# [Ru6( μ3-H)( η2-μ4-CO)2( μ-CO)(CO)12( η5-C5R5)] (R = H or Me): syntheses, X-ray structures and spectroscopic characterization

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## Abstract

The reaction of $[Ru_3(CO)_{12}]$ (1) with nickelocene, $Ni(Cp)_2$ (used as a source of Cp for the first time in the cluster chemistry) under reflux in *n*-heptane or with pentamethylcyclopentadiene in *n*-octane yielded novel thermally stable hexaruthenium clusters $[Ru_6(\mu_3$-H$)(\eta^2$-$\mu_4$-CO$)_2(\mu$-CO$)(CO)_{12}(\eta^5$-$C_5R_5)]$, where R = H (2) or R = Me (3). Their structures have been determined by X-ray diffraction and characterized by IR, $^1$H, $^{13}$C NMR and mass spectroscopy. A $^{13}$C NMR spectral assignment is reported for the first time for the cluster (3) characterized by a tetrahedral $Ru_4$ arrangement with two edge-bridging Ru-atoms containing 15 CO groups and an $\eta^5$-Cp*-ligand.

*Keywords:* Hexaruthenium cluster; $NiCp_2$, Cp and Cp* ligands; X-ray diffraction; NMR

## 1. Introduction

Octahedral hexaruthenium carbido cluster $Ru_6C(CO)_{17}$ (4) and its arene derivatives have been known since 1967 and have been well documented [1–12], while a limited number of papers describe other hexaruthenium clusters, such as a tetrahedral $Ru_4$ arrangement with two edge-bridging ruthenium atoms [8,13–15] or a cyclohexane-like ruthenium framework [16,17]. The hexaruthenium clusters $[Ru_6(\eta^2$-$\mu_4$-CO$)_2(CO)_{13}(\eta^6$-$C_6H_3Me_3)]$ (5) [13] and $[HRu_6(\eta^2$-$\mu_4$-CO$)_2(CO)_{13}(\eta^7$-$\mu_2$-$C_6H_3Me_2CH_2)]$ (6) [13], $[H_2Ru_6(CO)_{17}]$ (7) [14], as well as $[Ru_6(\mu_3$-H$)(\eta^2$-$\mu_4$-CO$)_2(CO)_{13}(\eta^5$-$C_5H_4Me)]$ (8) [15], possess the same ruthenium skeleton as the clusters 2 and 3 determined in this study. A special bonding mode of methyl-substituted arenes, as found in toluene and mesitylene where a methyl is transformed to a methylene group forming a bridge between adjacent ruthenium atoms ($C_6H_3Me_2CH_2$-moiety in 6 [13]), was also found in our recent investigations for pentamethylcyclopentadiene in an octahedral carbido cluster $Ru_6C(CO)_{14}(\mu$-$\eta^1$-$\eta^5$-

$C_5Me_4CH_2$) (9) [9,10], as well as in fulvene derivatives [12] of 4. So, Cp* can also show variable bonding modes as in six-membered ring systems when coordinated with hexaruthenium clusters. The conditions for the formation of the clusters 2 and 3 suggest that especially an $\eta^5$-coordinated Cp*-ligand can stabilize the formed cluster. This finding can be of great importance regarding the formation and isolation of other related structures, which can also be valuable in establishing the mechanism leading to formation of carbido clusters [15].

## 2. Results and discussion

### 2.1. X-ray diffraction

X-ray structure analyses of 2 and 3 reveal unambiguously the hexaruthenium framework with a tetrahedral $Ru_4$ arrangement, two edge-bridging ruthenium atoms and the Cp and Cp* ligands adopting the $\eta^5$-terminal bonding mode, as illustrated in Fig. 1 for 3. The clusters 2 and 3 are isostructural with each other, and also with a monomethyl cluster $[Ru_6(\mu_3$-H$)(\eta^2$-$\mu_4$-CO$)_2(CO)_{13}(\eta^5$-$C_5H_4Me)]$ (8) reported recently [15].

