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# Synthesis and Catalytic Properties of Niobium Indenyl Peroxo Complexes

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**Abstract**—Synthesis of four niobium sandwich peroxo complexes containing fragments of substituted indenes was performed and their structure was proved by NMR spectroscopy and ESI-MS mass spectrometry. Catalytic activity of the complexes in the oxidation of sulfides with hydrogen peroxide was studied, and a high selectivity in the oxidation of sulfides to sulfoxides and sulfones of the sandwich peroxo complexes was found.

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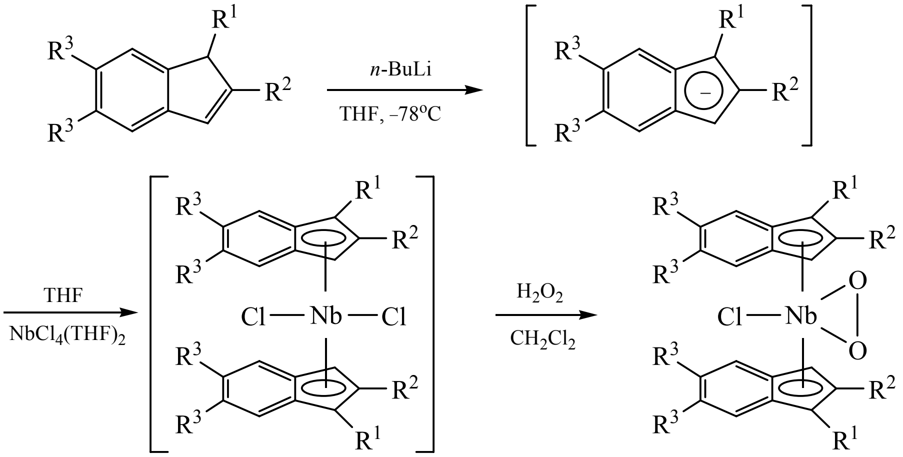
A large class of transition metal complexes are sandwich complexes of titanium, zirconium, niobium, and vanadium with ligands containing fragments of cyclopentadiene and its derivatives [1, 2]. Many of these complexes are able to catalyze various organic reactions with high efficiency and selectivity [3]. Among these reactions a significant synthetic value belongs to the oxidation reaction opening a way to the direct asymmetric synthesis of optically active oxygen- and sulfur-containing compounds [1, 2].

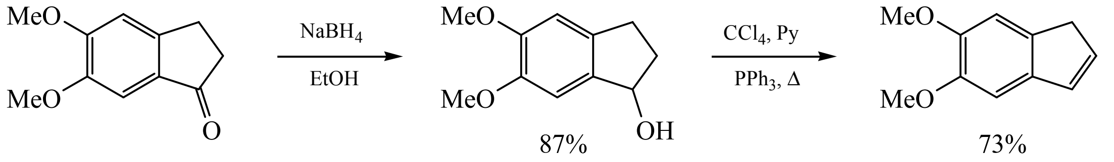
The aim of this work was to obtain niobium indenyl peroxo complexes with different structures and to use them as catalysts of oxidation of some organosulfur compounds with peroxides.

The niobium peroxo complexes with different indenyl ligands were obtained according to the following scheme:



**I**, $R^1 = H$, $R^2 = H$, $R^3 = H$ (31%); **II**, $R^1 = Ph$, $R^2 = H$, $R^3 = H$ (37%); **III**, $R^1 = H$, $2R^2 = (CH_2)_2$, $R^3 = H$ (38%); **IV**, $R^1 = H$, $R^2 = H$, $R^3 = OMe$ (50%).

The starting substances were commercially available indenes with substituents in the five-membered ring, as well as 5,6-dimethoxyindene synthesized specially from the available 5.6-dimethoxyindanone [4, 5].



