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Cluster Expansion Reactions of $HRu_3(CO)_9MeC\overset{\cdot\cdot\cdot}{-}CH\overset{\cdot\cdot\cdot}{-}CMe$, a *nido*-Pentagonal-bipyramidal Complex

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The condensation of $[(\eta\text{-}C_5H_5)Fe(CO)_2]_2$ with $HRu_3(CO)_9C_5H_7$ leads to a novel heterometallic cluster, $(\eta\text{-}C_5H_5)FeRu_3(CO)_9C_5H_7$, whose structure is inferred from i.r., mass and ^1H n.m.r. spectral data and discussed with that of isoelectronic complex $(\eta\text{-}C_5H_5)NiRu_3(CO)_8C_5H_7$. The formation of both compounds can be rationalized in terms of Wade's approach as a cluster expansion from a nido *to a* closo *polyhedron. The reaction of the title compound with $Ru_3(CO)_{12}$ affords $Ru_4(CO)_{12}C_5H_8$ in very low yield, for which a* closo-*octahedral geometry is suggested on the basis of spectroscopical evidence.*

Introduction

Over the past few years, transition metal carbonyl clusters have received wide attention from organometallic chemists, and the interest towards them has further increased since it was suggested that their structures and properties can contribute to a better understanding of chemisorption and catalytic processes [1]. It is often difficult to design a rational synthetic procedure of particular metal clusters. Wade's approach [2] might be a powerful tool for planning these reactions. The so called 'cluster expansion' reactions are in principle possible if neutral units can be incorporated into an existing polyhedral cluster. A favourable polyhedron should be the 'allylic' cluster $HRu_3(CO)_9C_5H_7$ (I), one of the main products of the reactions of $Ru_3(CO)_{12}$ with pentenes [3], pentadienes [4] and 2-pentyne [5]. Its solid state structure can be inferred from the X-ray analysis of the higher homologous $HRu_3(CO)_9C_6H_9$ [6] and envisaged as a *nido*-pentagonal-bipyramid (8 skeletal electron pairs (S), 6 skeletal atoms (n)), suitable to accommodate a neutral fragment into its vacant vertex (see Fig. 1). In order to test the versatility of (I) as reagent for cluster expansion syntheses, we have carried out the reactions of (I) with $[(\eta\text{-}C_5H_5)Fe(CO)_2]_2$ and $Ru_3(CO)_{12}$, from which the fragments '$(\eta\text{-}C_5H_5)Fe$' and '$Ru(CO)_3$' should be easily produced.

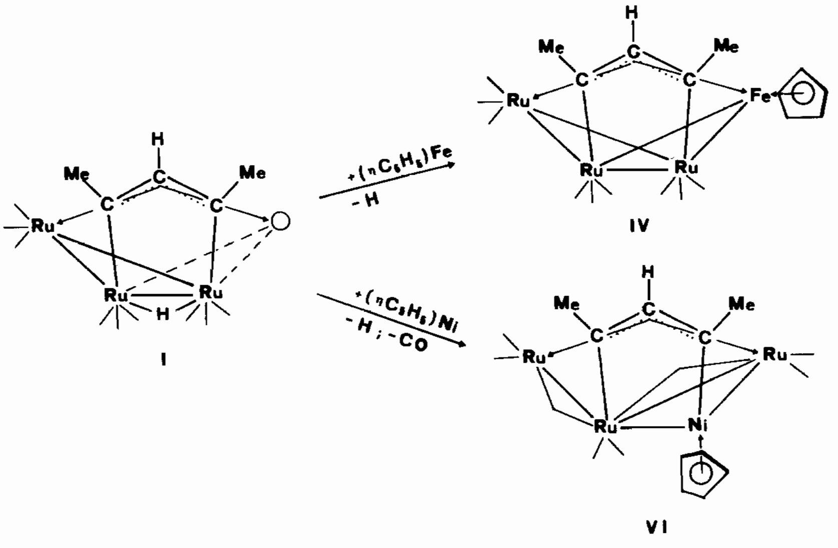


Fig. 1. Cluster expansion reactions of *nido*-pentagonal-bipyramid (I) with heterometallic fragments. o: vacant vertex; (IV): proposed structure; (VI): determined structure [7].

