Journal of Organometallic Chemistry, 290 (1985) 301–305
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

^{1}H NMR SPECTRA AND ELECTRONIC STRUCTURE OF BINUCLEAR NIOBOCENE AND TITANOCENE CONTAINING FULVALENE LIGANDS

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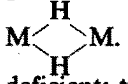
(Received February 18th, 1985)

Summary

^{1}H NMR spectra of binuclear metallocene hydride complexes, $(\eta^5:\eta^5\text{-}C_{10}H_8)(C_5H_5)_2M_2(\mu\text{-}H)_2$ (M = Nb, 20°C and Ti, (−60 to +25°C), were studied. The Nb complex is diamagnetic and gives a high resolution spectrum. The coordination of bridging hydride H atoms provides Nb atoms with complete 18 electron configuration. In its ground state, the Ti complex is also diamagnetic (the spectrum at −60°C agrees to that) in spite of only 17 electron configuration of each Ti atom. However, the population of the excited triplet state in the case of the Ti complex is appreciable at temperatures higher than −30°C, the proton resonance lines being shifted downfield and significantly broadened as compared with the spectrum at −60°C.

Results and discussion

Binuclear metallocene complexes $(\eta^5:\eta^5\text{-}C_{10}H_8)(C_5H_5)_2M_2H_2$, $C_{20}H_{20}M_2$ (I) with a fulvalene ligand and two hydride H atoms are reported for three transition metals, Ti, Nb and Mo of Groups IV, V and VI of the Periodic System [1–3]. A direct diffraction study of their structures was not yet carried out so we lack information on their angular and distance data, and little is known about valence and nonvalence interactions in these molecules. However, the general geometry of the complexes is reliably shown by the spectral characteristics and derived from the X-ray investigated structures of some compounds related to I [1–6]. Unlike the Mo complex (Ia), with an open linear fragment H–Mo–Mo–H, the corresponding Nb and Ti complexes (Ib), contain a ring



$M\overset{H}{\underset{H}{\diamond}}M$.

Complexes I are formally electron-deficient; two Mo atoms possess 34 electrons, two Nb atoms 32 electrons and two Ti atoms 30 electrons. Intermetallic interactions,

0022-328X/85/$03.30
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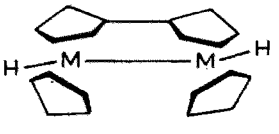
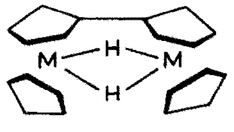
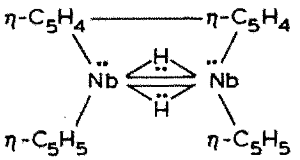


(Ia, M = Mo)

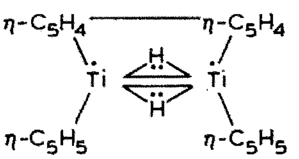


(Ib, M = Nb or Ti)

however, make up for this deficiency. These interactions adjust the electron configuration of each metal atom to the 18 electron rule. In the Mo complex, for example, a simple two electron Mo–Mo bond gives the Mo atoms 18 electron configuration. However, in corresponding Ib molecules the 18 electron configuration by Nb and Ti atoms is reached by formation of multicentre bonds in closed cluster-like fragments $\mathrm{M}\overset{\mathrm{H}}{\underset{\mathrm{H}}{\langle\;\rangle}}\mathrm{M}$, with at least four shared electrons. An accepted rule for calculation of electron numbers of metal atoms in such systems allows two electron tricentre bonds, $\mathrm{M}\overset{\mathrm{H}}{\diagup\!\!\underline{\;\;}\!\!\diagdown}\mathrm{M}$ [3,7,8]. So the electron structure of complexes II and III may be presented as follows:



(II)



(III)

The presence of bridging hydride H atoms in molecules II and III provides Nb atoms in II with 18 electron configuration and Ti atoms in III with 17 electron configuration. As a result electron deficiency of each metal centre in these compounds transforms into delocalized inside the $\mathrm{M}\overset{\mathrm{H}}{\underset{\mathrm{H}}{\langle\;\rangle}}\mathrm{M}$ fragments low lying MO of non-bonding or weakly anti-bonding types.

The above models of electron distribution suppose that the Nb complex is diamagnetic both in the solid state and in solution. There is no such certainty in the case of the Ti complex.

