Journal of Organometallic Chemistry, 132 (1977) C14—C16

Preliminary communication

PREPARATION AND PROPERTIES OF DICYCLOPENTADIENYLNIOBIUM(III) CHLORIDE

D.A. LEMENOVSKII*, T.V. BAUKOVA and V.P. FEDIN

Laboratory of Organo-Element Compounds, Chemical Department, University of Moscow, Moscow B234 (U.S.S.R.)

(Received March 24th, 1977)

Summary

The preparation of an air-sensitive 16-electron complex, Cp_2NbCl, is described. Its main property is easy transformation to 18-electron mononuclear compounds. $Cp_2Nb(=O)Cl$ and $Cp_2Nb(CO)Cl$ are obtained in oxidation and carbon monoxide gas addition processes, respectively. The physical properties of these complexes are described.

Results and discussion

At present we have hardly any data on 16-electron niobocene derivatives, in contrast to the few, but well-known vanadium compounds of this kind [1—3]. Cp_2NbCl was once mentioned to be a possible product of a reaction of $Cp_2Nb(\pi\text{-}C_3H_5)$ with HCl. No properties of the compound were reported [4]. A number of problems must first be resolved in the investigation of these electron-deficient complexes. Namely, we must know the reactivity as compared with corresponding complexes of adjacent elements, whether the structure is dimeric* or monomeric, and finally, the electron structure, since there may be two unpaired electrons in the molecule or none at all.

In this paper we report the synthesis of the electron-deficient niobocene(III) chloride and some of its reactions.

All experiments were performed in vacuum, or under argon using Schlenk-type glassware. ESR spectra were recorded with a Varian E-4 ESR spectrometer. ^1H NMR spectra were obtained with a Varian T-60 instrument. For the IR spectra investigation a Zeiss UR-20 machine was used. Good analyses were obtained for all compounds.

A very air-sensitive compound, Cp_2NbCl, was prepared following a typical reduction method (eq. 1).

---

*In this case the compound is only a pseudo-16-electron complex.

$$(C_5H_5)_2NbCl_2 \xrightarrow{+1\bar{e}} (C_5H_5)_2NbCl \qquad (1)$$

$$\text{(dec. temp. 220—222°C)}$$

Active metals such as Na, Mg, Zn and Al in ether-type or aromatic solvents accomplish this process. The best method, however, is the action of sodium naphthalene (NaphNa) in THF (eq. 2).

$$(C_5H_5)_2NbCl_2 + \text{NaphNa} \rightarrow (C_5H_5)_2NbCl \qquad (2)$$

$$(58\%)$$

In the course of the reduction reaction the strong ten-line ESR signal (g 1.9970; A_M 116.5 G) of the initial Cp_2NbCl_2 [5] decreased and finally vanished almost completely.

Cp_2NbCl is a dark-brown complex readily soluble in the usual organic solvents, except for alkanes. Special measures had to be taken to eliminate traces of oxygen in solvents during the synthesis and work-up.

Recently we carried out a reaction of n-C_4H_9Li with Cp_2NbCl_2 [6,7]. In this reaction a trivalent transitory niobium complex, apparently of structure $Li[Cp_2Nb(C_4H_9)Cl]$, was formed before the complexes finally isolated. In the present work we show that unstable $Li[Cp_2Nb(C_4H_9)Cl]$ is easily transformed to Cp_2NbCl by the action of HCl in ether (eq. 3)..

$$Li[(C_5H_5)_2Nb(C_4H_9)Cl] + HCl \xrightarrow{-LiCl, -C_4H_{10}} (C_5H_5)_2NbCl \qquad (3)$$

The main feature in the chemical behaviour of Cp_2NbCl is its fast transformation to 18-electron complexes under the action of a suitable reagent. We investigated two processes (eq. 4a, 4b).

$$(C_5H_5)_2NbCl \begin{cases} \xrightarrow{O_2\ \text{(air)}} (C_5H_5)_2Nb(=O)Cl & (4a) \\ \qquad (51\%, \text{ dec. temp.} > 190°C) & \\ \xrightarrow{CO\ \text{(gas)}} (C_5H_5)_2Nb(CO)Cl & (4b) \\ \qquad (56\%, \text{ dec. temp.} > 180°C) & \end{cases}$$

Reaction 4a is oxidation of niobium(III) to niobium(V). The yield of the resulting oxoniobocene chloride is similar to that reported in previous papers [6,8]. The Nb=O stretching frequency is 867 cm^{-1}.