Experimental

All reactions were carried out in an atmosphere of nitrogen. n-Octane was dried over molecular sieves before use. $[(\eta\text{-}C_5H_5)Fe(CO)_2]_2$ was purchased from Strem Chemicals Inc. and $Ru_3(CO)_{12}$ and $HRu_3(CO)_9C_5H_7$ (I) were prepared according to the literature [4]. Separations of the reaction mixtures were performed by t.l.c. preparative plates (Kieselgel PF, Merck; eluent diethyl ether 10% and light petroleum mixture). The complexes were analyzed by means of an F & M 185 C, H, N Analyzer and a Perkin Elmer 303 Atomic Absorption Spectrophotometer. The i.r. spectra were recorded on a Beckman IR-12. ^1H n.m.r. spectra were obtained on a Jeol 60-HL instrument, chemical shifts were reported as downfield positive with respect to TMS. Mass spectra were measured on a Hitachi Perkin-Elmer RMN 6H spectrometer.

Reaction of (I) with $[(\eta\text{-}C_5H_5)Fe(CO)_2]_2$

1.0 g (1.60 mmol) of complex (I) was dissolved in 200 ml of n-octane and added with 1.0 g (2.82 mmol) of cyclopentadienyl-iron dicarbonyl dimer. The mixture was refluxed for 20 hours. After cooling and filtration, the solvent and traces of $Fe(CO)_5$ were removed under reduced pressure and the residue, dissolved in CH_2Cl_2, was chromatographed by t.l.c. Beside unreacted (I) and $[(\eta\text{-}C_5H_5)Fe(CO)_2]_2$, the following derivatives have been eluted: $Ru_2(CO)_6C_5H_6$ (II), yellow powder (10%). *Anal.* Calcd. for $C_{11}H_6O_6Ru_2$: C, 30.14; H, 1.37; Ru, 46.57. Found: C, 29.90; H, 1.22; Ru, 46.80. Mol w. 438, mass spectrum: m/e 438 [M^+] followed by loss of six carbonyl groups. I.r. spectrum (n-heptane), ν_{CO} (cm^{-1}): 2083m, 2052vs, 2013s, 1998m, 1988m. ^1H n.m.r. ($CDCl_3$) δ: 6.68 (m,1), 6.09 (m,1), 5.83 (m,1) and 2.33 (s,3). $Ru_3(CO)_7(\eta\text{-}C_5H_5)C_5H_7$ (III), deep red crystals (15%). *Anal.* Calcd. for $C_{17}H_{12}O_7Ru_3$: C, 32.18; H, 1.89; Ru, 48.26. Found: C, 32.03; H, 1.67; Ru, 48.68. Mol. w. 634, mass spectrum: m/e 634 [M^+] followed by loss of seven carbonyl groups. I.r. spectrum (n-heptane), ν_{CO} (cm^{-1}): 2069 s, 2035 vs, 2001s(sh), 1995vs, 1984s, 1953w, 1897m. ^1H n.m.r. spectrum ($CDCl_3$) δ: 2.69 (s,3), 2.94 (s,3), 5.13 (s,5) and 6.61 (s,1). $(\eta\text{-}C_5H_5)FeRu_3(CO)_9C_5H_7$ (IV), dark brown powder (3%). *Anal.* Calcd. for $C_{19}H_{12}O_9FeRu_3$: C, 30.56; H, 1.61; Fe, 7.51; Ru, 41.02. Found: C, 30.33; H, 1.54; Fe, 7.65; Ru, 40.77. Mol. w. 746, mass spectrum: m/e 746 [M^+] followed by loss of nine carbonyl groups. I.r. spectrum (n-heptane), ν_{CO} (cm^{-1}): 2071s, 2034vs, 2024vs, 1993m, 1983w, 1966m.

Reaction of $Ru_3(CO)_{12}$ with $[(\eta\text{-}C_5H_5)Fe(CO)_2]_2$ in Presence of 1,3-pentadiene

1.0 g of $Ru_3(CO)_{12}$ (1.56 mmol) was suspended in 200 ml of n-octane and added with 1.0 g of cyclopentadienyliron dicarbonyl dimer and 2.0 ml of 1,3-pentadiene (20.1 mmol). The mixture was refluxed for 20 hours. Similar separation work-up afforded $Fe(CO)_5$ (trace), unreacted (I) and $[(\eta\text{-}C_5H_5)Fe(CO)_2]_2$, (II) (5%), (III) (5%) and (IV) (15%).

Pyrolysis of (I) Alone

0.2 g of (I) was dissolved in 50 ml of n-octane and refluxed under nitrogen. The course of the pyrolysis was checked by t.l.c. and i.r. monitoring. During 20 hours (II), $Ru_3(CO)_{12}$ and metallic ruthenium were the only detectable products.

