Octahedral rhodium cluster $[Rh_6Cp_6(\mu_6\text{-}C)]^{2+}(PF_6^-)_2$

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The 86-electron dicationic octahedral rhodium cluster $[Rh_6Cp_6(\mu_6\text{-}C)]^{2+}(PF_6^-)_2$ containing Cp ligands and the interstitial carbon atom was synthesized by the reaction of $Rh_3Cp_3(\mu\text{-}CO)_3$ with $RhCp(C_2H_4)_2$.

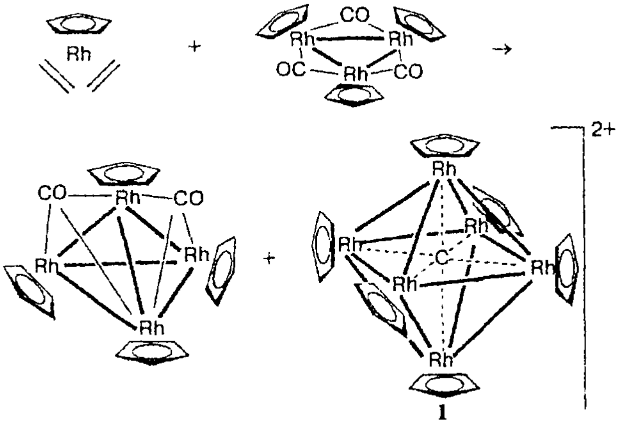
Key words: rhodium clusters, octahedral clusters.

Octahedral rhodium clusters containing the interstitial carbon atom have been widely covered in the literature using carbonyl clusters as examples.[1]

Octahedral rhodium clusters containing exclusively cyclopentadienyl ligands at the metal atoms have not be reported. Only two clusters of other metals with this structure, namely, the 86-electron titanium cluster $Ti_6Cp_6(\mu_3\text{-}O)_8$,[2] which follows Wade's rule, and the octahedral nickel clusters Ni_6Cp_6 and $[Ni_6Cp_6]^+PF_6^-$, which do not satisfy Wade's rule and have 90 and 89 electrons, respectively,[3] were structurally characterized.

In the present work, we report a procedure for the preparation of the rhodium cluster $[Rh_6Cp_6(\mu_6\text{-}C)]^{2+}(PF_6^-)_2$ (**1**), which is the first example of octahedral clusters containing Cp ligands and the interstitial carbon atom.

Previously,[4] we have studied the reaction of the bis-ethylene complex $RhCp(C_2H_4)_2$ with the trinuclear cluster $Rh_3Cp_3(\mu\text{-}CO)_3$. In addition to the major reaction product, namely, the tetranuclear rhodium cluster $Rh_4Cp_4(\mu_3\text{-}CO)_2$, we obtained a blue water-soluble cationic product.[5] After addition of NH_4PF_6 to an aqueous solution of this cation, the latter was isolated as the salt with the PF_6^- anion. Structure **1** was assigned to the resulting product based on the spectral data and the data of elemental analysis as well as on the preliminary results of X-ray diffraction analysis* of this cluster.



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Dicationic cluster **1** is an air-stable compound, which is moderately soluble in nitromethane and acetonitrile, poorly soluble in methanol, and virtually insoluble in less polar solvents. The IR spectrum of this compound (in nitromethane) has no absorption bands in the region typical of carbonyl groups. The ^1H NMR spectrum (in CD_3NO_2) contains only a singlet for the protons of the cyclopentadienyl ring at δ 5.85. The mass spectrum has peaks of a molecular ion and of its fragmentation ions (*m/z* 1020 $[M]^+$, 840 $[M - RhCp - C]^+$, 510 $[M]^{2+}$).

It should be noted that both initial components, $RhCp(C_2H_4)_2$ and $Rh_3Cp_3(\mu\text{-}CO)_3$, are necessary for cluster **1** to form. A special study demonstrated that heating of the above-mentioned compounds separately under the same conditions did not afford cluster **1**. It is reasonable to suggest that carbon monoxide or ethylene can serve as a source of the interstitial carbon atom.

The surprising fact is that the dicationic cluster was formed from neutral initial compounds in the nonpolar solvent under an inert atmosphere. Apparently, this is due to the exceptional stability of the product. The Rh^I atom from the RhCp fragment can serve as an oxidant, as indicated by the formation of a substantial amount of metallic rhodium during the reaction.

