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Mendeleev Commun., 2012, **22**, 70–72
Mendeleev Communications

Co^{II} complex of *N*-[2-(phenylseleno)cyclohexyl]-*N*-(pyridin-2-ylmethylene)amine: synthesis, electrochemistry and catalysis of triphenylphosphine and norbornene oxidation by nitrous oxide

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DOI: 10.1016/j.mencom.2012.03.005

The selenoorganic ligand *N*-[2-(phenylseleno)cyclohexyl]-*N*-(pyridin-2-ylmethylene)amine and its coordination compound with $CoCl_2$ have been obtained and investigated by cyclic voltammetry. The oxidation reactions of triphenylphosphine and norbornene using N_2O as the oxidant and the synthesized complex as a catalyst are described.

Nitrous oxide (N_2O) is thermodynamically powerful oxidant. The oxidation of organic compounds by N_2O is thermodynamically favourable but extremely slow except for high temperatures.[1] Alkenes and alkynes can be oxidized by N_2O, however, the reactions required temperatures of at least 200 °C.[2,3] Some small secondary alcohols and primary amines were oxidized by N_2O at room temperature in the presence of platinum black.[4] Meantime, there is almost no information on the low-temperature oxidation of organic functional groups by N_2O. The high-temperature heterogeneously catalyzed oxidation of benzene to phenol[5] and the oxidation of phosphines by supercritical N_2O at 100 °C without catalyst[6] were described.

The low-temperature oxidation of inorganic compounds by N_2O has been more fully explored. For example, the catalyzed oxidation of CO[7–9] and low-valent organometallic complexes[10–16] have been investigated.

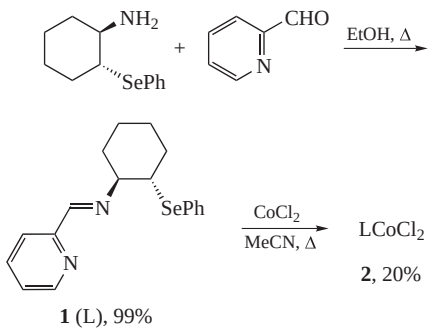
Nitrous oxide is an under-utilized by-product of chemical processes involving nitric acid. The attractive option for N_2O is its use as an oxidant for organic compounds from the viewpoint of green chemistry, nitrous oxide would be preferable to many other oxidants because the only by-product is N_2.

Obviously, the success of N_2O application depends on finding a proper catalyst and some attempts were assumed. Thus, the heterogeneous catalytic oxidation of benzene into phenol by N_2O has been reported.[5]

Although N_2O reacts with several metal complexes, it is generally regarded as kinetically inert toward reduction and a poor ligand.[17] Despite current interest in transition metal-mediated N_2O activation, only small numbers of metal complexes containing the N_2O ligand with Ru[18–21] and Fe[22] have been identified.

Earlier, we synthesized a Co^{II} complex with 3-phenyl-5-(2-pyridinemethylene)-2-thiohydantoin ligand,[23] which manifested capability to react with N_2O and catalyzed the oxidation of alkenes and phosphines.[24] Here we describe new selenoorganic ligand **1**, its coordination compound with $CoCl_2$ **2** and the capability of complex **2** to activate nitrous oxide in oxidation reactions with triphenylphosphine and norbornene.

Compound **1** was synthesized by *trans*-2-(phenylseleno)-cyclohexylamine[25] interaction with pyridine-2-carboxaldehyde in an almost quantitative yield.† Complex **2** precipitated after boiling ligand **1** with an equimolar amount of cobalt(II) chloride for 4 h (Scheme 1).‡



Scheme 1

Compounds **1** and **2** were studied by cyclic voltammetry (CV) and rotating disk electrode (RDE) techniques at a glass carbon (GC) electrode in DMF.§ The electrochemical oxidation and reduction potentials are given in Table 1.

† N-*[2-(Phenylseleno)cyclohexyl]*-N-*(pyridin-2-ylmethylene)amine* **1**. The solution of 0.13 g (0.5 mmol) of *trans*-2-phenylselenocyclohexylamine and 0.05 g (0.5 mmol) of pyridine-2-carboxaldehyde in EtOH (7 ml) was boiled for 3 h. After removing the solvent in a vacuum, 0.17 g (99%) of compound **1** as brown oil was obtained. ^{1}H NMR ($CDCl_3$) δ: 8.59 (d, 1H, Py, *J* 4.1 Hz), 8.35 (s, 1H, HC=N), 7.80 (d, 1H, Py, *J* 7.8 Hz), 7.62 (dt, 1H, Py, J_1 1.2 Hz, J_2 7.8 Hz), 7.47 (m, 2H, Ph), 7.24 (ddd, 1H, Py, J_1 1.2 Hz, J_2 4.1 Hz, J_3 7.8 Hz), 7.14 (m, 3H, Ar), 3.46 (ddd, 1H, HCN, J_1 4.1 Hz, J_2 9.7 Hz, J_3 13.7 Hz), 3.33 (dt, 1H, HCSe, J_1 4.1 Hz, J_2 9.7 Hz), 2.21 (d, 1H, HC^3, *J* 4.1 Hz), 1.75 (m, 4H, HC^6, HC^3, HC^4), 1.55 (m, 1H, HC^5), 1.38 (m, 2H, HC^5, HC^4). MS (MALDI), *m*/*z*: 344 (M^+).