Pyrolysis of (I) in Presence of $Ru_3(CO)_{12}$

1.0 g of (I) was dissolved in 200 ml of n-octane, added with 1.0 g of $Ru_3(CO)_{12}$ and refluxed for 20 hours. Similar separation procedure gave unreacted (I) and $Ru_3(CO)_{12}$, (II) (15%), $H_2Ru_4(CO)_{13}$ (trace), $H_4Ru_4(CO)_{12}$ (trace), $Ru_6(CO)_{17}C$ (5%), readily identified by means of i.r. and ms spectroscopy and $Ru_4(CO)_{12}C_5H_8$ (V), brown powder (trace). Mass spectrum: m/e 812 [M^+] followed by loss of twelve carbonyl groups and by a complicated fragmentation of the organic moiety to give ultimately the ion $Ru_4C_2^+$. I.r. spectrum (n-heptane), νCO (cm^{-1}): 2089w, 2064vs, 2038s(sh), 2034vs, 2008m, 1966w.

Results and Discussion

Condensation of (I) with Fragment from $[(\eta\text{-}C_5H_5)Fe(CO)_2]_2$

The heterometallic product of the reaction of (I) with $[(\eta\text{-}C_5H_5)Fe(CO)_2]_2$ is the tetranuclear cluster $(\eta\text{-}C_5H_5)FeRu_3(CO)_9C_5H_7$ (IV). Its yield can be increased when $Ru_3(CO)_{12}$ and $[(\eta\text{-}C_5H_5)Fe(CO)_2]_2$ are refluxed in presence of 1,3-pentadiene. The mass spectrum shows stepwise loss of 9 carbonyl groups from the molecular ion. Doubly charged ions corresponding to CO loss are present as intense peaks, indicating a great stability of the organometallic core. The i.r. spectrum in the CO stretching region shows absorptions characteristic of terminal carbonyl groups only. The chemical shifts, the pattern and the integrated intensities of the ^1H n.m.r. resonances suggest the presence in the molecule of a cyclopentadienyl group and a 1,3-dimethyl-allyl moiety symmetrically coordinated. No resonance is detected in the hydride region. In particular the signal attributed to the cyclopentadienyl group falls in the range found for $(\eta^5\text{-}C_5H_5)Fe$ units in heterobimetallic complexes (4.00–4.32) [8]. The resonance assigned in (IV) to C_2H is observed in (I) at an almost identical chemical shift, as found in tetranuclear butterfly systems that retain the allylic configuration of the organic moiety [7, 9]. The methyl groups in (IV)

TABLE I. N.m.r. Data.

Complex	δ/ppm[a]
$HRu_3(CO)_9MeCCHCMe$ (I)[b]	C_2H, 6.68(1,d): CH_3, 2.84(6,s); hydride, 30.1(1,d)
(η-C_5H_5)$NiRu_3(CO)_8MeCCHCMe$ (VI)[b]	C_2H, 6.65(1,s); C_5H_5, 4.97(5,s); C_1CH_3 3.59(3,s); C_3CH_3, 1.86(3,s)
(η-C_5H_5)$FeRu_3(CO)_9MeCCHCMe$ (IV)	C_2H, 6.58(1,s); C_5H_5, 4.11(5,s); CH_3, 3.47(6,s)

[a] In $CDCl_3$. [b] See reference 7.

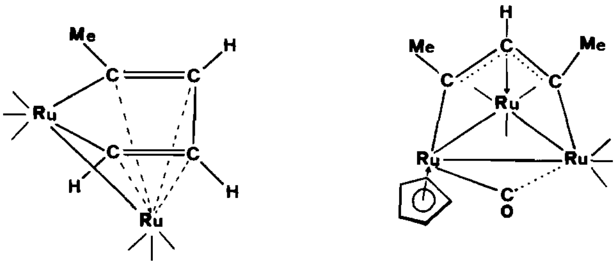
are still equivalent and show, with respect to (I), a downfield shift.

These spectroscopic data suggest that the addition of (η-C_5H_5)Fe fragment to (I) has simply occurred into the vacant vertex of the *nido*-pentagonal-bipyramid to give the *closo*-structure, in which the Fe atom results in an apical position or, in other words, in a wing side of the metallic butterfly core. This result can be related to the synthesis of (η-C_5H_5)-$NiRu_3(CO)_8C_5H_7$ (VI), obtained from the reaction of (I) with $[(\eta\text{-}C_5H_5)Ni(CO)]_2$ [7]. Now (VI) can be envisaged as a *closo*-pentagonal-bipyramid derived by cluster expansion of (I) and insertion of (η-C_5H_5)-Ni fragment into the Ru_3 triangle. The Ni atom occupies an equatorial position or, in other words, a hinge side of the metallic butterfly core. The different arrangement that the metals undergo in the cluster skeleton in (IV) and (VI) might reflect only the different electronic requirements of the two metallic fragments. Incidentally we note that (VI) shows two bridging COs, whose presence can be thought to reduce electron density differences within the cluster. It is noteworthy that the overall molecular formula of (VI) and (IV) can be easily predicted by Wade's theory [2]. A (η-C_5H_5)Ni fragment can contribute 3 skeletal bonding electrons to the growing polyhedron, while a (η-C_5H_5)Fe unit only 1. Therefore in order to maintain $S = 8$ required for the *closo*-pentagonal-bipyramidal structure found for (VI) and proposed for (IV), the complex (I) has to lose the hydride and a CO group in the former reaction and the hydride only in the latter. Unfortunately so far we have not been able to grow crystals of (IV) suitable for X-ray analysis.

