*Russian Journal of General Chemistry, Vol. 71, No. 6, 2001, pp. 905–906. Translated from Zhurnal Obshchei Khimii, Vol. 71, No. 6, 2001, pp. 964–965.*
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# Reaction of Nitrogen(I) Oxide with Nitrogen-fixing Systems on the Basis of Lithium, Chlorotrimethylsilane, and Transition Metal Compounds

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Received February 1, 2000

**Abstract**—Reaction of nitrogen(I) oxide with nitrogen-fixing systems Li/$Me_3SiCl/MCl_n$ ($MCl_n$ = $CrCl_3$, $CoCl_2$, $Cp_2TiCl_2$, $FeCl_3$, $CuCl_2$) was studied. In these systems nitrogen(I) oxide, molecular nitrogen, and air nitrogen undergo reductive silylation to tris(trimethylsilyl)amine. The efficiency of the process was estimated by the molar ratio of the tris(trimethylsilyl)amine formed to metal chloride $MCl_n$. The reaction of $N_2O$ with the nitrogen-fixing systems including $CoCl_2$ and $Cp_2TiCl_2$ is not exhausted by the reduction of the former to molecular nitrogen and its subsequent fixation by transition metal complexes.

Fixation of molecular nitrogen under mild conditions is one of the fundamental problems of modern chemistry [1]. The discovery by Vol'pin and Shur of the ability of transition metal compounds to fixing nitrogen gave rise to the development of a great variety of nitrogen-fixing systems. However, reaction of $N_2O$ with synthetic nitrogen-fixing systems has not yet been studied. The principle possibility of such reaction follows primarily from the fact that molecular nitrogen is formed by reduction of $N_2O$ in the coordination sphere of the metal. The formation of a series of dinitrogen transition metal complexes by such reductions has been reported. Thus, for instance, $(Cp)\cdot Re(CO)_2N_2$ is readily formed by the reaction of $(Cr)Re(CO)_2(THF)$ with $N_2O$ [2], $CoH(N_2)(PPh_3)_3$ can be obtained from $CoH_3(PPh_3)_3$ (in the presence of $PPh_3$ which reduces $N_2O$, thereby being oxidized to triphenylphosphine oxide) [3], and $[Ru(NH_3)_5N_2]^{2+}$, from $[Ru(NH_3)_5(H_2O)]^{2+}$ ($N_2O$ is reduced with Zn/Hg, $Cr^{2+}$, or $V^{2+}$) [4]. In the latter work the intermediate ruthenium nitrogen(I) oxide complex $[Ru(NH_3)_5\cdot(N_2O)]^{2+}$ could also be isolated [4].

On the other hand, coordination and activation of nitrogen(I) oxide followed by N–N bond clevage must not be ruled out. Laplaza *et al.* [5] showed that $N_2O$ reacts with molybdenum complexes $Mo(NRAr)_3$ [R = $C(CD_3)_2CH_3$, Ar = 3,5-$C_6H_5Me_2$] to give the corresponding nitride $N{\equiv}Mo(NRAr)_3$ and nitrosyl $O{=}N{-}Mo(NRAr)_3$ complexes.

The aim of the present work was to study reaction of nitrogen(I) oxide with nitrogen-fixing systems Li/$Me_3SiCl/MCl_n$ ($MCl_n$ = $CrCl_3$, $CoCl_2$, $Cp_2TiCl_2$, $FeCl_3$, and $CuCl_2$), since it is these systems which, among a great variety of related systems, are capable of fixing molecular nitrogen at room temperature and atmospheric pressure [6–8].

$$\mathrm{Li/Me_3SiCl/MCl}_n + \mathrm{N_2} \longrightarrow \mathrm{(Me_3Si)_3N} + \mathrm{M{-}N(SiMe_3)}_n.$$

The reactions were performed by the following procedure. A mixture of 33 mmol of lithium granules (0.3–0.8 mm in diameter), 33 mmol of chlorotrimethylsilane, and 0.66 mmol of $MCl_n$ in 10 ml of THF was stirred at room temperature under nitrogen, air, or nitrogen(I) oxide for 24 h, after which a sample was taken and analyzed by GLC. The main by-products were always hexamethyldisilane and hexamethyldisiloxane. The efficiency of nitrogen fixation from all the three gases was estimated by the molar ratios of formed amine **I** to taken transition metal chloride $MCl_n$. The resulting data are given in the table.