‡ *Complex* **2**. To the solution of compound **1** (0.14 g, 0.3 mmol) in 3 ml of MeCN, $CoCl_2$ (0.038 g, 0.3 mol) in 5 ml of MeCN was added. The mixture was boiled for 4 h; then, the solution was cooled to room temperature, and the precipitate was filtered off, washed with Et_2O and dried in air. Complex **2** (0.027 g, 20%) was obtained as brown powder, mp 140 °C. IR (Nujol, ν/cm^{-1}): 1630 (C=N), 1600 (C=C), 1570 (C=C). UV-VIS [DMF, λ/nm (ε/dm^3 mol^{-1} cm^{-1})]: 325.5 (37518), 372.0 (25655), 498.5 (437), 660.0 (176). MS (MALDI), *m*/*z*: 438 (M^+).

§ Electrochemical studies were carried out on a PI-50-1.1 potentiostat. Glassy-carbon (2 mm in diameter) disks polished by Al_2O_3 (<10 μm) were used as working electrodes; a 0.1 M Bu_4NClO_4 solution in DMF served as a supporting electrolyte; $Ag/AgCl/KCl_{sat.}$ was used as a reference electrode. All measurements were carried out under argon; the samples were dissolved in a deaerated solvent. N_2O was bubbled through the aqueous solution, and the positive pressure of N_2O was maintained in an electrochemical cell during the experiment.

Table 1 Electrochemical oxidation (E_{pa}^{Ox}) and reduction (E_{pc}^{Red}) potentials for compounds **1** and **2** measured by CV at GC electrode in DMF in the presence of 0.1 M Bu_4NClO_4. Potential scan rate is 200 mV s^{-1}; the values after slash marks refer to peak potentials relevant to reverse scans of CV curves.

Compound	E_{pc}^{Red}	E_{pa}^{Ox}
1	–1.83 / –1.75 (2:1); –2.51	1.16; 1.46
2	–0.92 / –0.85; –1.64; –1.95	1.16 (3–4 e)

Ligand **1** undergoes two-step reduction at greatly negative potentials (Table 1); it oxidizes in two irreversible steps. The additional quasi-reversible peak at E_{pc} = –0.92 V on complex **2** CV curves corresponds to two-electron reduction at metal; the following cathodic peaks are due to organic fragment reduction at a less negative potential compared to free ligand **1**. The oxidation of **2** occurs in one stage at E_{pa} = 1.16 V; under this potential, both organic ligand fragment and coordinated chloride anion are oxidized.

Under the reduction of complex **2** in the presence of N_2O (Figure 1) at slow scan rates (50 and 20 mV s^{-1}), the intensity of the first cathodic peak increases (at 20 mV s^{-1} the accretion of current magnitude is ~60%) along with the concomitant loss of reversibility. At the same time, the following peaks became low-intensive. In RDE experiments, when the reduction product can be removed from the electrode surface, permitting to new substrate molecules to approach the electrode face, the intensity of the first cathodic peak increases dramatically, while the following peaks almost disappear. If complex **2** was reduced at enhanced N_2O pressure, the first cathodic peak also increased. These facts consist with an electrocatalytic process at the formal potential of the Co^{II}/Co^0 redox couple. The loss of reversibility indicates that the reduced form of complex **1** undergoes an irreversible reaction with N_2O. Apparently, only N_2 (not NH_3) is formed under catalytic N_2O reduction because the NH_3 re-oxidation peak under E_{pa} ~ 1.0 V is not observed at CV reverse scan in the anodic region after the carrying of cathodic potential E_{pc} = = –1.0 V.

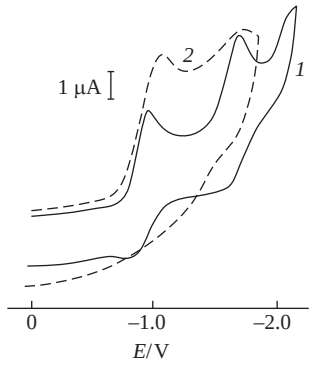


Figure 1 Cyclic voltammograms of complex **2** in DMF solution (1 mM, GC electrode, Bu_4NClO_4, 20 mV s^{-1}): (*1*) without N_2O, (*2*) in the presence of N_2O.