The carbonylation reaction (like the oxidation) occurs instantaneously, even at 1 atm pressure of CO, and the monocarbonyl complex is the result. Carbonylniobocene chloride is a grey crystalline compound, soluble in benzene, toluene, THF, and insoluble in ether, alkanes, and alcohols. The stability of this complex in air is much higher than that of Cp_2NbCl. The carbonylated chloride can easily be exposed to air for several days and only slow conversion to $Cp_2Nb(=O)Cl$ takes place. The CO stretching frequency is 1902 cm^{-1}. It is in good agreement with that of $Cp_2Nb(CO)H$ briefly described by Parshall and Tebbe in 1971 [9]. The compound $Cp_2Nb(CO)Cl$ belongs to the somewhat rarer trivalent, 18-electron niobium complexes [9—14].

Details concerning the structures of the compounds were obtained from the chemical reactions described above and from the physical properties.

The IR spectra of all compounds show absorption characteristics of π-bonded cyclopentadienyl groups (absorption at 3100—3080, 1430, 1370, 1120, 1010 and 800 cm^{-1}) [15].

All compounds are diamagnetic and have no unpaired electrons on the niobium atom. Evidence for diamagnetism of Cp_2NbCl in solution was obtained from the ESR spectra of the 10^{-3}—10^{-4} M solutions in various solvents. No signal associated with this compound was observed. Another proof is the uncomplicated PMR spectrum of Cp_2NbCl.

Parameters of PMR spectra (δ, ppm, from internal TMS) of π-bonded cyclopentadienyl ligands in the niobocene complexes synthetised are as follows: Cp_2NbCl 5.04 (acetone-d_6), $Cp_2Nb(=O)Cl$ 6.42 (acetone-d_6), and $Cp_2Nb(CO)Cl$ 4.88 (benzene-d_6).

References

1 H.J. Liefde Meijer, M.J. Janssen and G.J.M. van der Kerk, Rec. Trav. Chim. Pays Bas, 80 (1961) 831.
2 D. Ytsma, J.S. Hartsuiker and J.H. Teuben, J. Organometal. Chem., 74 (1974) 239.
3 H. Bouman and J.H. Teuben, J. Organometal. Chem., 110 (1976) 327.
4 F.W. Siegert and H.J. Liefde Meijer, Proc. 4th Intern. Conf. Organometal. Chem. London, 1969, p. J-23.
5 I.H. Elson, J.K. Kochi, U. Klabunde, L.E. Manzer, G.W. Parshall and F.N. Tebbe, J. Amer. Chem. Soc., 96 (1974) 7374.
6 D.A. Lemenovskii, T.V. Baukova, V.A. Knignikov, E.G. Perevalova, and A.N. Nesmeyanov, Doklady Akad. Nauk SSSR, 226 (1976) 585.
7 D.A. Lemenovskii, T.V. Baukova, E.G. Perevalova and A.N. Nesmeyanov, Izv. Akad. Nauk SSR, Ser. Khim., (1976) 2404.
8 P.M. Treichel and G.P. Werber, J. Amer. Chem. Soc., 90 (1968) 1753.
9 F.N. Tebbe and G.W. Parshall, J. Amer. Chem. Soc., 93 (1971) 3793.
10 N.N. Kirillova, A.I. Gusev, A.A. Passinskii and Yu.T. Struchkov, Zh. Strukt. Khim., 14 (1973) 868.
11 W.A. Fowbs, L.S. Ru and D.A. Rice, J. Organometal. Chem., 54 (1973) C17.
12 C.R. Lucas and M.L.H. Green, J. Chem. Soc. Chem. Commun., (1972) 1005.
13 F.N. Tebbe, J. Amer. Chem. Soc., 95 (1973) 5412.
14 L.J. Guggenberger, P. Meakin and F.N. Tebbe, J. Amer. Chem. Soc., 96 (1974) 5420.
15 F.A. Cotton and T.J. Marks, J. Amer. Chem. Soc., 91 (1969) 7281.