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Preliminary communication

Electrochemical studies on organometallic compounds

XL *. Reactivity of organometallic niobium complexes towards diphenylacetaldehyde. Electrogeneration and ESR characterization of [Nb(η^5-$C_5H_4SiMe_3$)$_2$(η^2-Ph_2CHCHO-*C*,*O*)]

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Abstract

The two-electron-reduction of [Nb(η^5-$C_5H_4SiMe_3$)$_2Cl_2$] in the presence of one equivalent of Ph_2CHCHO yields [Nb(η^5-$C_5H_4SiMe_3$)$_2$(η^2-Ph_2CHCHO-*C*,*O*)] which has been characterized by ESR spectroscopy.

There are several transition-metal-catalyzed reactions that involve aldehyde or ketone. Two industrially important examples are CO hydrogenation [1] and alcohol synthesis [2] by the oxo reaction. The study of stable aldehyde and ketone complexes is necessary to provide insight into the key steps of the catalytic reactions. Excellent review articles are available [3].

We describe here the electrochemical behaviour of [Nb(η^5-$C_5H_4SiMe_3$)$_2Cl_2$] (**1**) in the presence of Ph_2CHCHO.

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* For part XXXIX, see ref. 12.

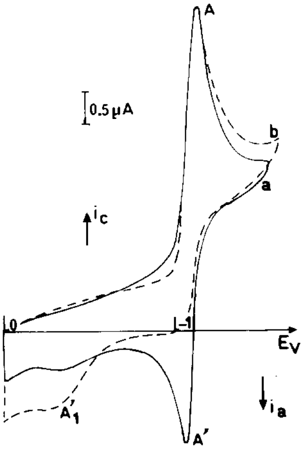

Fig. 1. Cyclic voltammogram of **1** in THF at a platinum electrode. Starting potential 0 V. Sweep rate 0.050 V s^{-1} (a) **1** alone (b) in the presence of one equivalent of Ph_2CHCHO.

The cyclic voltammogram of **1** at room temperature in tetrahydrofuran (THF) in the presence of 0.2 *M* tetrabutylammonium hexafluorophosphate as supporting electrolyte exhibits a reversible A/A' system where A' corresponds to the oxidation of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2]^-$ [4].

In the presence of one equivalent of Ph_2CHCHO the oxidation peak A' disappears and another peak, A'_1 is obtained (Fig. 1).

Figure 2a shows the polarogram of **1** in the presence of one equivalent of Ph_2CHCHO. During electrolysis at room temperature at −1.2 V two faradays were consumed and the brown electrolyzed solution exhibits in polarography [5*] a reduction wave B_1 and an ill-defined oxidation wave A'_1 (Fig. 2b).

The ESR spectrum ($g = 2.0028$) of the electrolyzed product **3** is shown in Fig. 3. Its shape is very special, consisting of ill-resolved lines reflecting coupling of the unpaired electron with the nuclear spin of niobium. The small coupling constant ($a_{Nb} = 8.35$ G) indicates that there is little unpaired spin density on the metal.

We formulate that the electrolyzed complex **3** as $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2\text{-}Ph_2CHCHO\text{-}C,O)]$, but we could not obtain it pure [6*]. A similar behaviour has been observed in other Nb^{IV} complexes [7,8].

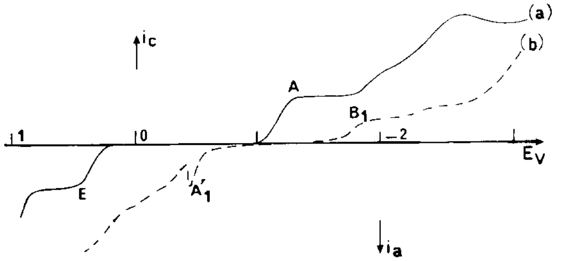

Fig. 2. Polarogram (average current, $\tau = 0.5$ s) in THF in the presence of one equivalent of Ph_2CHCHO: (a) before electrolysis; (b) after two-electron reduction at −1.2 V.

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

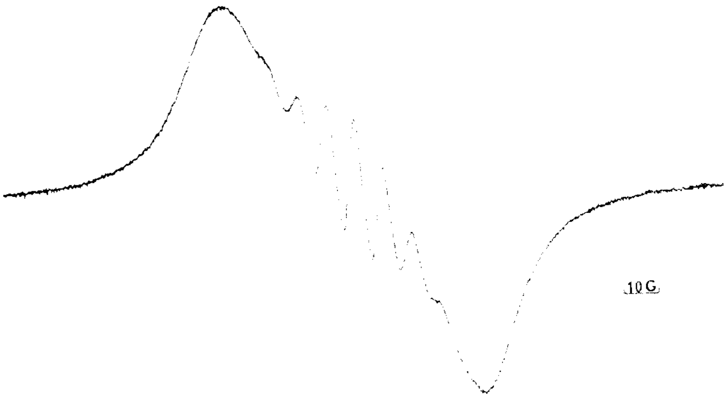

Fig. 3. ESR spectrum of **3** in THF.

