In the present work we report a new highly effective phase transfer nitration catalyst, mercury-containing macrocycle **2**, which is able also to bind the halide anions with formation of complexes.

In the typical experiment, to 5.8 mL of 0.23 *M* solution of acenaphthene in a benzene—nitrobenzene mixture (100 : 8.4 v/v) 0.008 g of **2** and 2.5 mL of 21.3 % HNO_3, containing NaCl (0.75 mol per mol of HNO_3) were added. Then to the reaction mixture, $NaNO_3$ (0.034 mol per mol of HNO_3) was introduced and vigorous stirring at 21 ± 1°C was started.

In the course of the reaction, rapid nitration of acenaphthene was observed, leading to the formation of 5-nitro- and 3-nitro-derivatives (in the ratio of (90—93) : (10—7)), the yield of which after ~10 min was almost quantitative (98%). Under similar conditions, but in the absence of **2**, the convertion of acenaphthene to nitroproducts did not exceed 1 % even after 2 h. According to the kinetic data, compound **2** increases the initial rate of acenaphthene nitration (determined by the slope of the tangent to the initial area of the kinetic curve) by 3300 times.

An important feature of **2**, distinguishing it from **1**, is that in this case acenaphthene nitration also proceeds without NaCl, although at a lower rate. The yield of nitroproducts under such conditions reaches ~100 % only after 2 h. However, if 31.2 % HNO_3 is used instead of 21.3 % HNO_3, the process of nitration is finished quantitatively after 3 min. Thus, one can suppose, that **2**, in contrast to **1**, coordinates efficiently enough not only chloride, but also nitrate anions. This assumption conforms with the fact that macrocycle **2**, in contrast to **1**,[3] is able to transfer protons into the benzene phase both from the aqueous solutions of hydrochloric acid and from the aqueous solutions of nitric acid. This transfer of proton into the organic phase can be monitored by the change in the color of the benzene layer, which contains dissolved triphenylcarbinol, from colorless to yellow due to formation of triphenylmethyl cation.

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Reaction of 1,4-diphenylbut-1-en-3-yne with $Ru_3(CO)_{12}$. Crystal structure of $Ru_3(CO)_8\{\mu_3\text{-}2\eta^1\text{-}\eta^4\text{-}\eta^2\text{-}PhCH{=}CHC{=}C(Ph)C(Ph){=}CCH{=}CHPh\}$

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In continuation of systematic investigations of reactions of heteroatom-substituted and functionalized alkynes with metal carbonyl clusters, we initated a study of the behavior of enynes in these reactions. Our interest in enynes is due to the fact of their participation as intermediates in the oligomerization/cyclization reactions of alkynes promoted by metal complexes; moreover, the presence of an olefinic bond in enynes offers

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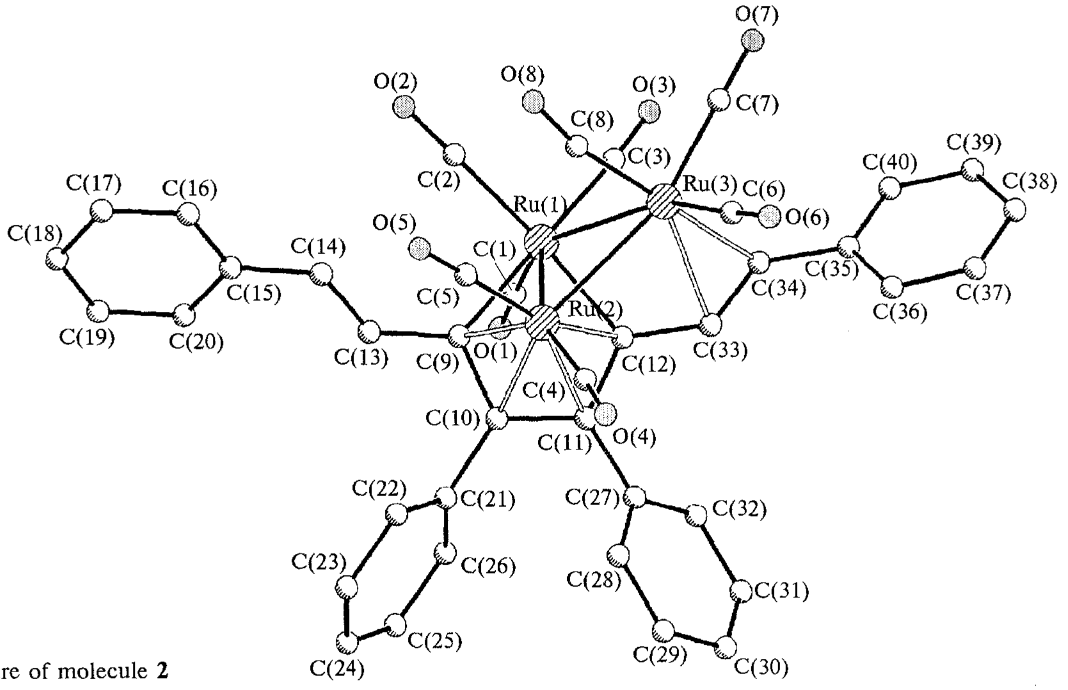

