Reaction of ruthenium carbonylcarbide cluster $Ru_6C(CO)_{17}$ with nickelocene and pentamethylcyclopentadiene

V. S. Kaganovich, Z. A. Kerzina, M. I. Rybinskaya, and E. Kolehmainen*

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085

The reaction of cluster $Ru_6C(CO)_{17}$ (**1**) with nickelocene is studied. Five CO ligands rather than a metal-ligand crown are substituted for two cyclopentadienyl groups to give a new complex $Ru_6C(\eta^5\text{-}Cp)_2(CO)_{12}$ (**2**). The reaction of cluster **1** with pentamethylcyclopentadiene leads to new complex $Ru_6C(\mu\text{-}\eta^1{:}\eta^5\text{-}CH_2C_5Me_4)(CO)_{14}$ (**3**) containing the σ-bond CH_2—Ru, along with an η^5-coordinated cyclopentadienyl ring.

Key word: ruthenium clusters; ligands exchange.

One of the most common reactions in the chemistry of transition metal clusters is the substitution of metal-ligand crowns ML_n by isolobal metal-ligand groups $M'L'_m$. These reactions have been well studied for many types of clusters, for example, carbyne[1] or tetrahedral[2] clusters, while for the well-known octahedral ruthenium cluster $Ru_6C(CO)_{17}$ (**1**) with an interstitial carbon atom such reactions remain to be studied.[3,4] In the present paper the reaction of **1** with nickelocene that is frequently used for the introduction of Ni crowns in other types of clusters[5] is carried out. It was found that in the case under consideration, only a part of the carbonyl ligands are substituted by cyclopentadienyl ligands with no change of the metal framework:

$$\underset{\mathbf{1}}{Ru_6C(CO)_{17}} + Cp_2Ni \rightarrow \underset{\mathbf{2}}{Ru_6C(\eta^5\text{-}Cp)_2(CO)_{12}}$$

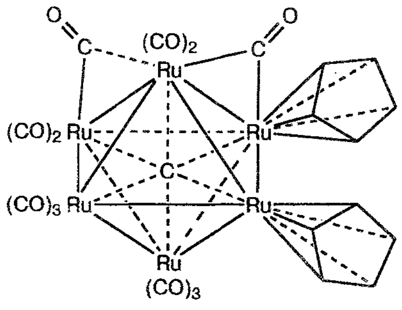
The structure of complex **2** is confirmed by preliminary X-ray data.* Previously analogous reaction of nickelocene with carbyne clusters of cobalt was noted.[6]

The substitution of carbonyl groups in complex **1** with cyclopentadienyl ligands under the action of nickelocene gave impetus to carry out such substitution by direct action of cyclopentadiene. However, from the fact that unsubstituted cyclopentadiene polymerizes significantly on refluxing in heptane, pentamethylcyclopentadiene was applied in this reaction. It was found that refluxing **1** with C_5Me_5H in heptane gives compound **3** containing only one Cp-ring:

$$\underset{\mathbf{1}}{Ru_6C(CO)_{17}} + C_5Me_5H \longrightarrow$$

$$\longrightarrow \underset{\mathbf{3}}{Ru_6C(\mu\text{-}\eta^1{:}\eta^5\text{-}CH_2C_5Me_4)(CO)_{14}}$$

The structure of product **3** was determined by mass- and ^1H NMR spectroscopy data (see Experimental) and by preliminary X-ray study,* which showed that σ-bond CH_2—Ru with the adjacent metal atom takes place along with η^5-coordinated cyclopentadiene ring. As a result, chelate complex with different metal atoms in the cluster including bimetal cycle was obtained.



2

Experimental

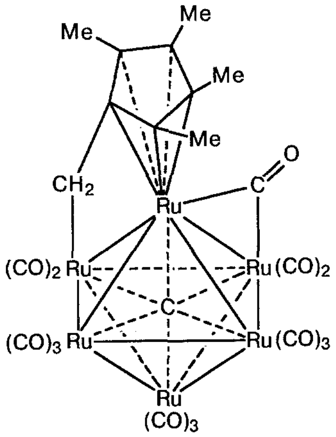
Cluster **1** was prepared according to the conventional procedure.[7] The IR spectrum in heptane was recorded on a Specord 75 IR spectrophotometer.

Reaction of 1 with Cp_2Ni. A mixture of 120 mg (0.1 mmol) of $Ru_6C(CO)_{17}$ (**1**) and 50 mg (0.26 mmol) of nickelocene in hexane was refluxed for 3 h under argon. After that solvent was removed *in vacuo*, and the remaining solid was chromatographed on silica gel (preparative TLC). The second of two brown zones yielded 6.5 mg of complex **2** (the structure of

---

* Detailed X-ray data will be presented in a later paper.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 6, pp. 1171—1172, June, 1995.



another product is under study). IR spectrum, ν(C≡O)/cm^{-1}: 2058 m, 2026 s, 1978 m, 1962 m, 1876 w.

Reaction of 1 with C_5Me_5H. A mixture of 0.12 g (0.1 mmol) of **1** and 0.4 g (0.3 mmol) of C_5Me_5H in 50 mL of heptane was refluxed for 5 h under argon. Then the solution was evaporated *in vacuo*, and the remaining solid was chromatographed (see above). The first brown zone yielded 4.2 mg (3.4 %) of complex **3**. IR spectrum, ν(C≡O)/cm^{-1}: 2072 m, 2042 s, 2024 s, 2016 s, 2004 w, 1986 w, 1820 m. Mass spectrum, *m/z*, 1146 $[M]^+$ (theor. 1144) and further sequential splitting out of 14 carbonyl fragments. ^1H NMR spectrum ($CDCl_3$), δ: 1.52 (s, Me); 2.10 (s, CH_2); ratio of intensities 6:1.

References

1. H. Vahrenkamp, *Comments Inorg. Chem.*, 1985, **4**, 253.
2. T. A. Pakkanen, J. Pursianen, R. Venäläinen, and T. T. Pakkanen, *J. Organomet. Chem.*, 1989, **372**, 129.
3. B. F. G. Johnson, R. D. Johston, and J. Lewis, *J. Chem. Soc. A*, 1968, 2865.
4. B. F. G. Johnson, J. Lewis, and I. G. Williams, *J. Chem. Soc. A*, 1970, 901.
5. M. Mlekuz, P. Bougeard, B. G. Sauer, R. Faggiani, C. J. L. Lock, M. J. McGlinchey, and G. Jaouen, *Organometallics*, 1985, **4**, 2046.
6. M. Mlekuz, P. Bougeard, M. J. McGlinchey, and G. Jaouen, *J. Organomet. Chem.*, 1983, **253**, 117.
7. V. S. Kaganovich, V. A. Petrakova, and M. I. Rybinskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 1893 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1990, **39**, 1720 (Engl. Transl.)].

Received December 20, 1994