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Reaction of Nitrous Oxide with Cyclopentadienyl Complexes of Cobalt, Rhodium, and Titanium[*]

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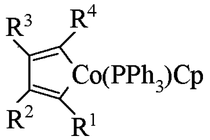
Abstract—The reaction of nitrous oxide with some cyclopentadienyl compounds of cobalt, rhodium, and titanium was studied. The corresponding furans were obtained in low to moderate yields.

We reported lately that reaction of 1-cyclopentadienyl-1-triphenylphosphine-2,3,4,5-tetraphenylcobaltacyclopenta-2,4-diene (**Ia**) with N_2O yielded substituted furan derivatives and but-2-ene-1,4-dione [1]. In this study within the framework of our systematic investigation we carried out reactions of nitrous oxide with some cyclopentadienyl complexes of cobalt (**Ib–d**), rhodium (**II**), and titanium (**III**). This class of organometallic compounds is frequently used as starting materials for preparation of a wide variety of 5- and 6-membered heterocyclic compounds [2], but the reaction of these metallocycles with the nitrous oxide was not investigated before.

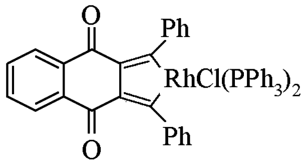
Reaction of complexes **Ib**–**d, II, III** with nitrous oxide

Compd. no.	Conditions	Reaction products
Ib	80°C	**Ib**, 25%; 3,4-dimethyl-2,5-diphenylfuran, 20%, mp 113–114°C (publ. mp 115–116°C [20]); $OPPh_3$, 72%
Ic	80°C	**Ic**, 17%; 3,4-dimethoxycarbonyl-2,5-diphenylfuran, 35%, mp 79–81°C (publ. mp 83–84°C [21]); $OPPh_3$, 82%
Id	80°C	**Id**, 16%; 3,5-dimethoxycarbonyl-2,4-diphenylfuran, 35%, mp 92–94°C; $OPPh_3$, 80%
II	130°C	1,3-Diphenylbenzo[*f*]isobenzofuran-4,9-dione, 15%, mp 219–221°C (publ. mp 220–222°C [18]); $OPPh_3$, 80%
III	130°C	2,3,4,5-Tetraphenylfuran, 29%, mp 169–170°C (publ. mp 169–171°C [22])

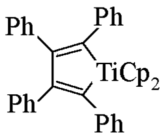


Ia–d

$R^1 = R^2 = R^3 = R^4 = Ph$ (**Ia**); $R^1 = R^4 = Ph, R^2 = R^3 = Me$ (**Ib**); $R^1 = R^4 = Ph, R^2 = R^3 = CO_2Me$ (**Ic**); $R^1 = R^3 = CO_2Me, R^2 = R^4 = Ph$ (**Id**).



II



III

The reduction of N_2O by solutions of low-valence complexes of transition metals was first described in [3]. Later on quite a number of titanium, chromium, vanadium, tin, and zirconium compounds [4–6] with terminal or bridging oxygen atoms was prepared with the use of nitrous oxide as oxygen donor. Besides it was possible in the presence of cobalt, molybdenum, and ruthenium complexes [7–9] to effect oxygen transfer from N_2O to triphenylphosphine and styrene. Johnson *et al.* [10] recently reported on an unusual reaction between N_2O and $Mo(N[R]Ar)_3$ with the rupture of the N≡N bond in the nitrous oxide resulting in formation of nitride Mo≡N and nitrosyl Mo=N=O complexes. Up till now this is a single example of such N_2O reaction with a metallocomplex. The reaction of $(\eta^5\text{-}C_5Me_5)_2M(RC{\equiv}CR)$ (M = Zr, Ti) with nitrous oxide gives rise to an oxometallocyclobutene derivative and molecular nitrogen, but an intermediate complex where N_2O inserted into the M–C bond to form a five-membered metallocycle was

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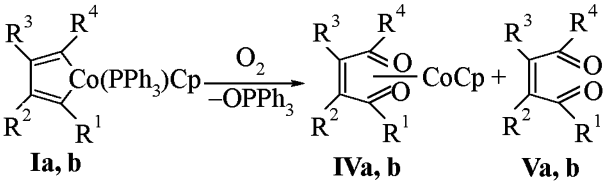
isolated and characterized [11]. It is also known that a simple saturation with the nitrous oxide of a solution of $[Ru(NH_3)_5(H_2O)]^{2+}$ resulted in a complex $[Ru(NH_3)_5(N_2O)]^{2+}$ where N_2O plays the role of a ligand [12].

In the course of our study were obtained the corresponding furans in low to moderate yields in reactions between the metal complexes **Ib–d, II, III** and nitrous oxide. We did not detect any nitrogen-containing compounds. Note that under the applied conditions N_2O as potential oxygen donor in the reaction of furan synthesis from rhodium complex **II** apparently is no better than commonly used molecular oxygen or hydrogen peroxide [13]. Our data on reaction with cyclopentadienyl compounds of cobalt **Ib–d** should be compared with investigation published by Wakatsuki and Yamazaki [14]. There was studied thermal and photochemical reaction of complexes **Ia, b** with molecular oxygen that afforded as main products dione complex **IVa, b** and dibenzoylstilbene (**Va**) or 2,3-dibenzoylbut-2-ene (**Vb**). The reaction scheme is as follows:



Ia, b   **IVa, b** 10–30%   **Va, b** 20–80%

It was presumed [14] that the thermal reaction (70°C, 2–8 h) proceeded via dissociation of the phosphine ligand followed by coordination of the oxygen molecule at the vacant place in the cobalt coordination sphere. As photochemical reaction (under the light of a high pressure mercury lamp, 15°C, 8–9 h) the process may occur as phosphine–oxygen exchange or along the mechanism of [4+2]-cycloaddition with participation of the forming singlet oxygen acting as a reactive dienophile. With nitrous oxide we failed to observe any dione complexes apparently due to the used microamounts. However it is well known that the reaction of but-2-ene-1,4-diones with PPh_3 under mild conditions affords the corresponding furans [15]. We did not try to carry out our reaction under photochemical conditions, but it should be mentioned that N_2O photolysis was a convenient method for preparation of oxygen atoms $O(^3P)$ [16]. The mechanism of reactions between cyclopentadienyl compounds of cobalt and nitrous oxide requires further investigation.

EXPERIMENTAL

Compounds **Ib–d, II, III** were prepared along the published procedures [17–19]. The process of experiment is described with **Ib** complex. All the data obtained are presented in the table.

Reaction of N_2O with cobalt complex Ib. A solution of complex **Ib** (0.25 g, 0.4 mmol) in 10 ml of benzene was charged into a reactor. On cooling the bottom of the reactor we condensed thereto about 5 ml of nitrous oxide. The reaction was carried out for 6 h at 80°C. The reaction mixture was separated by column chromatography on neutral alumina, Brockmann activity **II** grade. By gradient elution with hexane–ethyl acetate mixture we separated and identified the following compounds: initial complex **Ib** (0.06 g, 0.1 mmol); 3,4-dimethyl-2,5-diphenylfuran (0.02 g, 0.08 mmol); triphenylphosphine oxide (0.08 g, 0.3 mmol).

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