The stability of cluster **1** is determined by a number of factors. First, the cluster has a stable configuration consisting of 86 valence electrons, which satisfies Wade's rule. Second, this compound is stable to oxidation and electrophilic attack due to its dicationic character. Third, cluster **1** is inert with respect to nucleophilic reagents due to high delocalization of the positive charge (over six metal atoms) and to steric shielding by the bulky Cp ligands. Finally, the tightening effect of the interstitial carbide carbon atom, which is simultaneously bound to all rhodium atoms, imparts additional stability to the system.

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* The average Rh—Rh, $Rh-C_{int}$, and $Rh-C_{Cp}$ distances are 2.774, 1.967, and 2.174 Å, respectively.

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Experimental

The mass spectrum was measured on a Varian MAT AEI-MS-30 spectrometer with the use of the fast-atom bombardment technique. The ^{1}H NMR spectrum was recorded on a Bruker AMX-400 instrument (400 MHz). The chemical shifts were measured relative to internal standard (Me_4Si).

The initial compounds were prepared according to procedures reported in the literature: $Rh_3Cp_3(\mu\text{-}CO)_3 \cdot 0.5CH_2Cl_2$[5] and $RhCp(C_2H_4)_2$.[6]

A mixture of $Rh_3Cp_3(\mu\text{-}CO)_3 \cdot 0.5CH_2Cl_2$ (0.63 g, 1 mmol) and $RhCp(C_2H_4)_2$ (0.224 g, 1 mmol) was refluxed in *m*-xylene (50 mL) under an atmosphere of argon for 30 h. The solvent was evaporated, and the residue was extracted with CH_2Cl_2 until the extract was colorless. Chromatography of the extract gave $Rh_4Cp_4(\mu_3\text{-}CO)_2$ in a yield of 0.331 g (45%). Then the residue was washed with water until the extracts were colorless. When an aqueous solution of NH_4PF_6 was added to the resulting solution, a dark-blue finely crystalline precipitate of salt **1** was obtained. The yield was 0.027 g (~3% with respect to Rh). Found (%): C, 29.05; H, 2.54; P, 4.48. $C_{31}H_{30}F_{12}P_2Rh_6$. Calculated (%): C, 28.41; H, 2.31; P, 4.73.

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Methyl *N*-(benzylsulfonyl)oxamate as a probable intermediate in the synthesis of 4-hydroxy-5-phenyl-3(2*H*)-isothiazolone 1,1-dioxide from phenylmethanesulfamide and dimethyl oxalate in the presence of bases

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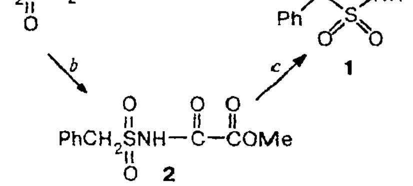
The formation of 4-hydroxy-5-phenyl-3(2*H*)-isothiazolone 1,1-dioxide from phenylmethanesulfamide and dimethyl oxalate under the action of bases is apparently a two-stage process involving the formation of linear methyl *N*-(benzylsulfonyl)oxamate followed by its cyclization. A stable complex of the heterocycle with dimethylformamide was synthesized.

Key words: phenylmethanesulfamide, dimethyl oxalate, 3(2*H*)-isothiazolone 1,1-dioxides.

Previously, it has been reported that 4-hydroxy-5-phenyl-3(2*H*)-isothiazolone 1,1-dioxide[1] (**1**), which possesses biological activity,[2] was synthesized from phenylmethanesulfamide and diethyl oxalate under the action of Bu^tOK in DMF. Compound **1** was also prepared, while in lower yield, by cyclization of methyl *N*-(benzylsulfonyl)oxamate (**2**), which has been synthesized by an independent procedure, under analogous conditions.[1]

We demonstrated that compound **2** was formed in the first step of condensation of phenylmethanesulfamide with dimethyl oxalate in the presence of a base. Apparently, compound **2** is an immediate precursor of heterocycle **1** in the above-mentioned reaction.



Reagents: *a*. 1) MeO_2CCO_2Me, Bu^tONa/Bu^tOH; 2) HCl/H_2O; *b*. 1) MeO_2CCO_2Me, $MeONa/MeOH$; 2) HCl/H_2O; *c*. 1) Bu^tONa/Bu^tOH; 2) HCl/H_2O.

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