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Preliminary communication

ELECTROCHEMICAL STUDIES ON ORGANOMETALLIC COMPOUNDS

VI*. ELECTROGENERATION OF STABLE COMPLEXES OF CYCLOPENTADIENYL DERIVATIVES OF NIOBIUM(III)

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Summary

The one electron reduction in THF ($Bu_4N^+PF_6^-$) of the complex (η^5-MeCp)$_2$-NbCl$_2$ in the presence of trimethylphosphite (TMP) yields the complex (η^5-MeCp)$_2$-NbCl(TMP), which reacts with CO to give the species (η^5-MeCp)$_2$NbCl(CO).

There has been increasing interest in recent years in studies of cyclopentadienyl derivatives of niobium in which the metal is in a low oxidation state, especially with the objective of activating small molecules. These complexes have been obtained by chemical reduction [1] and despite its potential advantages, the electrochemical method has not previously been used. We now report the results of an electrochemical study of dichlorobis(methylcyclopentadienyl)niobium (MeCp)$_2$NbCl$_2$ (1) in tetrahydrofuran (THF) in the presence of an excess of trimethylphosphite (TMP), which is capable of stabilizing the niobium(III) complexes. (The behaviour in the absence of TMP will be described later.)

On a platinum rotating disc electrode (r.d.e.) (with a five-fold excess of TMP, and 0.2 *M* tetrabutylammonium hexafluorophosphate as supporting salt), two reduction waves A and B, and one oxidation wave E′ are obtained; the half-wave potentials are respectively −1.28, −1.92 and +0.35 V versus an aqueous saturated calomel electrode. Wave B is ill-defined and irreversible; wave E′ corresponds to oxidation to a niobium(V) compound. Inversion of the potential scan after peak A in cyclic voltammetry causes an oxidation peak A'_1 to appear; the difference between the peak potentials of A and A'_1 is about 800 mV (Fig. 1). During the second cathodic scan, a new peak A_1, which forms a reversible system

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*For part V see ref. 6.

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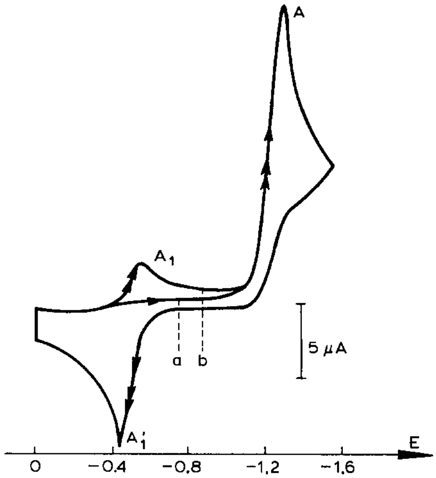


Fig. 1. Voltammograms of η^5-$(MeCp)_2NbCl_2$ in THF in presence of TMP at room temperature. Starting potential; 0 V. Sweep rate 0.100 V s^{-1}; a, first sweep; b, second sweep.

with A'_1, appears when the sweep rate is large enough or when the temperature is lowered (Fig. 1); peak A is obtained whether A_1 appears or not.

An electrolysis carried out at a potential (−1.4 V) corresponding to the plateau of wave A consumes 1 F; a brown solution is obtained. The r.d.e. voltammogram shows wave A'_1 at −0.4 V. The solution was evaporated and the residue was dissolved in toluene to remove the supporting salt. The solid obtained after evaporation of the toluene solution was recrystallized from a toluene/heptane mixture and characterized as $(MeCp)_2NbCl[P(OMe)_3]$ (2); mass spectrum with parent ion at *m/e* 410 and characteristic fragment ions $(MeCp)_2NbCl[P(OMe)_2]^+$ at *m/e* 379 and $(MeCp)_2NbCl^+$ at *m/e* 286. NMR spectrum (benzene-d_6): δ 5.09 (m, 4, Cp); 4.41 (m, 2, Cp); 4.13 (m, 2, Cp); 3.39 (d, 9, *J* 10 Hz, P—O—Me); 1.87 (s, 6, Me).