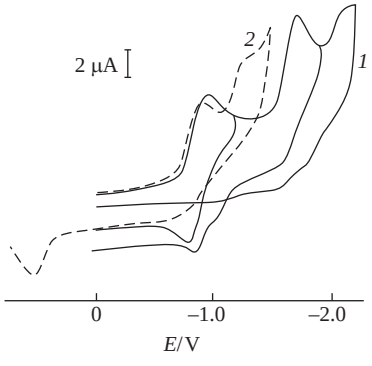
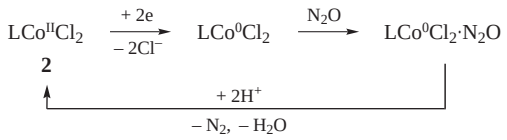


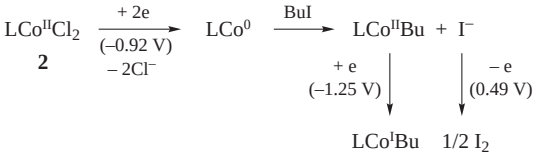
Figure 2 Cyclic voltammograms of complex **2** (1 mM, GC electrode, Bu_4NClO_4, 20 mV s^{-1}): (*1*) without BuI, (*2*) in the presence of BuI (10-fold excess).

The product of complex **2** reduction takes possibility to bond N_2O at a vacant coordination position. Probably, the formed complex can be protonated by the solvent with the regeneration of complex **2** (Scheme 2). This process results in a growth of the first cathodic peak intensity. Thus, complex **2** catalyzes the reduction of nitrous oxide to N_2 under mild conditions at moderate potentials (E_{pc} < –1.0 V). This catalysis mimics the behaviour of the N_2O reductase enzymes, which reduce nitrous oxide with two electrons, yielding dinitrogen and water. Note that N_2O undergoes the same reduction in electrochemical cell only at high potentials (E_{pc} < –2.0 V).[26]



Scheme 2

If complex **2** is reduced in the presence of BuI, the additional peak with E_{pc} = –1.25 V is observed at the cathodic branch of CV curve (Figure 2). This peak corresponds to Co-alkylated derivatives, formed as a result of the reaction of *n*-butyl iodide with LCo^0 (Scheme 3).[27] Further, the peak of I^- re-oxidation at E_p = = 0.49 V appears at CV reverse scan, and the reversibility of the first reduction peak is breaking down. Hence, the reduced form of complex **2** is stable enough time for catch to react with BuI with the formation of an alkylation product.



Scheme 3

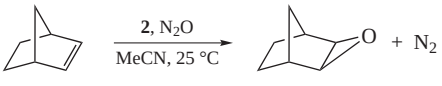
Thereby, the data of electrochemical investigation confirm the stability of complex **2** in a reduced form and the capacity of this complex to associate with nitrous oxide.

In the tests of the effect of the N_2O/**2** system on various compounds,¶ we found that norbornene reacts with nitrous oxide in the presence of complex **2** under normal pressure at room temperature to form 3-oxatricyclo[3.2.1.$0^{2,4}$]octane **3** in yields up to 90% (Scheme 4).

It is unlikely that the oxygen source was anything other than N_2O. The reactions of norbornene with air in the presence of **2**

¶ *Oxidation of norbornene.* A solution of 0.094 g (1 mmol) of norbornene and 0.047 g (0.1 mmol) of complex **2** in 10 ml of MeCN was placed in a two-necked flask equipped with a gas supply pipe and a condenser. N_2O (medical quality; from Criogen, http://cryogen-firma.ru/) was bubbled through a solution for 4 h at room temperature; gas flow rate ~2 dm^3 h^{-1}. The mixture was passed through a short (h = 3 cm) SiO_2 column using CH_2Cl_2 as an eluent. After the evaporation of the solvent, the mixture was analyzed by ^1H and ^{13}C NMR spectroscopy and GLC. The yield of 3-oxatricyclo[3.2.1.$0^{2,4}$]octane **3** was 90%.

Oxidation of triphenylphosphine. A solution of 0.05 g (2 mmol) of Ph_3P and 0.047 g (0.1 mmol) of complex **2** in 10 ml of MeCN was placed in a two-necked flask equipped with a gas supply pipe and a condenser. N_2O (medical quality; from Criogen) was bubbled through a solution for 4 h at room temperature; gas flow rate ~1 dm^3 h^{-1}. After the evaporation of the solvent, the mixture was analyzed by ^1H and ^{31}P NMR spectroscopy. The yield of Ph_3PO **4**, calculated on the basis of the integral intensity of Ph_3P (–5 ppm) and Ph_3PO (29 ppm) peaks in ^{31}P NMR spectra, was 91%.

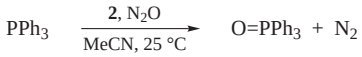


3, 90%

Scheme 4

or with N_2O in the presence of $CoCl_2$ under the same conditions did not afford oxidation products. The N_2 by-product is assumed but not experimentally confirmed.

Thus, it has been found that, if the N_2O is introduced to a solution of $LCoCl_2$ **2** and PPh_3 at room temperature, the catalytic oxidation of triphenylphosphine to triphenylphosphine oxide **4** occurs (Scheme 5).



4, 91%

Scheme 5

The reactions of PPh_3 with N_2O under the same conditions in the absence of complex **2** gave only 8% of oxidation product **4**.

In conclusion, Co^{II} complex **2** is capable to catalyze the oxidation reactions of norbornene and triphenylphosphine by nitrous oxide under ambient conditions.

This work was supported by the Russian Foundation for Basic Research (project no. 10-03-00677a).

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Received: 17th October 2011; Com. 11/3819