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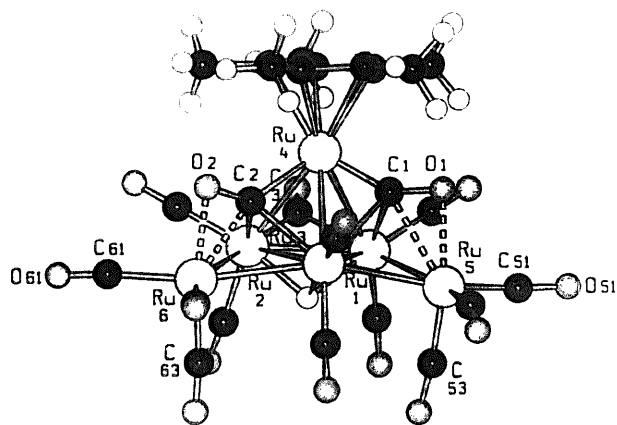
Fig. 1. The molecular structure of [Ru$_6$($\mu_3$-H)($\eta^2$-$\mu_4$-CO)$_2$($\mu$-CO)(CO)$_{12}$($\eta^5$-C$_5$Me$_5$)] (3). The principal bond lengths (Å) in the crystal are: Ru–Ru (1)–(2) 2.720, (1)–(3) 2.851, (1)–(4) 2.848, (1)–(5) 2.756, (2)–(3) 2.868, (2)–(4) 2.838, (2)–(6) 2.758, (3)–(4) 2.759, (3)–(5) 2.815, (3)–(6) 2.833; Ru(4)–C(cyclopentadienyl): 2.32, 2.29, 2.28, 2.29 and 2.22.

Therefore, only some X-ray structural details such as the Ru–Ru bond lengths and Ru–Cp* distances of 3 are given in Fig. 1. As expected, the X-ray structural parameters for the molecular farmework of 2 are practically the same as in 3. One interesting structural feature that should be mentioned is the two triply bridging carbonyls (numbered as C$_1$O$_1$ and C$_2$O$_2$ in Fig. 1) also forming a $\pi$-bond to an edge-bridging ruthenium atom (5 and 6). The third carbonyl bridge (C$_3$O$_3$) is formed between Ru-1 and Ru-2. The $\mu_3$-H moiety is located symmetrically below the basal plane (Ru-1, Ru-2 and Ru-3) of the Ru$_4$ tetrahedron. The complete lists of the atomic coordinates, bond lengths and bond angles for 2 and 3, as well as other supplementary material, have been deposited at the Cambridge Crystallographic Data Centre and are available also from E.K. or K.R. on request.

### 2.2. NMR spectroscopy

The $^1$H NMR spectrum of 2 measured in CDCl$_3$ at 30 °C showed the presence of one hydride in the molecular framework resonating at $\delta = -20.00$ ppm, while the protons of the Cp-ring gave a signal at 5.58 ppm. Unfortunately, the amount of 2 was too limited for an exhaustive $^{13}$C NMR spectral assignment. Only the signal of five identical carbons of the Cp-moiety resonating at 92.40 ppm can be reliably assigned. In the case of 3 the amount of sample was sufficient for full $^1$H and $^{13}$C NMR spectral analyses. As in 2, the hydride moiety of 3 gave a strongly shielded signal at $\delta = -24.66$ ppm, while five identical methyls of the Cp*-ligand gave a strong signal at 1.53 ppm. The $^{13}$C NMR

spectrum of 3 in CDCl$_3$ at 30 °C (Fig. 2) shows nine well-resolved CO signals at $\delta = 285.6$, 215.3, 205.3, 200.3, 192.7, 191.3, 190.2, 186.2 and 185.8 ppm with the relative intensities (based on signal integration, since significant differences existed in the line widths) of 2:1:2:1:2:1:2:2:2. These intensity ratios can be explained directly by the molecular symmetry of 3 giving three lines with a relative intensity of one ($\mu$-CO bridging between Ru-1 and Ru-2, axial CO at Ru-3 and equatorial CO at Ru-3) and six lines with relative intensity of two (two triply bridging $\eta^2$-$\mu_4$-CO groups at Ru-1/Ru-3/Ru-4 and Ru-2/Ru-3/Ru-4, axial CO groups at Ru-1 and Ru-2, equatorial CO groups at Ru-1 and Ru-2, axial CO groups at Ru-5 and Ru-6 and two pairs of equatorial CO groups at Ru-5 and Ru-6).

