Electrochemical synthesis of π-cyclopentadienyl(nitrosyl)nickel complexes

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The dependence of the yield of π-cyclopentadienyl(nitrosyl)nickel on the conditions of its electrochemical synthesis from cyclopentadiene under an atmosphere of nitric oxide has been studied with the use of a nickel anode. The general character of the reaction has been demonstrated by its extention to monosubstituted ethyl-, isopropyl-, and benzoylcyclopentadienes.

Key words: cyclopentadienyl (nitrosyl)nickel, electrochemical synthesis; nickelocene.

Previously[1] it was demonstrated that the electrolysis of cyclopentadiene in acetonitrile under an atmosphere of nitric oxide using a nickel anode affords π-cyclopentadienyl(nitrosyl)nickel (**1**). In this work, the dependence of the yield of compound **1** on the conditions of the electrochemical reaction has been studied. The electrolysis was performed with direct current in an undivided cell.[1] Experimental results are given in Table 1.

In preliminary experiments, the most favorable conditions were found for performing the electrochemical synthesis, namely, 40 °C and low current density (*cf.*, for example, Table 1, experiments 1 and 2). Moreover, the yields of compound **1** under comparable conditions are somewhat better with tetraethylammonium chloride than with bromide (experiments 1 and 3). Therefore, subsequent experiments were carried out at low current density, and in most experiments, triethylammonium chloride was used as the supporting electrolyte.

The yield of compound **1** substantially depends on the quantity of passed electricity. In the range of 50—100 mF, this dependence is nearly linear, and the yield of the compound increases from 16 to 33 % (experiments 3—5). However, we failed to obtain higher yields by increasing the quantity of electricity passed because after prolonged electrolysis marked passivation of the electrodes occurred.

The general character of the reaction of the electrochemical synthesis of cyclopentadienyl(nitrosyl) complexes was demonstrated for monosubstituted cyclopentadienes, C_5H_5R (R = ethyl, isopropyl, and benzyl), where electrolysis afforded the corresponding RC_5H_4NiNO complexes. The regularities of the electrochemical synthesis of these complexes are similar to those reported for compound **1** (see Table 1). The highest yields of ethyl-, isopropyl-, and benzylcyclopentadienyl(nitrosyl)nickel were 32, 24, and 42 %, respectively, in terms of the initial cyclopentadiene (experiments 9, 13, and 17).

Table 1. Synthesis of cyclopentadienyl(nitrosyl)nickel derivatives, RC_5H_4NiNO, by electrolysis of cyclopentadienes C_5H_5R at a nickel anode under a NO atmosphere

Experiment	R	Duration of electrolysis /min	Quantity of passed electricity /mF	Yield of RC_5H_4NiNO /mmol
1*	H	316	50.9	7.2
2*,**	H	162	51.2	5.8
3	H	314	50.8	7.8
4	H	460	71.3	10.7
5	H	645	100.0	16.7
6*	Ethyl	320	52.3	6.9
7	Ethyl	310	50.7	7.2
8	Ethyl	465	70.7	9.8
9	Ethyl	630	95.4	16.1
10*	Isopropyl	330	54.4	4.5
11	Isopropyl	315	48.7	5.3
12	Isopropyl	440	68.6	7.3
13	Isopropyl	625	88.0	12.0
14*	Benzyl	318	51.9	9.5
15	Benzyl	335	52.3	10.3
16	Benzyl	470	73.0	14.1
17	Benzyl	650	107.2	21.0

Note. Initial amount of C_5H_5 was 50 mmol; acetonitrile was used as the solvent; 0.1 *N* Et_4NCL was used as the supporting electrolyte; the solvent volume in a cell was 75 mL; the temperature was 40 °C; the current density was 2.5 mA cm^{-2}. * Et_4NBr was used as the supporting electrolyte. ** The experiment was performed at a current density of 50 mA cm^{-2}.