As seen from the table, all the metal chlorides, except for copper(II) chloride, in the reductive system

Efficiency of nitrogen fixation by systems Li/$Me_3SiCl/MCl_n$

| $MCl_n$ | Air nitrogen | Nitrogen | $N_2O$ |
|---|---|---|---|
| $CrCl_3$ | 0.6 | 3.0 | 0.7 |
| $CoCl_2$ | 0.6 | 0.8 | 1.6 |
| $Cp_2TiCl_2$ | 0.6 | 0.8 | 1.6 |
| $FeCl_3$ | 0.5 | 0.6 | 0.3 |
| $CuCl_2$ | 0 | 0 | 0 |

$Li/Me_3SiCl/MCl_n$ are capable to effect conversion of of nitrogen to tris(trimethylsilyl)amine (**I**), using as substrates molecular nitrogen, air, or $N_2O$. Such reaction with nitrogen has first been described by Shiina [6], and our results are in general agreement with his data. Oxygen reduces the yields of the nitrogen reduction reactions by destroying the reductive systems [9, 10]. In our case the effect of oxygen on the nitrogen-fixing systems is that it reduces the activity of the transition metal compounds, thus limiting the nitrogen conversion by 0.5–0.6. Interesting results were obtained in experiments with nitrogen(I) oxide. In the systems including $CoCl_2$ and $Cp_2TiCl_2$, twice as much amine **I** is formed, when the source of nitrogen is $N_2O$ rather than molecular nitrogen. We consider this result as clear evidence against primary formation of nitrogen from nitrogen(I) oxide and in favor of another mechanism of tris(trimethylsilyl)-amine formation in this case. More probably that here coordination and activation of $N_2O$ with transition metal complexes occurs, like with the ruthenium complexe $[Ru(NH_3)_5(N_2O)]^{2+}$ [4]. After that dinitrogen complexes are formed under the action of chlorotrimethylsilane and with N–O bond cleavage, which further undergo reductive silylation. Oxygen transfer from nitrogen is facilitated by the high affinity of oxygen to silicon and is accompanied by abundant polysiloxane formation. The poor activity of nitrogen-fixing systems on the basis of chromium(III) and iron(III) chlorides with respect to nitrogen(I) oxide is probably associated with the intrinsic oxidative activity of $N_2O$.

## EXPERIMENTAL

All operations were performed with dry gases. Nitrogen(I) oxide was of medical grade. Tetrahydrofuran and chlorotrimethylsilane were distilled under argon over lithium aluminum hydride and calcium carbide, respectively. The other reagents were purified, when required, by known procedures. Chromatography was perfomed on a Chrom-5 chromatograph (carrier gas nitrogen, flame-ionization detector, column 3000 × 3 mm, packing 15% SE-30 on Spherone, injector temperature 230°C, oven temperature 100°C, and detector temperature 150°C). Tris(trimethylsilyl)amine (**I**) was synthesized by the procedure described in [11].

**Reaction of air, nitrogen, and nitrogen(I) oxide with nitrogen-fixing systems $Li/Me_3SiCl/MCl_n$.** Transition metal salt, solvent, and chlorotrimethylsilane were placed in a Schlenk vassel (50 ml) filled with one of the gases, and the mixture was stirred under the same gas, filtered, the precipitate was washed with hexane, and the filtrate was reduced to required volume and analyzed by GLC.

## ACKNOWLEDGMENTS

The work was financially supported by the Russian Foundation for Basic Research (project no. 99-03-33055).

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