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Reactivity of niobocene dihalogenides toward nitroso derivatives. EPR and IR characterization of the first niobium(IV) complexes containing an ArNO-*N*,*O* ligand

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Abstract

The reaction of $[Nb(\eta^5\text{-}C_5H_4R)_2X_2]$ [**1**: R = $SiMe_3$, X = Cl; **2**: R = $SiMe_3$, X = Br; **3**: R = H, X = Cl; **4**: R = ^tBu, X = Cl] with nitroso derivatives ArNO [*a*: Ar = Ph; *b*: Ar = $o\text{-}CH_3\text{-}C_6H_4$; *c*: Ar = $p\text{-}(CH_3)_2NC_6H_4$] yields paramagnetic complexes formulated as $[Nb(\eta^5\text{-}C_5H_4R)(\eta^3\text{-}C_5H_4R)X_2(ArNO\text{-}N,O)$ **1a**, **1b**, **1c**, **2a**, **3a**, **4a** and **4c**, which have been characterized by ESR and IR spectroscopy.

Keywords: Niobium; Nitrosobenzene complexes; EPR; Electrochemistry

1. Introduction

Nitrosobenzene and its derivatives are interesting ligands because metal-promoted deoxygenation can generate nitrenes and oxo fragments [1]. In most nitrosobenzene [2,3] or substituted nitrosobenzene complexes [1d,4–6] so far prepared, the ligand is coordinated as a *N* or *O* σ base, allowing a very wide range of coordination modes [7]. A general correlation of coordination mode with the ν(NO) has been frequently developed [8]. Although several paramagnetic d^1 niobocene complexes, such as $[Cp_2NbX_2]$ (Cp = cyclopentadienyl group; X = halogen) show a well-documented [9] reactivity in redox and substitution processes, its behaviour as an inorganic radical has been scarcely studied [10]. As free radicals tend to attack the nitroso group [11], we became interested in the studies of the reactivity of nitroso derivatives towards some d^1 niobocene complexes which can be considered as inorganic radicals. We report here the reactions of $[Nb(\eta^5\text{-}C_5H_4R)_2X_2]$ with several nitroso compounds, ArNO, which lead to the isolation of paramagnetic (ArNO-*N*,*O*) niobium(IV) complexes.

2. Results

When one equivalent of nitrosobenzene (PhNO) was added at room temperature to a solution of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2]$ **1** in toluene a colour change in the solution from green to red was observed, along with the formation of a brown precipitate **1a**, which was collected by filtration under argon. The ESR spectrum of **1a** in THF consists of a singlet at $g = 2.002$, and no observable hyperfine interactions with niobium, nitrogen or protons. Its IR spectrum shows ν(NO) characteristic of a nitrosoaryl ligand at 1069 cm^{-1} (see Table 1).

Similar results were obtained using THF or CH_2Cl_2 as solvents. Complex **1a** is poorly soluble in these solvents, and from their solutions after evaporation of solvent and chromatography on silica column (eluent: mixture of hexane/CH_2Cl_2) azoxybenzene (12% yield) the *oxo*-complex $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2\text{-}$

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Table 1
ESR and IR spectroscopic data for $[Nb(\eta^5\text{-}C_5H_4R)(\eta^3\text{-}C_5H_4R)X_2(ArNO\text{-}N,O)]$ complexes

Complex	g_{iso} [a]	ν(N–O) [b]
1a	2.002 [c]	1073 [g]
1b	2.001 [c]	1097 [g]
1c	2.0032 [d]	1045 [h]
2a	2.0059 [e]	1095 [g]
3a	1.979 [f]	1072 [g]
4a	2.0037 [f]	1069 [g]
4c	2.0037 [f]	1064 [g]

[a] DPPH used as reference.
[b] Expressed in cm^{-1}.
[c] Determined in THF solution.
[d] Determined in toluene solution.
[e] Determined in CH_2Cl_2 solution.
[f] In solid state.
[g] Measured in KBr.
[h] Measured in $CHCl_3$.

Cl(O)] and other (unidentified) products in small amounts were isolated.

We have also studied the reactivity of **1** toward PhNO using electrochemical methods. Fig. 1 shows the polarogram of a mixture of **1** and PhNO (1/1). Oxidation wave E′ and reduction waves N and A were observed. E′ and A correspond to the oxidation and reduction of **1** respectively [12]. The wave N corresponds to the reduction of PhNO. After 1 h, the polarogram was drastically modified; thus one oxidation wave A'_1 together with three new reduction waves A_1, A_2 and B appear [Fig. 1]. We have verified that the isolated derivative **1a** exhibits the same polarogram.

Similar chemical (in toluene, CH_2Cl_2 or THF) or electrochemical (in THF) studies with both other niobocene and nitroso compounds have been carried out. Table 1 shows some ESR and IR spectroscopic data of the isolated nitrosoniobium(IV) paramagnetic compounds. No reaction was found between $[Nb\{1,3\text{-}C_5H_3(SiMe_3)_2\}_2Cl_2]$ and $[Nb(\eta^5\text{-}C_5Me_4Et)_2Cl_2]$ and nitroso compounds.