The compound obtained by reduction of 1 with sodium amalgam in toluene in the presence of an excess of trimethylphosphite is identical to 2.

Electrolysis of the brown solution at 0 V on the plateau of wave A'_1 regenerates 1, as shown by the r.d.e. voltammogram of the solution.

Air-oxidation of a solution of 2 yields $(MeCp)_2Nb(O)Cl$ [2]; this type of behaviour has already been observed for diverse complexes of niobium(III), in particular for Cp_2NbCl [3] and $Cp_2Nb(CH_3)L$ (L = CO, TMP, $P(C_2H_5)_3$, C_2H_4) [4].

When CO is bubbled through a solution of 2, the initially brown solution turns green. On the r.d.e., wave A'_1 disappears and is replaced by a new oxidation wave A'_2 at 0 V, due to the complex $(MeCp)_2NbCl(CO)$ (3). In cyclic voltammetry, the corresponding peak A'_2 appears during the anodic scan and peaks A_2 and A after switching the scan at +0.2 V (Fig. 2).

The shift of the oxidation wave towards more negative potentials as a result of the decrease of the electronic density on the metal is in good accord with the fact that the trimethylphosphite group is replaced by a CO group. The IR spectrum of 3 is identical to that of the product obtained by reduction of 1 by sodium

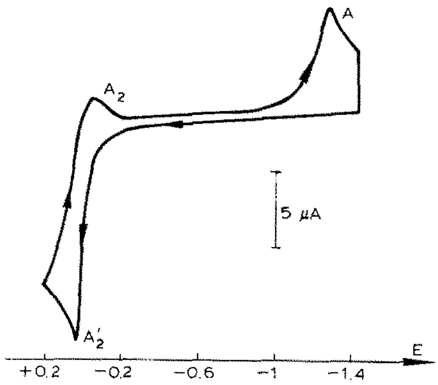
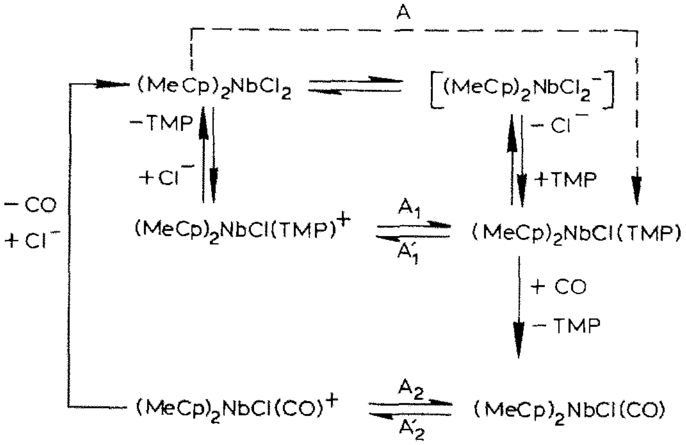


Fig. 2. Voltammogram of η^5-(MeCp)$_2$NbCl(CO) in THF. Starting potential −1.5 V. Sweep rate 0.200 V s^{-1}.

amalgam in the presence of CO (ν(CO) at 1914 cm^{-1}; THF). For (Cp)$_2$NbCl(CO) this band appears at 1920 cm^{-1} [5].

The results can be rationalized in terms of Scheme 1.



SCHEME 1

The uptake of the electron by (MeCp)$_2$NbCl$_2$ gives, with an excess of TMP, the complex (MeCp)$_2$NbCl(TMP) probably via the anonic species (MeCp)$_2$NbCl$_2$ Peak A'_1 corresponds to the oxidation of (MeCp)$_2$NbCl(TMP) to (MeCp)$_2$NbCl(TMP)$^+$ which is relatively stable. The cationic complex reacts slowly with Cl$^-$ ions present in solution to regenerate the complex (MeCp)$_2$NbCl$_2$. The behaviour is similar in the presence of CO (Scheme 1).

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