## The first example of chemiluminescence of fullerenes — oxidation of $C_{60}$ by ozone in solution

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Chemiluminescence (CL) was found during the oxidation of  $C_{60}$  (1) with ozone in solutions of toluene and methylnaphthalene. This CL is more intense  $(J_{max} =$  $6.2 \cdot 10^9$  photon (s mL)<sup>-1</sup>) than that observed during ozo-nization of toluene ( $J_{max} = 7.6 \cdot 10^5$  photon (s mL)<sup>-1</sup>). No chemiluminescence appears upon contact of solutions of 1 with  $O_2$ . It is most likely that the CL spectrum (Fig. 1) is mainly due to the emission of diketone  $O=C_{60}=O^*$ . Photoluminescence (PL) of the products of ozonolysis of 1 is much more intense than the weak PL of fullerene. The maximum PL coincides with  $\lambda_{max} =$ 685 nm of the CL spectrum. The kinetics of consumption of compound 1 and accumulation and consumption of diketones and epoxides  $C_{60}O_n$  (where n = 1-5) during ozonolysis of a toluene solution of 1 were studied by PL, IR spectroscopy, and HPLC. The data obtained were compared to the kinetic behavior of the CL intensity over time, which has a broad maximum at the fifth min. Ketones of fullerene are more stable than epoxides, which decompose 30 min after the beginning of ozonolysis of 1 in toluene. The kinetic curves of CL and yield of ketones are parallel. These data coupled with the absence of an influence of ionol inhibitor and the absence of CL at 1270 nm imply the following mechanism of CL. When the O-O bond is cleaved in the intermediate monoozonide, excited diketone (CL emit-



Fig. 1. Luminescence spectra during ozonization (1.2 mmol  $O_3$  per h) of toluene solutions of  $C_{60}$  (1.6  $\cdot$  10<sup>-4</sup> mol L<sup>-1</sup>): *I*, CL of  $C_{60} + O_3$ ; 2, CL of toluene +  $O_3$ ; 3, PL of  $C_{60}$  (77 K,  $\lambda_{exc} = 337$  nm); 4, PL of the reaction solution (at the fifth min, 77 K,  $\lambda_{exc} = 514$  nm). Spectra *I*-3 were measured using boundary light filters; 4, on an Aminco-Bowmen fluorimeter.

ter) and toluene epoxide are formed. The latter is further transformed into cresol with yields higher for ozonolysis of a toluene solution of 1 than for ozonolysis of toluene (identified by GLC).

> Received December 30, 1998; in revised form March 25, 1999

## New approach to the synthesis of benzoazacrown ethers

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Until recently, cross-linking of two different fragments has been used as the main approach to the development of macrocycles in the chemistry of macroheterocyclic compounds.<sup>1-3</sup> At the same time, for heterocyclic compounds containing three- and sevenmembered cycles, the following methods for designing

Translated from Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 6, pp. 1203-1205, June, 1999.

1066-5285/99/4806-1190 \$22.00 © 1999 Kluwer Academic/Plenum Publishers



the heterocyclic ring, apart from condensation from two fragments, have been studied in detail: methods based on opening of heterocycles and use of acyclic compounds formed in the synthesis of new heterocycles<sup>4-6</sup> by Zincke-Koenig reactions, the Yur'ev reaction, enamine rearrangement, <sup>5,6</sup> and others.

Only a few examples of opening of macroheterocycles are known.<sup>7,8</sup> Nevertheless, the development of new macroheterocyclic compounds from podands formed by opening of macrocycles of other, more accessible compounds seems to be one of the most promising directions in the synthesis of macroheterocyclic compounds.<sup>9</sup>

We have previously found<sup>10,11</sup> that heating of formyl derivatives of benzocrown ethers (for example, **1a,b**) with alkylamines ( $RNH_2$  and  $RNH_3^+Cl^-$ ) results in opening of the macroheterocycle to form nitrogen-containing podands (for example, **2a,b**) in a yield of at least 94%. The method of cyclization of podands **2a,b** to earlier unknown N-methylbenzoazacrown compounds **3a,b** was developed. The reaction of the podands with  $SOCl_2$  gave chloro-derivatives **4a,b** in a 97% yield. Their reaction with NaI resulted in the replacement of the chlorine atom in **4a,b** by the iodine atom in 75–97% yields. Heating of iodo-derivatives **5a,b** in the presence of alkali metal carbonates afforded benzoazacrown compounds **3a,b** in 52–61% yields.

The formation of benzoazacrown compounds 6a,b in 17-21% yields was observed along with N-methylbenzoazacrown compounds 3a,b.