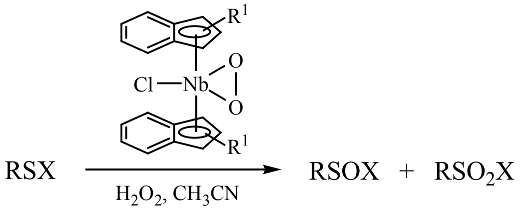
In the first stage of the reaction, the action of *n*-BuLi on the substituted indene leads to the formation of a yellow solution of the salt, which at the action of $NbCl_4(THF)_2$ followed by addition of 37% hydrogen peroxide affords sandwich niobium peroxo complexes **I–IV** as pale yellow powders via the intermediate halogenated complexes.

The synthesized niobium peroxo complexes are unstable in air and suffer gradual decomposition. Study of the complexes by NMR spectroscopy shows a downfield shift of proton signals and change in their multiplicity, which confirms the formation of metallocene complexes of sandwich type. The disappearance of the signals of protons of the indene $CH_2$ fragments and comparison of chemical shifts with literature data allowed a reliable identification of the compounds [3].

An additional information about the structure of the synthesized peroxo complexes **I–IV** was obtained using ESI-MS (electrospray ionization mass spectrometry). A characteristic feature of the mass spectrum of each peroxo complex is a peak of the cation formed at the cleavage of the chloride anion from the parent peroxo complex molecule (see the table).

As an example, the figure shows the mass spectrum of the peroxo complex **II**. The presence of low-intensity ion peaks is due to the instability of the indenyl peroxo complexes under the analysis conditions. A similar pattern is typical of the mass spectra of the other peroxo complexes.

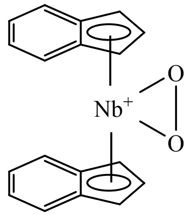
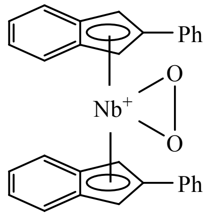
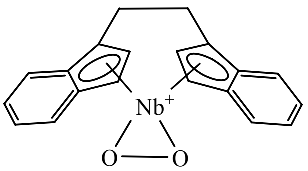
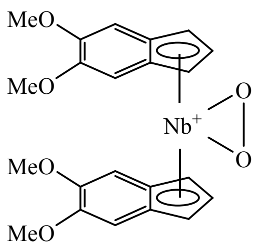
As the model substances for the study of catalytic activity of indenyl niobium peroxo complexes methyl phenyl sulfide, benzothiophene, and dibenzothiophene were taken. Such a choice of the objects originates from the difference in the reactivity of these sulfides in the oxidation reaction ranging from the readily oxidized methyl phenyl sulfide to difficultly oxidized benzo- and dibenzothiophenes.