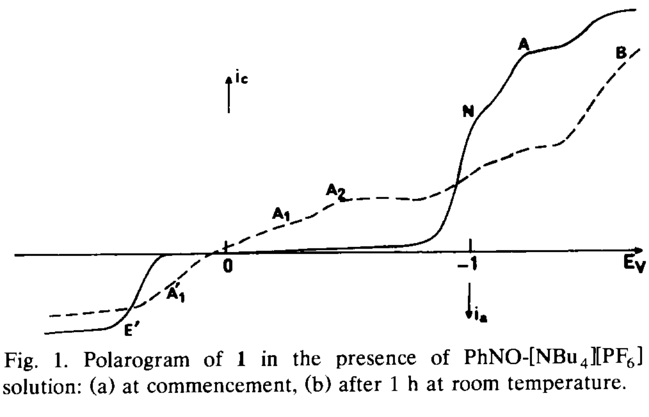

Fig. 1. Polarogram of **1** in the presence of PhNO-$[NBu_4][PF_6]$ solution: (a) at commencement, (b) after 1 h at room temperature.

3. Discussion

The complexes **1a**, **1b**, **1c**, **2a**, **3a**, **4a** and **4c** are formulated as $[Nb(\eta^5\text{-}C_5H_4R)(\eta^3\text{-}C_5H_4R)X_2(ArNO\text{-}N,O)$ (**1a**: R = $SiMe_3$, X = Cl, Ar = Ph; **1b**: R = $SiMe_3$, X = Cl, Ar = $o\text{-}CH_3C_6H_4$; **1c**: R = $SiMe_3$, X = Cl, Ar = $p\text{-}(CH_3)_2NC_6H_4$; **2a**: R = $SiMe_3$, X = Br, Ar = Ph; **3a**: R = H, X = Cl, Ar = Ph; **4a**: R = ${}^tBu$, X = Cl, Ar = Ph; **4c**: R = ${}^tBu$, X = Cl, Ar = $3\text{-}(CH_3)_2NC_6H_4$] for the following reasons.

(a) The ESR spectra of these complexes are related with those previously found for several paramagnetic bis(silylcyclopentadienyl)niobocene complexes with different unsaturated molecules, such as ketenimine [13], ketene [14], acetylene [15], aldehyde [16], and carbon disulfide [17]. These complexes, as well as the nitroso compounds, constitute an unusual family of paramagnetic niobocene complexes where the small values for the coupling constants indicate an appreciable delocalization of the unpaired spin density onto the ligands. Extended Hückel calculations performed for some of our complexes [18] give an insight into the role of the electronic properties of the ligands in the electron delocalization. These show that in the nitroso complexes, parallel to the carbon disulfide complex, $[Nb(\eta^5C_5H_4SiMe_3)_2(CS_2\text{-}C,S)]$, the unpaired electron is highly delocalized onto the nitroso ligand.

(b) The IR spectra for the nitroso complexes show a characteristic band at ca. 1045–1097 cm^{-1}, assignable to the ν(N-O) of an η^2-nitroso group. Values in the range of 973 at 1039 cm^{-1} have been previously ascribed to η^2-nitroso complexes of Pt, Ni, and Pd [19–21].

(c) The new oxidation wave (A'_1) and reduction waves (A_1, A_2) (see Fig. 1b) in the polarogram of a mixture of **1** and PhNO after 1 h indicate that a chemical reaction takes place between **1** and the nitroso ligand. This has been confirmed by comparison of this polarogram with that of genuine **1a**.

In order to keep the most general 17-electron configuration of niobium(IV) metallocenes, we propose η^3-coordination (Fig. 2) for one cyclopentadienyl ring. Unfortunately we could not isolate suitable crystals to

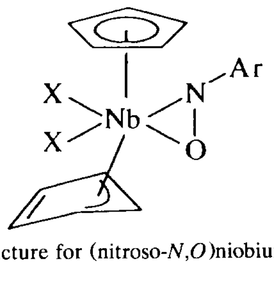

Fig. 2. Proposed structure for (nitroso-*N*,*O*)niobium (IV) complexes.

carry out an X-ray diffraction study. Obviously this is a tentative proposal, and other possibilities cannot be excluded. Several examples of a "ring-slippage" have been reported in the chemistry of transition-metal cyclopentadienyl complexes [22]. For example, in 1969 Cotton reported the X-ray crystal structure of $[(C_5H_5)_3Mo(NO)]$ for which an $[(\eta^1\text{-}C_5H_5)(\eta^3\text{-}C_5H_5)(\eta^5\text{-}C_5H_5)Mo(NO)]$ formulation seemed plausible [23], but the X-ray structure failed to show a distinct η^3-ligand [24]. The proposal of an η^3-cyclopentadienyl ligand was unambiguously substantiated in 1978 [25] with the crystal structure of $[(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_5H_5)W(CO)_2]$.

We have no conclusive data to explain the unreactivity of $[\{1,3\text{-}C_5H_3(SiMe_3)_2\}_2NbCl_2]$ and $[(\eta^5\text{-}C_5Me_4Et)_2NbCl_2]$ towards PhNO. The additional trimethylsilyl group or a peralkylated cyclopentadienyl ring, hindering η^5–η^3 ring slippage, could play an important role in the lack of reactivity. η^5–η^3 ring slippage has only been previously observed for complexes containing unsubstituted cyclopentadienyl groups.