In addition to the relative intensity data, the $^{13}$C NMR chemical shift assignment of 3 is based on $^nJ$(C,H) ($n = 2$ or 3) spin–spin coupling constants and reference data [18]. The low field signal at $\delta = 285.6$ ppm is assigned to two identical, triply bridging $\eta^2$-$\mu_4$-CO groups being close to the values of 281.1 and 280.9 ppm of the bridging CO groups in a related tetrahedral ruthenium cluster K$_2$H$_2$Ru$_4$(CO)$_{12}$ (10) [18]. In the proton-coupled $^{13}$C NMR spectrum at 30 °C the majority of the CO signals were split into doublets as follows: 215.3 ppm, 1.3 Hz; 200.3 ppm, 3.4 Hz; 192.7 ppm, 12.1 Hz; 191.3 ppm, 12.1 Hz; 190.2 ppm, 3.4 Hz (Fig. 3). The signal of the $\eta^2$-$\mu_4$-CO groups at 285.6 ppm and the two most shielded signals were somewhat broadened in the proton-coupled spectrum but no clear couplings were observed. Similarly, the signal at 205.3 ppm also remained as a singlet in the proton-coupled $^{13}$C NMR spectrum. The direct coupling constant of the methyl groups ($\delta = 9.6$ ppm) in Cp* is $^1J$(C,H) = 128.4 Hz while the skeletal carbons ($\delta = 105.1$ ppm) of
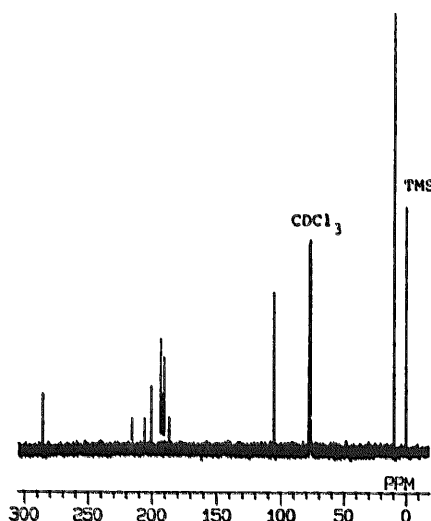


Fig. 2. The $^{13}$C NMR spectrum of [Ru$_6$($\mu_3$-H)($\eta^2$-$\mu_4$-CO)$_2$($\mu$-CO)(CO)$_{12}$($\eta^5$-C$_5$Me$_5$)] (3) in CDCl$_3$ at 30 °C.
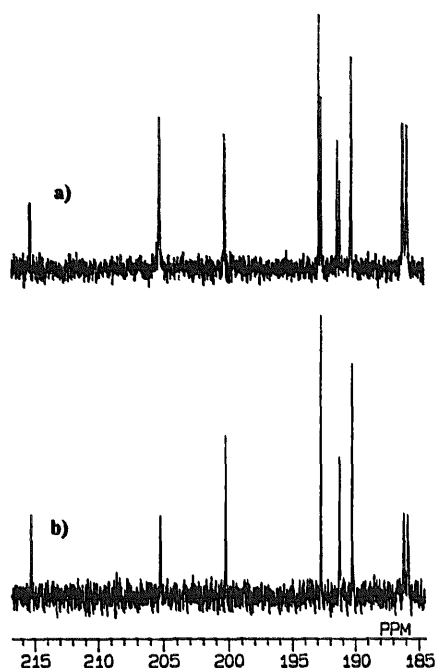
Fig. 3. Expansion (185–215 ppm) of the $^{13}$C NMR spectrum of [Ru$_6$($\mu_3$-H)($\eta^2$-$\mu_4$-CO)$_2$($\mu$-CO)(CO)$_{12}$($\eta^5$-C$_5$Me$_5$)] (3): (a) $^1$H coupled; (b) $^1$H decoupled.

Cp* gave a complex coupling pattern from which unique coupling constants were impossible to resolve.

The signals at 192.7 and 191.3 ppm (relative intensity 2:1), both characterized by a large coupling of 12.1 Hz, are assigned to the equatorial CO groups at Ru-1/2 and at Ru-3 based on the general bond angle dependencies of the geminal $^2J$(C,H) coupling constants [19], as well as the observed large $^2J$(CO, trans-H) coupling constant of 10.3 Hz in (10) [18]. Similarly, the signals at 190.2 and 200.3 ppm (relative intensity 2:1) characterized by an intermediate coupling of 3.4 Hz are assigned to the axial CO groups at Ru-1/2 and at Ru-3 respectively. The only remaining resonance line of an intensity one at 215.3 ppm must originate from the $\mu$-CO bridging between Ru-1 and Ru-2 and shows a small coupling of 1.3 Hz.