All compounds obtained are oils. Their structure was investigated by <sup>1</sup>H and <sup>13</sup>C NMR mass spectrometry, including NOESY spectra, and confirmed by the mass spectrometric data.

The approach suggested makes it possible to synthesize previously unknown derivatives of benzoazacrown compounds from accessible formyl derivatives of benzocrown ethers, which are used as synthons. This provides a possibility for synthesis of new promising groups of ion-selective luminophores.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 97-03-33033).

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Received February 26, 1999; in revised form March 25, 1999

# Coupling of dehydrobenzene, CO, and an enyne on an Ru<sub>3</sub> cluster. Crystal structure of the complex $Ru_3(CO)_6{\mu_3-P(Ph)CH_2PPh_2}{\mu_3-C(Ph)=CHCC(Ph)(1,2-C_6H_4)C(=O)}$

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Continuing the study of transformations of enyness on Ru<sub>3</sub>-carbonyl clusters,<sup>1</sup> we carried out the thermal reaction of the Ru<sub>3</sub>(CO)<sub>10</sub>( $\mu$ -dppm) cluster (dppm = Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>) with PhC=CCH=CHPh and obtained the red complex Ru<sub>3</sub>(CO)<sub>6</sub>{ $\mu_3$ -P(Ph)CH<sub>2</sub>PPh<sub>2</sub>}{ $\mu_3$ -C(Ph)=CHCC(Ph)(1,2-C<sub>6</sub>H<sub>4</sub>)C(=O)} (1) in ~20% yield.



The <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 25 °C) of complex 1 contains a complex multiplet from 29 aromatic protons in the region of  $\delta$  6.6–8.2, a signal for the olefinic hydrogen atom at  $\delta$  5.60 (dd, 1 H, J = 7.3 Hz, J =2.5 Hz), and two signals for the methylene protons at  $\delta$ 4.38 (ddd, 1 H) and 4.68 (ddd, 1 H). The <sup>31</sup>P NMR spectrum exhibits two doublet signals at  $\delta$  210.3 and 16.5 with splitting  $J_{PP} = 24.8$  Hz, which indicates the transformation of the dppm ligand into the phosphido-phosphine ligand during the formation of complex 1.

The IR spectrum  $(CH_2Cl_2)$  showed the presence of terminal CO groups (v(CO)/cm<sup>-1</sup>: 2030 m, 2005 s, 1983 s, 1973 sh, 1941 m, and 1921 m), and weak absorption at 1533 cm<sup>-1</sup> characteristic of the ketone group coordinated with the metal atom<sup>2</sup> was also observed.

According to the X-ray diffraction analysis data, the crystals of complex 1 are monoclinic, at T = 293 K a =14.672(6) Å, b = 20.397(6) Å, c = 15.551(5) Å,  $\beta =$ 104.54(3)°, V = 4505(3) Å<sup>3</sup>, Z = 4,  $d_{calc} = 1.672$  g cm<sup>-3</sup>, space group  $P2_1n$ , 12022 independent reflections,  $R_1 =$ 0.0595 for 7761 observed reflections with  $I = 2\sigma(I)$ , three ruthenium atoms are arranged in an open fashion (the Ru(1)-Ru(2) and Ru(2)-Ru(3) bond lengths are equal to 2.778(1) and 3.028(1) Å, respectively; the Ru(1)-Ru(2)-Ru(3) angle is equal to  $102.09(3)^{\circ}$ , and the nonbonding Ru(1)...Ru(3) distance is equal to 4.517(1) Å), and each ruthenium atom coordinates two terminal CO groups (Fig. 1). The complex organic ligand bound to three ruthenium atoms is formed upon coupling of dehydrobenzene (derived from dppm), CO, and metallated enyne and can be considered as an indenone derivative (one of the ethylene hydrogen atoms of the starting enyne is replaced by the Ru(1) atom, and the second hydrogen atom is at C(8)). The Ru(1)atom forms a  $\sigma$ -bond with the ethylenic C(7) atom with a distance of 2.070(5) Å; the same atom coordinates the oxygen atom of the ketone group (Ru(1)-O(7) 2.133(3))A) and phosphinic P(1) atom of the phosphido-phosphine ligand (Ru(1)-P(1) 2.410(1) Å). The phosphidic P(2) atom serves as a bridge between the Ru(2) and

Translated from Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 6, pp. 1206-1207, June, 1999.

1066-5285/99/4806-1192 \$22.00 © 1999 Kluwer Academic/Plenum Publishers