The complex $Ru_2(CO)_6C_5H_6$ (II), obtained as a side-product, derives from the thermal degradation of (I) as shown from the pyrolysis of (I) alone in the same experimental conditions. The following equations represent an attempt to explain the formation of the recovered products:

$$HRu_3(CO)_9C_5H_7 \xrightarrow{\Delta} Ru_2(CO)_6C_5H_6 + H_2 + \text{`}Ru(CO)_3\text{'}$$

$$4\text{`}Ru(CO)_3\text{'} \rightarrow Ru_3(CO)_{12} + Ru$$



II III

Fig. 2. Proposed structure for (II) and (III).

I.r. mass and ^1H n.m.r. spectra are very similar to those of complexes $Ru_2(CO)_6L_2$ [L = alkyne] [10] and $Ru_2(CO)_6$ [L – 2H] [L = diene] [4] and strongly suggest the presence of a ruthena-cyclopentadienyl ring. The extensive rearrangement of the organic ligand with the elimination of a molecule of H_2 is remarkable.

The other by-product is the trimetallic cluster (η-C_5H_5)$Ru_3(CO)_7C_5H_7$ (III). The mass spectrum suggests that a cyclopentadienyl group has replaced two CO's and the hydride ligand. The i.r. spectrum displays a peak at 1897 cm^{-1} that might indicate the presence of an asymmetric bridging carbonyl group as found for $Ru_3(CO)_6(\eta\text{-}C_5H_5)(\eta^7\text{-}C_8H_9)$ and $Ru_3(CO)_6(\eta\text{-}C_5H_5)(\eta\text{-}C_7H_7)$ [11].

The ^1H n.m.r. spectrum indicates that the allylic arrangement is retained and the cyclopentadienyl group is η-coordinated to a Ru atom σ-bonded to the organic chain. The formation of (III) during the course of the reaction can then be accounted for by simple migration of cyclopentadienyl group from iron to ruthenium and the recovery of $Fe(CO)_5$ in the reaction products supports this proposal.

Condensation of (I) with Fragment from $Ru_3(CO)_{12}$

A few years ago it was reported that the treatment of $HRu_3(CO)_9C_{12}H_{15}$ (VII) (a compound structurally analogous to (I)) with $Ru_3(CO)_{12}$ afforded the tetranuclear complex $Ru_4(CO)_{12}C_{12}H_{16}$ (VIII) [9]. This reaction can now be easily understood in terms of a *nido* to *closo* cluster expansion

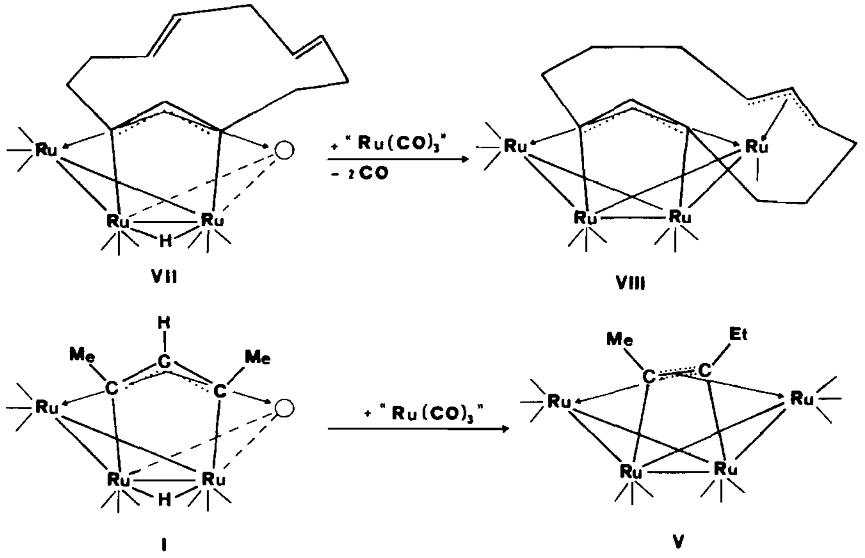


Fig. 3. Different reaction pathways of (VII) and (I) with fragments from $Ru_3(CO)_{12}$.

in the pentagonal-bipyramidal geometry. In the course of the reaction the large organic cycle is able to rearrange in order to satisfy the electronic requirement of a *closo*-pentagonal-bipyramid (S = 8, n = 7).