The three remaining double intensity signals at 205.3, 186.2 and 185.8 ppm come from three pairs of CO groups locating at two edge-bridging ruthenium atoms 5 and 6, which are spatially far away from $\mu_3$-H and, consequently, do not show any resolved couplings in the $^{13}$C NMR spectrum. Nevertheless, the assignment of

Table 1
Characteristic $\nu_{(CO)}$ (cm$^{-1}$) values for 2 and 3

| | |
|---|---|
| 2 | in n-heptane: 2088 w, 2056 s, 2028 s, 2008 m 1962 w, 1860 vw in KBr disc: 1464m, 1435s |
| 3 | in n-hexane: 2089 m, 2067 s, 2060 sh, 2032 s, 2020 s, 2009 s, 1998 w, 1980 m, 1972 w, 1964 m, 1862 w,br in KBr disc: 1441 m, 1419 s, 1377 m |

Table 2
Characteristic mass spectral ions for 2 and 3

| Ion | 2 | 3 |
|---|---|---|
| [M]$^+$ | 1093 [a] | 1163 [a] |
| [M–CO]$^+$ | 1065 | 1135 |
| [M–2CO]$^+$ | 1037 | 1107 |
| [M–3CO]$^+$ | 1009 | 1079 |
| [M–4CO]$^+$ | 981 [b] | 1051 |
| [M–5CO]$^+$ | 953 | 1023 [b] |
| [M–6CO]$^+$ | 925 | 995 |
| [M–7CO]$^+$ | 897 | 967 |
| [M–8CO]$^+$ | 869 | 939 |
| [M–9CO]$^+$ | 841 | 911 |
| [M–10CO]$^+$ | 813 | 883 |
| [M–11CO]$^+$ | 785 | 855 |
| [M–12CO]$^+$ | 757 | 827 |
| [M–13CO]$^+$ | 729 | 799 |
| [M–14CO]$^+$ | 701 | 771 |
| [M–15CO]$^+$ | 673 | 743 |

[a] The central line of the characteristic isotope pattern of hexaruthenium cluster. [b] Main peak.

these CO groups can be obtained by measurements at elevated temperatures. When the temperature is increased the two most shielded signals at 186.2 and 185.8 ppm are broadened and almost disappear at 55 °C. This means that at elevated temperatures an exchange process begins between these CO groups (unfortunately the fast exchange limit was not achieved owing to the low boiling point of the solvent). In a related structure (10) this behavior is explained by a cyclic exchange between bridging and equatorial CO groups around the basal plane of the Ru$_4$ tetrahedron [18]. In the present case the same reasoning is supported by an observation that the signal of the triply bridging CO groups at 285.6 ppm is also broadened at elevated temperatures. Consequently, the signals at 186.2 and 185.8 ppm can be assigned to two pairs of equatorial CO groups at Ru-5/6 and the only remaining signal at 205.3 ppm must come from two identical CO groups in axial orientation at Ru-5/6 respectively.

### 2.3. IR and mass spectra

Characteristic $\nu_{(CO)}$ (cm$^{-1}$) wavenumbers and mass spectral ions for 2 and 3 are collected in Tables 1 and 2 respectively. In the IR spectra, several CO-stretching bands were observed. In the mass spectra, sequential losses of fifteen CO groups were found.

## 3. Experimental section

### 3.1. Syntheses

All reactions were carried out in Ar atmosphere using absolute dry solvents.

*3.1.1.* $[Ru_6(\mu_3$-$H)(\eta^2$-$\mu_4$-$CO)_2(\mu$-$CO)(CO)_{12}(\eta^5$-$C_5H_5)]$ (2)

Ru$_3$(CO)$_{12}$ (270 mg; 0.42 mmol) was mixed in *n*-heptane (50 ml) and refluxed with Ni(Cp)$_2$ (100 mg, 0.53 mmol, Aldrich AG) for 5 h. The solvent was evaporated under reduced pressure and the dark brown reaction product [Ru$_6$($\mu_3$-H)($\eta^2$-$\mu_4$-CO)$_2$($\mu$-CO)(CO)$_{12}$($\eta^5$-C$_5$H$_5$)] (2) (20 mg, 0.018 mmol, 9%) was separated by column chromatography on silica gel by using CHCl$_3$–petroleum ether as an eluent with rising polarity. The reaction residues are uncharacterized products (in minor quantities) and decomposed material. As far as we know, this is the first time that NiCp$_2$ has been used as a source of Cp in an intermolecular ligand-transfer reaction in the cluster chemistry. A comparable intermolecular ligand-transfer of an $\eta$-C$_4$Ph$_4$ group in a redox-mediated reaction has also been reported previously [20].

