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Preliminary communication

Electrochemical studies on organometallic compounds

XXXIII *. Catalytic oxidation of triphenylphosphine by niobium(V) cationic complexes

H. Nabaoui, Y. Mugnier *, A. Fakhr and E. Laviron

Laboratoire de Synthèse et d'Electrosynthèse Organometalliques associé au CNRS (UA 33), Faculté des Sciences, 6 Bd Gabriel 21000 Dijon (France)

J. Mofidi

Department of Chemistry, University of Teheran (Iran)

A. Antiñolo, F.A. Jalon, M. Fajardo and A. Otero

Departamento de Quimica Inorganica, Universidad de Alcala de Henares, Campus Universitario, Alcala de Henares (Spain)

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Abstract

The cationic Nb^V species $Nb(\eta^5\text{-}Me_3SiC_5H_4)_2I_2^+$, has been shown to be an effective catalyst for the electrochemical oxidation of triphenylphosphine. Indirect anodic oxidation in the presence of water gives triphenylphosphine oxide in good yield.

Tertiary phosphine oxides can be made chemically in fair yields by several methods and, for example, Grignard and lithium reagents can be used [1]. More recently a few examples of catalytic oxygenations of arylphosphines by Pt complexes have been reported [2].

Direct electrochemical oxidation of tertiary phosphines is possible. In the presence of water, it gives phosphine oxides [3], but requires high anodic potentials. We show below that the overvoltage can be considerably lowered by use of cationic Nb^V complexes. As an example, we report here the catalytic oxidation of triphenylphosphine by the complex $Nb(Me_3SiC_5H_4)_2I_2$ (**1**).

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* Part XXXII, see ref. 8.

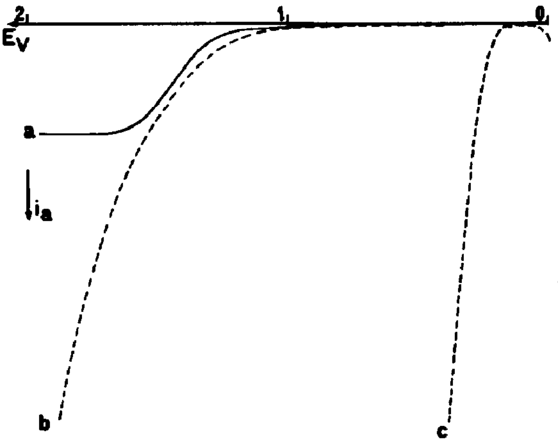

Fig. 1. Voltammograms on a platinum rotating disc electrode in tetrahydrofuran (a) of Ph_3P **3** alone, (b) **3** in the presence of water, (c) **3** in the presence of $Nb(Me_3SiC_5H_4)_2I_2$ (**1**) and water.

The rotating disc voltammogram at a Pt electrode of triphenylphosphine **3** in tetrahydrofuran (THF) (Bu_4NPF_6) is shown in Fig. 1a ($E_{1/2}$ +1.43 V versus SCE). Upon addition of water the height of the oxidation wave is increased (Fig. 1b). In the presence of catalytic amounts of the niobium derivative **1**, the wave is shifted towards less positive potentials (E 1.2 V) (Fig. 1c).

In cyclic voltammetry, **1** is oxidized along peak E', yielding $Nb(Me_3SiC_5H_4)_2I_2^+$ (**2**), which is reduced along peak E. In the presence of triphenylphosphine and water, a large increase in E' is observed (Fig. 2).

We carried out an electrolysis of a mixture of 0.011 g of **1** and 0.119 g of **3** in THF containing an excess of water. After consumption of 51 F per mole of the niobium complex (2 F per mole of **3**), the current fell almost to zero. Analysis of the solution by rotating disc voltammetry shows that the concentration of **1** has not changed (wave E'). The solution was extracted with diethyl ether. After chromatographic purification (Kieselgel, hexane/acetone 3/1) and recrystallization, crystals were obtained (mp 154 °C) and characterized by NMR spectrometry as triphenylphosphine oxide (yield 80%).

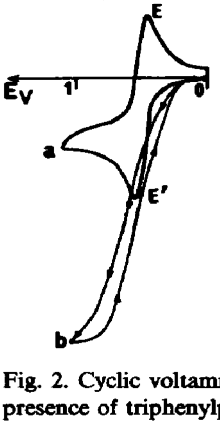

Fig. 2. Cyclic voltammograms on a platinum electrode: sweep rate 0.050 Vs^{-1} (a) **1** alone, (b) **1** in the presence of triphenylphosphine and water.

The increase in wave E' cannot be due to an outer sphere reaction between **2** and **4**, since the difference between the oxidation potentials of **1** and **3** is larger than 1 V. We suggest that a cationic intermediate complex of Nb^V $Nb(Me_3SiC_5H_4)(Ph_3P)I_2^+$ **4** is first formed by coordination of the phosphine ligand at the metallic atom (eq. 1 and 2). This is in keeping with the reaction of the Lewis acid (complex **2**, d_0 configuration) with phosphine, which has a nucleophilic character.

This is followed by a reductive elimination of a radical cation **5** Ph_3P^+ with regeneration of niobium complex **1** (eq. 3). The cation radical Ph_3P^+ then reacts with a molecule of water to form the oxide **6** (reaction 4).

$$\underset{\mathbf{1}}{Nb(Me_3SiC_5H_4)_2I_2} \underset{E}{\overset{E'}{\rightleftharpoons}} \underset{\mathbf{2}}{Nb(Me_3SiC_5H_4)_2I_2^+} \tag{1}$$

$$\underset{\mathbf{2}}{Nb(Me_3SiC_5H_4)_2I_2^+} + \underset{\mathbf{3}}{Ph_3P} \rightarrow \underset{\mathbf{4}}{Nb(Me_3SiC_5H_4)_2(Ph_3P)I_2^+} \tag{2}$$

$$\underset{\mathbf{4}}{Nb(Me_3SiC_5H_4)_2(Ph_3P)I_2^+} \rightarrow \underset{\mathbf{1}}{Nb(Me_3SiC_5H_4)_2I_2} + \underset{\mathbf{5}}{Ph_3P^+} \tag{3}$$

$$Ph_3P^+ + H_2O \rightarrow Ph_3PO + 2H^+ + e^- \tag{4}$$

Similar reductive eliminations of halogen atom [4] or $SiMe_3$ group [5] from niobium(V) complexes have been observed electrochemically. Elimination of a halogen atom has also been observed in the case of complexes of type Cp_2MCl_2 (M = Mo, W) [6].

We confirmed directly that reactions 2 and 3 occur. The cation **2** prepared quantitatively by chemical [7*] or electrochemical oxidation of **1** shows a reduction peak E. When triphenylphosphine **3** is added, wave E' (oxidation of **1**) appears.

We are currently investigating the reactions of **2** with other organic substrates.

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7 **2** can be obtained quantitatively by chemical oxidation of **1** with $(C_5H_5)_2Fe^+$ PF_6^-. ^1H NMR of **2** in $CDCl_3$: $C_5H_4SiMe_3$ 6.9 (m:4), $C_5H_4SiMe_3$ 0.38 (s:9) in ppm relative to TMS.

8 H. Nabaoui, Y. Mugnier, A. Fakhr, E. Laviron, A. Antinolo, F.A. Jalon, M. Fajardo and A. Otero, J. Organomet. Chem., in press.

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* Reference number with asterisk indicates a note in the list of references.