The formulation of complex **3** is consistent with the following data:

- A similar spectrum was observed in the case of niobium(IV) ketenimine complex $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2\text{-}PhN{=}C{=}CPh_2\text{-}C,N)]$ which has been well-characterized [7].
- **3** is obtained by two electron-reduction of **1**. A similar reduction process was observed with niobocene complexes of ketenimine [7] or ketene [8] or acetylenic [9].
- The ESR spectrum of Fig. 3 was also obtained after two-electron reduction of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Br_2]$ (**4**) in the presence of one equivalent of Ph_2CHCHO. This indicates that halide (chloride or bromide) is not present in complex **3**.
- The same reduction wave B_1 (see Fig. 2) was observed after two-electron reduction of complexes **1** and **4** in the presence of Ph_2CHCHO.
- The IR spectrum of **3** in THF shows a band at 1583 cm^{-1} which probably corresponds to $\nu(C{=}O)$ of the diphenylacetaldehyde coordinated η^2.

The formation of complex **3** can be rationalized by the following scheme:

$$\underset{(\mathbf{1})}{\left[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2\right]} \overset{e}{\rightleftharpoons} \underset{(\mathbf{2})}{\left[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2\right]} \qquad (a)$$

$$\mathbf{2} + Ph_2CHCHO \xrightarrow{\text{fast}} \underset{(\mathbf{2'})}{\left[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2(Ph_2CHCHO)\right]} \qquad (b)$$

$$\mathbf{2'} \xrightarrow{\text{slow}} \underset{(\mathbf{2''})}{\left[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(\eta^2\text{-}Ph_2CHCHO\text{-}C,O)\right]} + Cl^- \qquad (c)$$

$$\mathbf{2''} \xrightarrow{e} \underset{(\mathbf{3})}{\left[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2\text{-}Ph_2CHCHO\text{-}C,O)\right]} + Cl^- \qquad (d)$$

The anion **2** probably reacts rapidly with Ph_2CHCHO to give the intermediate **2'** because it is basic and the aldehyde is electrophilic. A similar reactivity in anionic Nb^{III} complexes has been proposed in the catalytic reduction of benzyl chloride [10]. The Nb^V intermediate **2'** is relatively stable on the cyclic voltammetry time scale; it is unstable on the electrolysis time scale and a slow evolution of **2'** occurs with the loss of the Cl^- ion (step c). Finally, a one-electron reduction of **2''** yields complex **3** [11*].

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References

1 B.D. Dombek, Adv. Catal., 32 (1983) 325; B.D. Dombek, J. Chem. Educ., 63 (1986) 210; M. Ishino, M. Tamura, T. Deguchi and S. Nakamues, J. Catal., 105 (1987) 478; I. Tkatchenko, in G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), comprehensive Organometallic Chemistry, Vol. 8, Pergamon Press, Chap. 50.3, pp. 102–15; R.P.A. Sneeden, *Ibid.*, 50.2 pp. 40–48; W.A. Hermann, Angew. Chem., Int. Ed. Engl., 21 (1982) 117; E.L. Muetterties and J. Stein, J. Chem. Rev., 79 (1979) 479; R. Eisenberg and D.E. Hendriksen, Adv. Catal., 28 (1979) 79; C.K. Rofer-De Poorter, Chem. Rev., 81 (1981) 447; J.R. Beackborow, R.J. Daroda and G. Wilkinson, Coord. Chem. Rev., 43 (1982) 17.

2 C.M. Masters, Homogeneous Transition Metal Catalysis, Chapman and Hall, New York, 1981, p. 110; R.L. Pruett, J. Chem. Educ., 63 (1986) 196.

3 Y.-H. Huang and J.A. Gladysz, J. Chem. Educ., 65 (1988) 298 and references therein.

4 H. Nabaoui, A. Fakhr, Y. Mugnier, A. Antinolo, M. Fajardo, A. Otero and P. Royo, J. Organomet. Chem., 338 (1988) C17.

5 The reduction wave of Ph_2CHCHO ($E_{1/2} = -2.53$ V in THF) does not appear.

6 After evaporation of THF and extraction in toluene, the electrolytic salt was eliminated by filtration. The ESR analysis of this resulting solution shows the same spectrum as Fig. 3. However, complex **3** decomposes when the solution in toluene is evaporated to dryness.

7 A. Antinolo, M. Fajardo, C.L. Mardomingo, A. Otero, Y. Mourad, Y. Mugnier, J. Sanz-Aparicio, I. Fonseca and F. Florencio, Organometallics, 9 (1990) 2919.

8 A. Antinolo, M. Fajardo, C.L. Mardomingo, A. Otero, D. Lucas, Y. Mugnier and A. Tiripicchio, in preparation.

9 H. Chollet, D. Lucas, Y. Mugnier, A. Antinolo, M. Fajardo and A. Otero, in preparation.

10 A. Fakhr, Y. Mugnier, E. Laviron and J. Mofidi, J. Organomet. Chem. 346 (1988) C49.

11 An electron transfer between **2** and **2″** is possible. This type of reaction has been proposed for the electrosynthesis of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2\text{-}Ph_2C{=}C{=}O\text{-}C,O)]$ see ref. 8.

12 L. Roullier, D. Lucas, Y. Mugnier, A. Antinolo, M. Fajardo and A. Otero, J. Organomet. Chem., 412 (1991) 353.