The formation of both azoxybenzene and the *oxo*-complex $[Nb(\eta^5\text{-}Me_3SiC_5H_4)_2Cl(O)]$ in the chromatography on silica column for complex **1a** can be explained by a mechanism similar to that proposed by Fochi and Floriani for nitrosotitanium complexes [1a]. The absence in our procedure of azobenzene may rule out the presence of a nitrene intermediate.

4. Experimental details

4.1. General procedures

All manipulations were performed by using Schlenk techniques under an atmosphere of dry, oxygen-free dinitrogen or argon. EPR spectra were recorded at X-band frequencies with a Bruker ESP 300 spectrometer. Elemental analyses were performed with a Perkin-Elmer 240B microanalyser. IR spectra were recorded at room temperature with a Nicolet 205 spectrophotometer. They were taken either in solution between NaCl plates (thickness: 0.020 mm) or in the solid state (using KBr as matrix). The mass spectrum was recorded with a Kratos Concept S (70 eV) machine.

4.2. Electrochemical equipment and cell

For the polarograms, a three-electrode Tacusssel Tipol polarograph was used in a standard three-electrode cell using a saturated calomel reference electrode separated from the solution by a sintered glass disk. The auxiliary electrode was a platinum wire. The dropping mercury electrode characteristics were $m = 3$ mg s^{-1} and $\tau = 0.5$ s. In all cases the electrolyte was a 0.2 M solution of $(NBu_4)PF_6$ in THF.

4.3. Reagents

Tetrahydrofuran and toluene were purified from sodium benzophenone ketyl under argon. Tetrabutylammonium hexafluorophosphate (Fluka) was twice recrystallized from ethanol, then dried and deoxygenated before use. Nitrosobenzene, *o*-nitrosotoluene and *p*-dimethylaminonitrosobenzene were all commercial products. $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2]$ [26], $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Br_2]$ [27], $[Nb(\eta^5\text{-}C_5H_5)Cl_2]$ [28], $[Nb(\eta^5\text{-}C_5H_4{}^tBu)_2Cl_2]$ [29], $[Nb(\eta^5\text{-}1,3\text{-}C_5H_3(SiMe_3)_2)_2Cl_2]$ [26] and $[Nb(\eta^5\text{-}C_5Me_4Et)_2Cl_2]$ were synthesized according to published methods.

4.4. Preparation of $Nb(\eta^5\text{-}C_5H_4SiMe_3)(\eta^3\text{-}C_5H_4SiMe_3)Cl_2(PhNO\text{-}N,O)]$ **1a**

To a solution of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2]$ (400 mg; 0.913 mmol) in 100 ml of toluene was added 100 mg of PhNO (1.02 equivalent). The mixture was allowed to react at room temperature with stirring over 1 d. ESR spectroscopy showed that niobocene dichloride had totally disappeared, and the solution became red to give finally a brown-red precipitate. This was collected by filtration, washed with toluene (three pars of 5 ml) and dried to give the air-sensitive complex **1a**. This derivative **1a** shows poor solubility in THF, CH_2Cl_2. Unfortunately it was not possible to recrystallize **1a**.

4.4.1. *1a*

Elemental analysis [Found (Calc. for $C_{30}H_{31}Cl_2NNbOSi_2$)]: C, 48.6 (48.44); H, 5.68 (5.72)%. ESR (THF): $g_{iso} = 2.002$. IR (KBr): $\nu(NO) = 1073$ cm^{-1}. Mass spectrum: $m/z = 437$ $[(\eta^5\text{-}C_5H_4SiMe_3)_2NbCl_2]$, 107 (PhNO).

For the preparation of **1b**, **1c**, **2a**, **3a**, **4a** and **4c** a similar proceeding was used.

4.4.2. *1b*

Elemental analysis [Found (Calc. for $C_{23}H_{33}Cl_2NNbOSi)_2$]: C, 49.70 (49.62); H. 5.81 (5.98); N, 2.63 (2.52)%.

4.4.3. *1c*

Elemental analysis [Found (Calc. for $C_{24}H_{36}Cl_2N_2NbOSi)_2$]: C, 48.31 (49.21); H, 6.18 (6.20); N, 4.63 (4.78)%.

4.4.4. *2a*

Elemental analysis [Found (Calc. for $C_{22}H_{31}Br_2NNbOSi)_2$]: C, 41.81 (41.63); H, 4.83 (4.92); N, 2.18 (2.20)%.

4.4.5. *3a*

Elemental analysis [Found (Calc. for $C_{16}H_{15}Cl_2NNbO$)]: C, 47.69 (47.88); H, 3.68 (3.77); N, 3.51 (3.49)%.

4.4.6. 4a

Elemental analysis [Found (Calc. for $C_{24}H_{31}Cl_2$-NNbO)]: C, 55.58 (56.26); H, 6.04 (6.05); N, 3.07 (2.73)%.

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