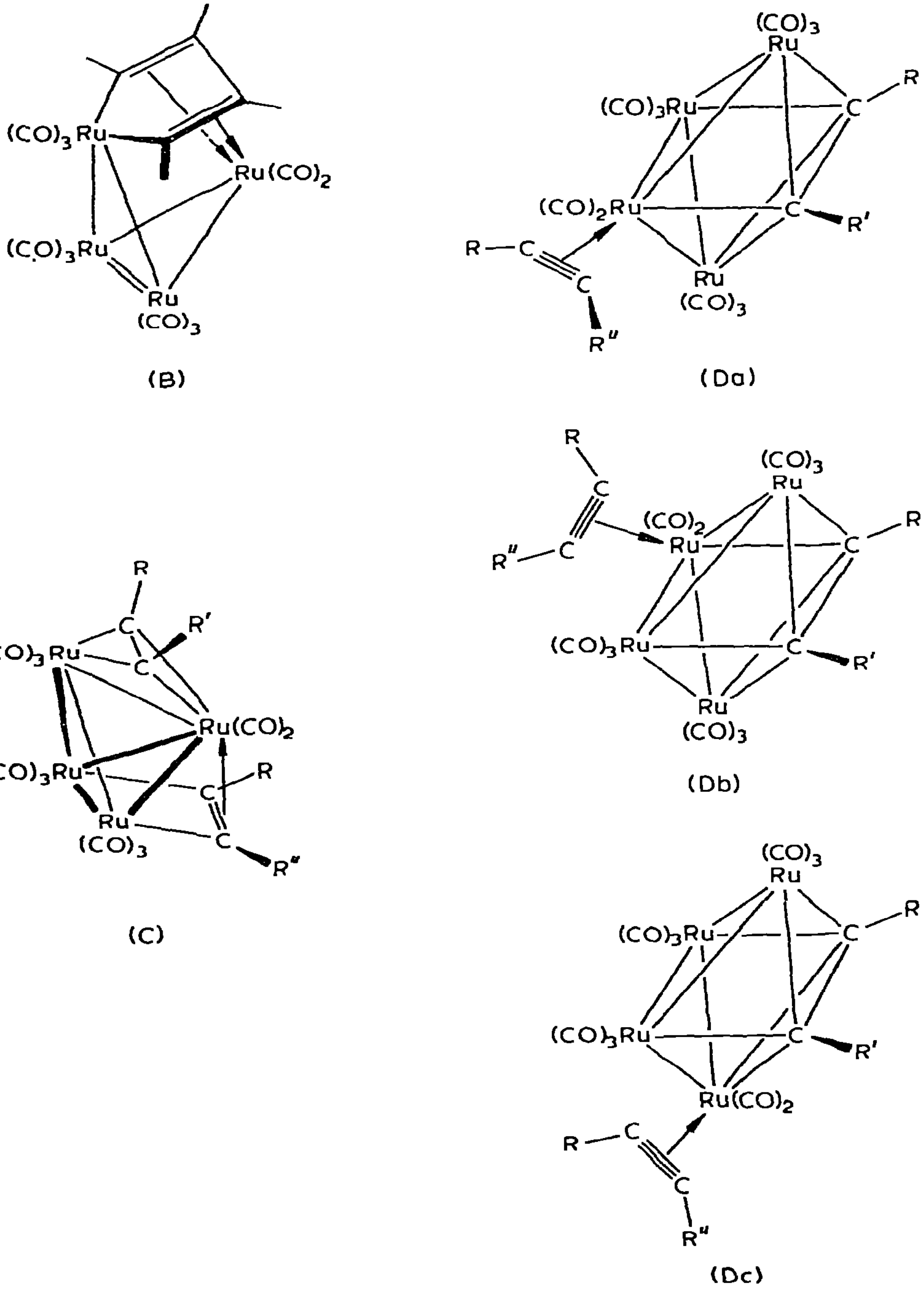

Fig. 2. Possible structures of $Ru_4(CO)_{11}(RC_2R')(PhC_2R'')$.

On allowing complexes Ia or Ib to react with additional alkyne ($PhC{\equiv}CR''$ in n-hexane) ($R'' =$ Me or Et), (see Scheme 1) under argon (reflux 6 h), carbon monoxide is evolved and new complexes based on a Ru_4 cluster unit are produced, which are obtained in yields of 50-60%, after TLC on silica. These new orange complexes are soluble in a wide range of organic solvents. On the basis of their mass spectra, which exhibit strong parent ions, they may be formulated as $Ru_4(CO)_{11}(PhC{\equiv}CR')(PhC{\equiv}CR'')$. This formulation is supported by analytical data and their infrared spectra which are similar to those reported for other $Ru_4(CO)_{11}$ species [2]. Their structures are unknown. Several possibilities are given in Fig.2. At present we have no way of differentiating these possibilities apart from the observation that a peak corresponding to $Ru_4C_4^+$ appears in the mass spectrum, which tends to imply that the two acetylenes have combined [8] thereby favouring structural possibility B.

TABLE 2

^1H NMR SPECTRA OF COMPLEXES (IIIa) AND (IIIb) IN LIQ. SO_2 + 1 drop HSO_3F [a]

Compound	Temp. (°C) [b]	Chemical shifts (τ, ppm)
IIIa	+ 10	2-3m (10H), 33.4s (1H)
IIIa	−10	2-3m (10H), 33.6s (1H)
IIIa	−40	2-3m (10H), 33.8s (1H)
IIIa	−60	2-3m (10H), 33.9s (1H)
IIIb	0	2-3m (5H), 6.3s (3H), 32.8s (1H)
IIIb	−20	2-3m (5H), 6.3s (3H), 32.8s (1H)
IIIb	−60	2-3m (5H), 6.3s (3H), 32.8s (1H)

[a] m = multiplet, s = singlet; relative intensities in parentheses. [b] ± 0.2 °C.

Complexes Ia and Ib also undergo protonation in strong acid (see Scheme 1) to yield the hydrido cations $[HRu_4(CO)_{12}(RC_2R')]^+$. The hydrido ligand was detected from the ^1H NMR spectrum (Table 2) and clearly must span a Ru—Ru edge in the cluster, although facile migration of H ligands from one polyhedral edge to another is commonly observed [9-11] for organometallic complexes of this type.

Hydrogenation of $Ru_4(CO)_{12}PhC_2Ph$ in n-heptane under reflux (15 min) gives an almost quantitative yield of $H_4Ru_4(CO)_{12}$ and *trans*-stilbene. The mechanism of this hydrogenation will be discussed in a subsequent paper.

We thank the SRC for financial support to K.T.S. and Johnson Matthey and Co. Ltd., for their generous loan of ruthenium trichloride.

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