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Preliminary communication

DICYCLOPENTADIENYLNIOBIUM, $(C_5H_5)_2Nb$; EVIDENCE FOR ITS EXISTENCE AND DESCRIPTION OF ITS PROPERTIES

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Summary

Monomeric dicyclopentadienylniobium, Cp_2Nb, was shown to form in high yield in solution by the action of electron donors on Cp_2NbCl_2. Two compounds Cp_2NbCl_2 and $[Cp_2Nb(Me)I]I$ are obtained from niobocene in oxidative addition reactions.

Results and discussion

The discovery of metallocenes has opened new avenues in organometallic chemistry. However, the synthesis of genuine high-symmetry metallocenes is by no means an easy task. This is true for many elements, especially at the beginning and end of the transition metal series. For some metals such derivatives have not been obtained so far. For instance 15-electron niobocene and tantalocene are not known for certain. The synthetic difficulties lie ultimately with the electronic structure of a metal atom of these complexes, which differs from the most stable 18-electron shell.

Recently in the investigation of the thermal decomposition of Cp_2NbH_2, Elson and Kochi [1] detected an unstable complex (ESR; g 1.9894; A_M 103 G). They supposed this complex to be most probably niobocene. In our report we describe another synthetic route to this compound. We employed the action of strong electron donors on Cp_2NbCl_2.

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.

Monomeric, 15-electron dicyclopentadienylniobium was obtained only in solution.

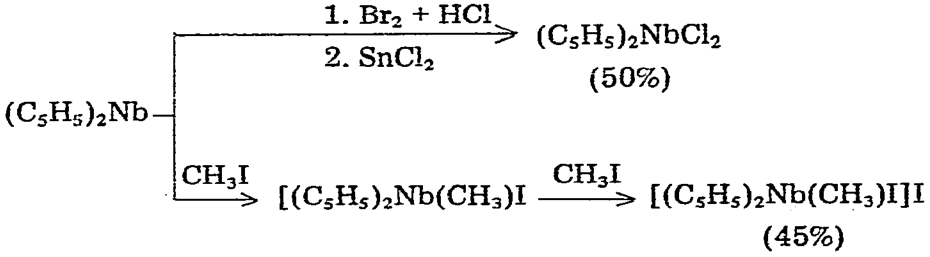
$$(C_5H_5)_2NbCl_2 \xrightarrow{+2\bar{e}} (C_5H_5)_2Nb$$

Two equivalents of reducing agent are necessary*. Metals (Na, Mg, Zn), sodium amalgam, sodium naphthalene, and large anionic species like $[Fe(CO)_2Cp]^-$ in ether-type or aromatic solvents can effectively be used as electron donors. In the course of the reduction reaction the ESR signal of the initial Cp_2NbCl_2 gradually decreases and then vanishes altogether. At the same time a new ten-line ESR signal (g 1.9864; A_M 103.6 G) rapidly increases. The main feature of the spectrum is the independence of its parameters on the nature of the solvent used. Such behavior may be expected only in the case of a high-symmetric, nonpolar organometallic complex in which solvent molecules do not enter the nearest coordination sphere of the metal. It is also noteworthy that ESR data of our complex are essentially equal to that obtained by Kochi [1] on the study of the thermal decomposition of Cp_2NbH_2.

The above considerations more or less confirm the metallocene, sandwich nature of this complex. Dimeric and oligomeric structures in this case may be discarded with confidence. Such aggregates must be either diamagnetic or have a more complicated ESR spectrum with more than ten lines.

The most prominent feature of the chemical behavior of niobocene, Cp_2Nb, is its easy transformation into 16—18-electron complexes. Besides π-cyclopentadienyl rings the resulting compounds include other ligands bonded to the metal atom. In reactions studied by us (vide infra) the metallocene, dicyclopentadienyl part of the molecule remains unchanged, which may serve as chemical evidence of the sandwich nature of niobocene.

We performed two oxidative-addition reactions, the reaction with Br_2 in hydrochloric acid solution and the reaction with CH_3I.



$$(C_5H_5)_2Nb \xrightarrow[2.\ SnCl_2]{1.\ Br_2 + HCl} \underset{(50\%)}{(C_5H_5)_2NbCl_2}$$

$$(C_5H_5)_2Nb \xrightarrow{CH_3I} [(C_5H_5)_2Nb(CH_3)I \xrightarrow{CH_3I} \underset{(45\%)}{[(C_5H_5)_2Nb(CH_3)I]I}$$

In the first case the methods of Cp_2NbCl_2 isolation were used which had been worked out for the synthesis of this compound from $NbCl_5$ and CpNa [2].

In the second reaction the unknown ionic compound $[Cp_2Nb(Me)I]I$ was formed. The complex was characterised by elemental analysis.

The location of the H_5 cyclopentadienyl signal in the PMR spectrum of $[Cp_2Nb(Me)I]I$ (δ 6.6 ppm, HMPT solution) is in good agreement with the chemical shifts of the ring protons in related dicyclopentadienyl complexes of niobium(V) [3,4].

We suppose that the interaction of niobocene with methyl iodide proceeds in two steps. After the addition of CH_3I to the Cp_2Nb solution, the ESR instrument instantly records the appearence of a new paramagnetic compound, (g 2.00 ± 0.01; A_M 92.2 G). At the same time the signal of niobocene vanishes

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*With 1 equivalent of the reducing agent instead of paramagnetic Cp_2Nb, a high yield of Cp_2NbCl is obtained. The diamagnetic complex Cp_2NbCl can be isolated in crystalline form.

completely. The magnitude of A_M for this new compound is intermediate between the corresponding values for Cp_2NbMe_2 (A_M 88.8 G), Cp_2NbCl_2 (A_M 116.5 G), and $Cp_2Nb(H)Cl$ (A_M 97.6 G) [1]. This signal most probably belongs to $Cp_2Nb(Me)I$.

In conclusion we must note that due to the great lability of niobocene all our attempts to get this metallocene in crystal form were unsuccessful, though it is quite evident that the complete confirmation of its structure requires its isolation. An additional complication arises due to the slow appearence of a number of other paramagnetic niobium complexes in the solution (ESR test). The distinguishing feature of these compounds is a striking dependence of their ESR spectra on the type of solvent used. Their nature will be discussed later.

References

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