Fig. 1. Structure of molecule **2**

additional possibilities, in compaison to simple alkynes, for coordination with metal atoms in clusters and for carbon-carbon bond formation.

The reaction of an excess of *trans*-PhCH=CHC≡CPh (**1**) with $Ru_3(CO)_{12}$ in boiling hexane gives ~50 % yield of the unusual cluster $Ru_3(CO)_8(PhCH{=}CHC_2Ph)_2$ (**2**) along with bi- and trinuclear complexes of well known types with a dimerized alkyne ligand. The ^1H NMR spectrum of **2** in acetone-d_6 indicates the π-coordination to one of the olefin groups of the dimerized ligand with a ruthenium atom: δ 5.13 (d, J_{H-H} = 12.3 Hz, 1 H), 5.32 (d, J_{H-H} = 12.3 Hz, 1 H), 6.87 (d, J_{H-H} = 15.7 Hz, 1 H), 7.28 (d, J_{H-H} = 15.7 Hz, 1 H), 7.1—7.4 (m, 20 H) (in starting enyne **1** the signals of olefin protons appear at δ 6.56 and 7.09 ppm, each as a doublet with J = 16.3 Hz).

According to the results of X-ray analysis (293 K, λMo*K*α, space group *C*2/*c*, $Z = 8$, $R = 0.043$ for 7566 reflexions with $I \geq 2\sigma(I)$) molecule **2** (Fig. 1) includes a triangle of ruthenium atoms, two of which coordinate three CO ligands, while the third one coordinates two CO, and a hydrocarbon ligand, formed by the "head-to-head" coupling of two molecules of enyne **1**.

The hydrocarbon ligand is bound to the Ru_3-framework in a complicated way : C(9) and C(12) atoms form σ-bonds with Ru(1) atom, giving a ruthenacyclopentadiene ring. The diene fragment C(9)C(10)C(11)C(12) of this ring is π-coordinated with the Ru(2) atom; finally, olefinic atoms C(33) and C(34) form a π-bond with the Ru(3) atom.

The side-on μ-$2\eta^1$-η^4-coordination of the metallacyclopentadiene fragment observed in molecule **2** is typical for trinuclear osmium clusters with a dimerized alkyne ligand; an alternative μ_3-$2\eta^1$-$2\eta^2$-bonding was only recently established for the $Os_3(CO)_9\{\mu_3\text{-}2\eta^1\text{-}2\eta^2\text{-}C(SiMe_3)C(Me)C(H)C(Ph)\}$ complex[6].

However, in contrast to other trinuclear complexes with a μ-$2\eta^1$-η^4-coordinated metallacyclopentadiene fragment which contains the $M(CO)_4$ unit in cluster **2** one CO group of the unit indicated is substituted by a π-ethylene group C(33)=C(34) of dimerized ligand.

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