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## LETTERS TO THE EDITOR

# New-Type Supercomplex Including a Mononuclear Ruthenium Complex and a Hexanuclear Rhodium Cluster

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The modern strategy of directed synthesis of polynuclear bridging complexes of transition metals is based on the use of so-called "complexes as metals" and "complexes as ligands" as building blocks. Complex compounds with labile ligands fall into the first group and those with ligands capable of acting as bridges fall into the second group [1]. Ruthenium(II) complexes are of special interest among such building blocks as their spectra contain strong charge-transfer bands from $d\pi$ metal orbitals onto $\pi$ antibonding ligand orbitals in the visible region. Therefore, polypyridine ruthenium(II) complexes are being intensively studied as "antennas" of polynuclear systems initiating electron or energy phototransfer [2].

In this work we have synthesized the polynuclear compound $[Cl(bpy)_2Ru(P–P)Rh_6(CO)_{15}](BF_4)$ (**I**) [bpy is 2,2'-bipyridyl, P–P is *trans*-1,2-bis(diphenylphosphino)ethylene]. This compound includes a classical Werner ruthenium(II) complex and a hexanuclear rhodium(0) carbonyl cluster, i.e., it is a polynuclear compound with metal–metal bonds, which is the subject for study of modern organometallic chemistry. The supercomplex was prepared using the compound $[Rh_6(CO)_{15}(CH_3CN)]$ with a labile acetonitrile molecule as a "complex as metal." The "complex as ligands" was $[Ru(bpy)2(P–P)Cl]^+$.

$$[Ru(bpy)_2(P\_P)Cl]^+ + [Rh_6(CO)_{15}(CH_3CN)]$$

$$\longrightarrow [Cl(bpy)_2Ru(P\_P)Rh_6(CO)_{15}]^+ + CH_3CN.$$

The polynuclear compound **I** is stable in the solid state and in solutions ($CHCl_3$, $CH_3OH$, and $CH_2Cl_2$). Its IR spectrum contains ν(CO) bands characteristic of monosubstituted phosphine derivatives of hexacarbonylhexarhodium [3]. The $d\pi(Ru) \rightarrow \pi^*(bpy)$ charge-transfer bands which almost coincide in position and intensity with the corresponding bands of the initial complex $[Ru(bpy)2(P–P)Cl]^+$ dominate in the visible absorption spectrum of compound **I**. The compound decomposes on oxidation on a platinum electrode (scan rate 100 mV/s) in methanol solution, as follows the observation of two irreversible halfwaves at 1.1 and 1.35 V in the cyclic voltammogram. This compound is also unstable on irradiation in solutions at wavelengths higher than that of the abovementioned long-wave charge-transfer band ($\lambda_{irr}$ 450 ± 10 nm). In this case, the characterstic ν(CO) bands at 2100, 2066, and 2036 $cm^{-1}$ disappear from the IR spectrum of the photolyte, implying decomposition of the $\{Rh_6(CO)_{15}\}$ fragment. This process results from energy or electron phototransfer from the $\{Ru(bpy)_2Cl\}^+$ "antenna" through the diphosphine bridging ligand on the cluster fragment, since phosphine derivatives of hexacarbonylhexarhodium, for example $[Rh_6(CO)_{15}(PPh_3)]$, in thereselves are not decomposed by visible light. The mechanism of the photoprocesses involving compound **I** is of special interest and requires additional detail studies.

**{μ-*trans*-1,2-Bis(diphenylphosphino)ethylene}-pentadecacarbonylhexarhodium(0)-chlorobis(2,2'-bipyridyl)ruthenium(II) tetrafluoroborate (I).** $[Rh_6(CO)_{15}(CH_3CN)]$ (50 mg) prepared by the procedure [3] and *cis*-$[Ru(bpy)_2(P–P)Cl](BF_4)$ (40 mg) synthesized by the procedure [4] were added to 20 ml of chloroform deaerated with argon. The solution was stirred for 30 min at room temperature and then applied to a column with silica gel (10 × 120 mm). The main brown-red fraction was eluted with a 1 : 1 ethyl acetate–acetone mixture. The solvent was distilled off in a vacuum, the dry residue was dissolved in chloroform, and the solution was filtered and concentrated by evaporation. The product was dried in a vacuum. Yield 63 mg (76%). Electronic absorption spectrum ($CHCl_3$), $\lambda_{max}$, nm ($\varepsilon \times 10^{-3}$, $mol^{-1} cm^{-1}$): 361 (12.2) and 428 (9.57). IR spectrum ($CHCl_3$), ν, $cm^{-1}$: 2100, 2066, 2036, and 1788 (CO). $^{31}P$ NMR spectrum ($CD_3CN$), $\delta_P$, ppm: 41.85 d ($^3J_{PP}$ 16.0 Hz), 15.17 d.d ($^1J_{PhP}$ 135.0 Hz). Found, %: C 37.32, 37.35; H 1.97, 2. 07; N 2.70, 2. 74. $C_{61}H_{38}BClF_4N_4O_{15}P_2 \cdot Rh_6Ru$. Calculated, %: C 37.20; H 1.94; N 2.84.

The technique of spectral and electrochemical experiments has been described in [4].

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