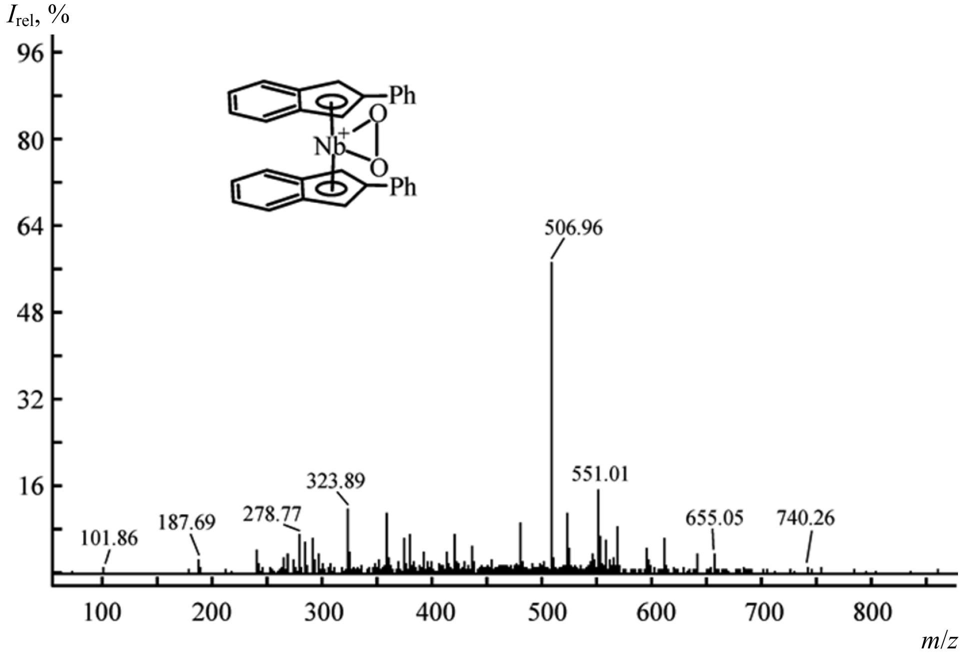


The oxidation of sulfides by hydrogen peroxide was carried out in acetonitrile at 70°C for 4 h. The composition of the formed mixture was analyzed by gas-liquid chromatography. Benzo- and dibenzothiophenes are practically not oxidized in these conditions, in contrast to methyl phenyl sulfide, which is oxidized to 96–100%.

| Peroxo complex | Yield, % | |
|---|---|---|
| | PhSOMe | $PhSO_2Me$ |
| **I** | 97 | 3 |
| **II** | 100 | 0 |
| **III** | 3 | 97 |
| **IV** | 96 | 4 |

The ESI–MS mass spectrometry data of indenyl peroxo complexes

| Comp. no. | Ligand | Ion | *m*/*z* |
|---|---|---|---|
| **I** | Indene |  | 355 |
| **II** | 2-Pheylindene |  | 507 |
| **III** | 1,2-Bis(1-indenyl)ethane |  | 381 |
| **IV** | 5,6-dimethoxyindene |  | 475 |



Mass spectrum of bis[$\eta^5$-(2-phenylindenyl)]chloroniobium(V)peroxide **II**.

Attention is attracted by the selectivity of oxidation of methyl phenyl sulfide in the presence of peroxo complexes of different structures. The complexes with the ligands that are separate indenyl fragments lead to MeSPh oxidation to sulfoxide, while the peroxo complex **III** with bis-indenyl ligand catalyzes the oxidation to sulfone. The presence of substituents not binding two indenyl moieties does not affect the selectivity or the rate of the methyl phenyl sulfide oxidation. Apparently, the presence of short $–(CH_2)_2–$ fragment makes the catalytic center of the peroxo complex **III** more sterically accessible, which increases its catalytic activity.

The data on the composition of oxidation products indicate that the nature of the indenyl peroxo complex plays an important role in the oxidation process. The high selectivity of the peroxo complexes makes it possible to expect that other complexes with rigidly connected ligands may lead to new highly selective catalytic systems.

## EXPEIMENTAL

The $^1$H NMR spectra were recorded on a Bruker DRX-400 spectrometer with the operating frequency 400 MHz, solvent $CDCl_3$, internal reference HMDS. Chemical shifts were measured with an accuracy of 0.01 ppm. The ESI-MS spectra were recorded on an Agilent LC/MS 1100 SL instrument in the electrospray ionization (ESI) mode of the sample ionization and with the registration of positive ions. The samples were prepared as solutions in chloroform (LS MS grade, Aldrich), the concentration 1 mg ml$^{-1}$. Conditions of analysis: flow rate 0.5 ml min$^{-1}$, pressure 50 psi, temperature 150°C, drying gas flow 12 l min$^{-1}$, voltage 4500 V.

The composition of reaction products and the purity control of the starting materials were monitored by the gas-liquid chromatography (GLC) on a Kristall-2000M chromatograph with a flame ionization detector, column Zebron, $l$ = 30 m, $d$ = 0.32 mm, the liquid phase ZB-1, ramp from 100 to 250°C.