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Table 2. Physicochemical characteristics of cyclopentadienyl(nitrosyl)nickel and its homologs, RC_5H_4NiNO

R	Found/Calculated (%)			Molecular formula	B.p./°C (p/Torr)	IR spectrum, ν/cm^{-1}	Mass spectrum, m/z, (I(%))
	C	H	N				
H	39.27 39.04	3.34 3.28	8.92 9.11	C_5H_5NNiO	19 (1)	3100, 1460, 1025,1010, 810 (C_5H_5); 1810 (NO)	154 (58), 124 (100), 98 (27), 65 (70), 59 (40)
Ethyl	46.33 46.23	5.14 4.99	7.53 7.70	C_7H_9NNiO	25—28 (1)	3070, 1460, 1025,1010, 810 (C_5H_4); 1815 (NO)	182 (90), 152 (70), 150 (61), 137 (46), 124 (100), 98 (26), 93 (50), 59 (28)
Isopropyl	49.33 49.05	5.78 5.66	7.03 7.15	$C_8H_{11}NNiO$	28—30 (1)	3070, 1465, 1030,1010, 810 (C_5H_4); 1815 (NO)	196 (100), 166 (51), 151 (62), 138 (11), 125 (45), 107 (53), 98 (5), 59 (37)
Benzyl	59.27 59.09	4.51 4.55	5.62 5.74	$C_{12}H_{11}NNiO$	65 (0.1)	3090, 1455, 1030, 1010, 810 (C_5H_4); 1810 (NO)	244 (50), 214 (100), 155 (48) 136 (22), 98 (2), 77 (73), 59 (28)

In all of the experiments, the corresponding cyclopentenes were formed as by-products. According to GLC data, their yields amounted to as much as 10—15 % (based on the starting cyclopentadiene). This makes it possible to advance some suggestions about the ways compound **1** and its homologs are formed. Although there are indications in the literature[2] that nickelocene cannot be prepared by the electrolysis of cyclopentadiene using a nickel anode owing to the electrochemical instability of the former, we assume that the transient formation of nickelocene and its reduction at the cathode to cyclopentadienylcyclopentenylnickel $C_5H_5NiC_5H_7$ (**2**) do actually take palce. This reduction occurs under rather mild conditions at a potential of −1.74 V (see Refs. 3 and 4). When compound **2** reacts with nitric oxide, the cyclopentene ligand is split off, and compound **1** is formed (see Ref. 5). Since the yield of cyclopentene is always lower than the yield of compound **1**, this splitting can also occur by the direct reaction of intermediate nickelocene with nitric oxide.[5]

When electrolysis was prolonged (see Table 1, experiment 5), a small amount of nickelocene (in about 3 % yield) was detected among the reaction products. Its formation may be attributed to a side process of the decomposition of compound **1** in the course of electrolysis. The electrochemical reduction of compound **1** to nickelocene at a potential of −1.83 V has been reported previously.[6] When electrolysis was performed under an inert atmosphere in the absence of nitric oxide, nickelocene was not found in the reaction products.

Experimental

Acetonitrile was purified according to the conventional procedure.[7] The water content of a solvent was determined by the method of Fischer. Tetraethylammonium bromide was twice recrystallized from ethanol; tetraethylammonium chloride was recrystallized from dimethoxyethane and ethanol (6:1) and then dried under a vacuum over P_2O_5. Cyclopentadiene was distilled just prior to each experiment. Alkylcyclopentadienes were prepared and tested for purity in the same manner as previously described.[8] An individed cell was used with a nickel anode and a St-3 steel cathode; the area of each electrode was 100 cm^2. IR spectra were recorded on a UR-20 spectrophotometer in a thin layer. Mass spectra were obtained on an MI-1305 instrument.

In all experiments, unsubstituted or substituted cyclopentadiene in a solution of tetraethylammonium chloride or bromide in acetonitrile was electrolyzed with direct current at 40 °C under an atmosphere of nitric oxide. The quantity of passed electricity was determined with a copper coulometer. When electrolysis was completed, the reaction mixture was diluted with a 5-fold volume of water, and then the reaction products were extracted with hexane. The extract was dried with magnesium sulfate and filtered and the solvent was distilled off. In the distillate, the corresponding cyclopentenes were determined by GLC. Cyclopentadienyl(nitrosyl)nickel complexes were separated by distilling the residue under a vacuum. The structures of the compounds were confirmed by elemental analysis, IR, and mass spectra (Table 2).

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