*3.1.2.* $[Ru_6(\mu_3$-$H)(\eta^2$-$\mu_4$-$CO)_2(\mu$-$CO)(CO)_{12}(\eta^5$-$C_5Me_5)]$ (3)

Ru$_3$(CO)$_{12}$ (510 mg; 0.79 mmol) was mixed in *n*-octane (100 ml) and refluxed with 0.8 ml of pentamethyl-cyclopentadiene (Merck AG) for 5 h. The work-up was performed as for (2). The dark brown reaction product [Ru$_6$($\mu_3$-H)($\eta^2$-$\mu_4$-CO)$_2$($\mu$-CO)(CO)$_{12}$($\eta^5$-C$_5$Me$_5$)] (3) (50 mg, 0.045 mmol, 11%) was separated by column chromatography on silica gel by using CHCl$_3$-petroleum ether as an eluent with rising polarity. The reaction residues are mainly uncharacterized products for which the structure elucidation is on-going.

## 3.2. Crystal structure determination

The crystals of 2 and 3 were grown from their solutions in the mixtures of CHCl$_3$-heptane by slow evaporation in a refrigerator at +5 °C. X-ray diffraction measurements of 2 and 3 were made on an Enraf-Nonius CAD-4 (graphite monochromator, Mo K$\alpha$ radiation, $\lambda = 0.71073$ Å, $\theta$-$2\theta$ scan mode, $T = 296$ K). Crystallographic data and the details of data collection and structure refinement for 2 and 3 are summarized in Table 3. The structures of 2 and 3 were solved using SHELXS [21]. All non-hydrogen atoms were refined anisotropically; the hydride H atoms were located from the $\Delta F$-map and were refined as riding atoms with a fixed isotropic temperature factor of 0.08 Å$^2$. The Cp* H-atoms of 3 were calculated to their idealized positions (C-H distance 1.05 Å) and included in the final structure factor calculations with fixed isotropic temperature factors ($U = 0.08$ Å$^2$) but not refined [22]. Both structures were solved and refined in an acentric space group $P2_1$. All attempts to solve and refine the structures in a higher symmetry space group ($P2_1/m$) were unsuccessful.

Table 3
Crystallographic data and details of measurements for 2 and 3

| | 2 | 3 |
|---|---|---|
| *Crystal data* | | |
| Molecular formula | C$_{20}$H$_6$O$_{15}$Ru$_6$ | C$_{25}$H$_{16}$O$_{15}$Ru$_6$ |
| Formula weight | 1092.67 | 1162.81 |
| Temperature (K) | 293(2) | 293(2) |
| Wavelength (Å) | 0.71073 | 0.71073 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | $P2_1$ (no. 4) | $P2_1$ (no. 4) |
| $a$ (Å) | 9.404(2) | 9.564(1) |
| $b$ (Å) | 17.067(4) | 17.415(2) |
| $c$ (Å) | 9.593(3) | 19.951(2) |
| $\alpha$ (deg) | 90 | 90 |
| $\beta$ (deg) | 118.21(2) | 92.93(1) |
| $\gamma$ (deg) | 90 | 90 |
| $V$ (Å$^3$) | 1356.8(6) | 3318(1) |
| $Z$ | 2 | 4 |
| $d_{calc}$ (g cm$^{-3}$) | 2.675 | 2.327 |
| $\mu$ (mm$^{-1}$) | 3.326 | 2.680 |
| *Data collection* | | |
| $2\theta_{max}$ (deg) | 50 | 50 |
| Collected data | 2815 | 6540 |
| Unique data | 2651 | 6046 |
| Observed data, for $I > 2\sigma(I)$ | 2649 | 4040 |
| Absorption correction | Empirical with $\Psi$-scans max 0.905 min 0.740 | max 0.99 min 0.65 |
| *Refinement* | | |
| Number of parameters | 373 | 829 |
| Final $R$ (%) | 1.7 | 2.6 |
| $R_w$ (%) | 3.7 | 2.8 |

The fractional coordinates and equivalent isotropic temperature factors, the bond distances (Ångstroms) and bond angles (in degrees), as well as other supplementary material, for 2 and 3 have been deposited at the Cambridge Crystallographic Data Centre.

## 3.3. Spectroscopy

Mass spectra of 2 and 3 were run with a VG Autospec mass spectrometer using direct inlet and 35 eV electron impact (EI) ionization. $^1$H and $^{13}$C NMR spectra were recorded on a Jeol JNM GSX 270 FT NMR spectrometer working at 270.17 MHz and 67.94 MHz respectively. IR spectra were measured using a Specord M-80 spectrometer.

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