**Synthesis of the niobium indenyl peroxo complexes I–IV.** A substituted indene (0.86 mmol) was dissolved in 2.6 ml of THF, the mixture was cooled to –78°C, and 0.6 mmol of 2.5 M *n*-BuLi in heptane was added. The resulting yellow solution was stirred for 30 min. Then 0.43 mmol of complex $NbCl_4(THF)_2$ (0.86 mmol in the case of compound **III**) dissolved in THF was added dropwise, the mixture was stirred at room temperature for 3 h. The resulting solution was evaporated to dryness on a rotary evaporator. The resulting product was dissolved in 6 ml of $CH_2Cl_2$ in a dry box, and 12 ml of hexane was added, the separated precipitate was filtered off, the organic phase was evaporated to dryness at 30°C. The resulting yellow material was dissolved in 6 ml of $CH_2Cl_2$, and 7.21

mmol of 37% $H_2O_2$ was added dropwise to the solution. After 30 min, to the resulting yellow-orange solution was added 5 ml of water, the organic layer was separated and dried over $Na_2SO_4$. After the evaporation of solvent the target peroxo complexes were isolated as pale yellow powders. Yields of the peroxo complexes **I–IV** were 31, 37, 38, and 50% respectively.

**Compound I.** $^1$H NMR spectrum ($CDCl_3$, 400 MHz): δ 7.44 m (8H, $H_{Ar}$), 5.39 m (2H, $H_{Cp}$), 5.22 m (2H, $H_{Cp}$), 4.40 (dd, 2H, $H_{Cp}$). ESI mass spectrum: *m*/*z* 355 [$M^+ - Cl^-$].

**Compound II.** $^1$H NMR spectrum ($CDCl_3$, 400 MHz): δ 7.84 m (4H, $H_{Ar}$), 7.74 d (2H, $H_{Ar}$), 7.54 d (2H, $H_{Ar}$), 7.58 m (4H, $H_{Ar}$), 7.00 m (2H, $H_{Ar}$), 6.81 m (4H, $H_{Cp}$), 5.56 s (2H, $H_{Cp}$), 5.01 s ( 2H, $H_{Cp}$). ESI mass spectrum: *m*/*z* 507 [$M^+ - Cl^-$].

**Compound III.** $^1$H NMR spectrum ($CDCl_3$, 400 MHz): δ = 7.69 m (4H, $H_{Ar}$), 7.52 m (4H, $H_{Ar}$), 7.52 m (4H, $H_{Ar}$), 4.20 m (4H, $H_{Cp}$) 3.33 s (4H, $CH_2$). ESI mass spectrum: *m*/*z* 381 [$M^+ - Cl^-$].

**Compound IV.** $^1$H NMR spectrum ($CDCl_3$, 400 MHz): δ 7.22 s (2H, $H_{Ar}$), 7.16 s (2H, $H_{Ar}$), 5.25 d (2H, HSr), 5.02 d (2H, $H_{Cp}$) 4.35 m (2H, $H_{Cp}$), 3.90 s (3H, $CH_3$), 3.89 s (3H, $CH_3$).

ESI mass spectrum: *m*/*z* 475 [$M^+ - Cl^-$].

**Oxidation of sulfides by hydrogen peroxide in the presence of the $Nb^{5+}$ indenyl peroxo complexes.** Under argon, to a solution of 0.8 mmol of sulfide in 5 ml of $CH_3CN$ was added 0.066 ml of 37% $H_2O_2$ and 0.008 mmol of a $Nb^{5+}$ peroxo complex. The reaction mixture was kept for 4 h at 70°C, and then cooled. Excess hydrogen peroxide was neutralized by adding sodium thiosulfate, the solution was dried over $Na_2SO_4$, filtered and evaporated. The reaction products were analyzed by GLC.

## ACKNOWLEDGMENTS

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