On the other hand, from the reaction of (I) with $Ru_3(CO)_{12}$ the tetranuclear cluster $Ru_4(CO)_{12}$-C_5H_8 (V) is achieved in trace only. Its mass and i.r. spectra are very similar to those of compounds $Ru_4(CO)_{12}PhC_2R$ [R = Ph, Me, Et] [12] and $Ru_4(CO)_{12}MeC_2Me$ [13] based on *closo*-Ru_4C_2 units. Thus the condensation of (I) with '$Ru(CO)_3$' fragment might be explained by cleavage and reformation of a Ru–C(σ) bond coupled with hydrogen shifts. A new coordination between the metallic butterfly core and only two atoms of the organic moiety occurs. For this bonding scheme values of S = 7 and n = 6 can be predicted in accordance with a *closo*-octahedral structure. We think that the insaturation available in the large organic cycle of (VII) is responsible for the different behaviour observed in the formation of (VIII) and (V).

The formation of the other products of the reaction is straightforward. (II) derives from thermal degradation of (I), $H_2Ru_4(CO)_{13}$ and $H_4Ru_4(CO)_{12}$ from reaction of $Ru_3(CO)_{12}$ with minute traces of water [14] and eventually $Ru_6(CO)_{17}C$ from pyrolysis of $Ru_3(CO)_{12}$ [15].

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References

1 E. L. Muetterties, T. N. Rhodin, E. Band, C. F. Brucker and W. R. Pretzer, *Chem. Rev.*, *79*, 91 (1979).
2 a) K. Wade, *Adv. Inorg. Chem. Radio-chem.*, *18*, 1 (1976);
b) 'Transition Metal Clusters', Edited by B. F. G. Johnson, Wiley, 1980.
3 M. Castiglioni, L. Milone, D. Osella, G. A. Vaglio and M. Valle, *Inorg. Chem.*, *15*, 394 (1976).
4 O. Gambino, M. Valle, S. Aime and G. A. Vaglio, *Inorg. Chim. Acta*, *8*, 71 (1974).
5 S. Aime, L. Milone, D. Osella and M. Valle, *J. Chem. Research*, *(S)* 77 (1978), *(M)* 0785–0797 (1978).
6 M. Evans, M. Hursthouse, E. W. Randall, E. Rosenberg, L. Milone and M. Valle, *J. Chem. Soc. Chem. Comm.*, 545 (1972).
7 D. Osella, E. Sappa, A. Tiripicchio and M. Tiripicchio Camellini, *Inorg. Chim. Acta*, *42*, 183 (1980).
8 Th. Madach and H. Vahrenkamp, *Chem. Ber.*, *113*, 2675 (1980).
9 a) M. I. Bruce, M. A. Cairns and M. Green, *J. Chem. Soc. Dalton Trans.*, 1293 (1972).
b) R. Belford, M. I. Bruce, M. A. Cairns, M. Green, H. P. Taylor and P. Woodward, *J. Chem. Soc. Chem. Comm.*, 1159 (1970).
10 G. Cetini, O. Gambino, E. Sappa and M. Valle, *J. Organomet. Chem.*, *17*, 437 (1969) and references therein.
11 A. P. Humphries and S. A. R. Knox, *J. Chem. Soc. Dalton Trans.*, 1523 (1978).
12 a) B. F. G. Johnson, J. Lewis and K. T. Shorpp, *J. Organometal. Chem.*, *91*, C13 (1975);
b) B. F. G. Johnson, J. Lewis, B. E. Reichert, K. T. Shorpp and G. M. Sheldrick, *J. Chem. Soc. Dalton Trans.*, 1417 (1977).
13 P. F. Jackson, B. F. G. Johnson, J. Lewis, P. R. Raithly and G. J. Will, *J. Chem. Soc. Chem. Comm.*, 1190 (1980).
14 C. R. Eady, B. F. G. Johnson and J. Lewis, *J. Organometal. Chem.*, *57*, C84 (1973).
15 B. F. G. Johnson, R. D. Johnston and J. Lewis, *J. Chem. Soc. A*, 2865 (1968).