In our present paper we provide ^{1}H NMR data of the Nb complex II and Ti complex III. We synthesized the Nb complex II recently [2]. The Ti complex III was obtained by a modified technique described in ref. 9. FT ^{1}H NMR spectra were obtained on an FX-100 JEOL instument using 16 k real points and digital quadrature detection with locking on the internal ^{2}D signals of toluene-d_8 or benzene-d_6. The spectrum of II was recorded in C_6D_6 and the spectrum of III in $C_6H_5CD_3$. The samples were run in standard 5 mm sealed tubes. Chemical shifts were measured from C_6D_5H for II and $C_6D_5CD_2H$ for III and are given on the δ-scale from TMS.

The Ti complex III, or bis-titanocene, was first reported long ago and its properties were thoroughly studied. We recall here some of its important (from our point of view) characteristics. It was stated that thoroughly purified crystalline samples of bis-titanocene III are diamagnetic [4,6], in addition several structurally studied adducts synthesized from III are also diamagnetic both in the solid state and in solution. Their ^1H NMR spectra are described in ref. 6. Surprisingly the ^1H NMR spectrum of bis-titanocene itself was not reported, but some attempts in that direction were made. It was noted almost 20 years ago [10] that the ^1H NMR spectrum of bis-titanocene III could not be registered. Later Guggenberger and Tebbe [11] stated that the ^1H NMR spectra of III and of the related complex $(\eta^5:\eta^5\text{-}C_{10}H_8)(C_5H_5)_2Ti_2(\mu\text{-}OH)_2$ were anomalous presumably because of paramagnetism of these compounds. Unfortunately, the spectral characteristics were not presented. The ^{13}C NMR spectrum of III was obtained meanwhile [5], but the spectral data reported were not sufficient to infer the cause of manifest broadening of resonanse lines, probably through the influence of slight paramagnetism of III.

We found that the Nb complex II is diamagnetic both in the solid state and in solutions. In the ^1H NMR spectrum at 20°C are a sharp singlet of free C_5H_5 rings at 4.90 ppm and an AA′XX′ system of proton signals of the fulvalene ligand at 5.49 ppm (H(2,5)) and 3.61 ppm (H(3,4)). The values of spectral parameters of the cyclopentadienyl protons are typical of metallocenes and of niobocenes in particular *. The hydride H atoms which are directly bonded with Nb atoms give a broad signal ($\Delta\nu_{1/2}$ 210 Hz) at high field -20.85 ppm in the spectrum. The bridging positions of these H atoms are derived from the general character of the spectrum reflecting C_{2v} symmetry of the molecule, the position of the signals at high field, and the significant width of it. This supposition is in agreement with general regularity [12]. Terminal hydride atoms directly bonded to the niobocene moiety, as in $Cp_2NbH(L)$, both in mononuclear and in binuclear complexes, are characterized by substantially weaker screening by the diffuse electron shell of the metal atom (δ(H) -2 to -6 ppm as a rule), the signal width of terminal H hydride atoms being also significantly smaller [13,14]. The latter effect is caused by the fact that in these compounds, unlike complex II, each terminal H hydride atom is spin-coupled to only one quadrupolar ^{93}Nb nucleus.

The proton spectrum of III was found to be temperature-dependent. The low field part of the spectrum of III, provided by protons of cyclopentadienyl ligands, is presented in Fig. 1. At room temperature the cyclopentadienyl ring proton signals are broad and appear at relatively low field ($\delta(H(C_5H_4)$ 5.5 and 8.1 ppm, and $\delta(H(C_5H_5)$ 6.9 ppm) as compared with complex II. The signal of the bridging hydride atoms was not registered at room temperature. As the temperature is lowered upfield shifts of the signals typical for the metallocenes region and line sharpening are observed. At -60°C a very broad resonance line of the hydride bridge H atom appears (δ(H) -21.2 ppm, $\Delta\nu_{1/2}$ 300 Hz). Unfortunately, further lowering of the temperature results in a sharp decrease of solubility of III, and that makes registration of its high resolution ^1H NMR spectrum impossible in toluene. In general, the spectrum of III resembles that of II, and this fact confirms the structural

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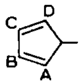
* For $(\eta^5:\eta^5\text{-}C_{10}H_8)(C_5H_5)_2Nb_2(\mu\text{-}H)(\mu\text{-}OMe)$ (synthetized as in ref. 2), for example, we found that the cyclopentadienyl fragment  or the fulvalene ligand has the following NMR parameters: δ(H(A)) 4.94, δ(H(B)) 2.61, δ(H(C)) 5.33 and δ(H(D)) 5.01 ppm; J_{AB} 3.25, J_{AC} 1.50, J_{AD} 1.20, J_{BC} 3.18, J_{BD} 2.18 and J_{CD} 3.39 Hz.

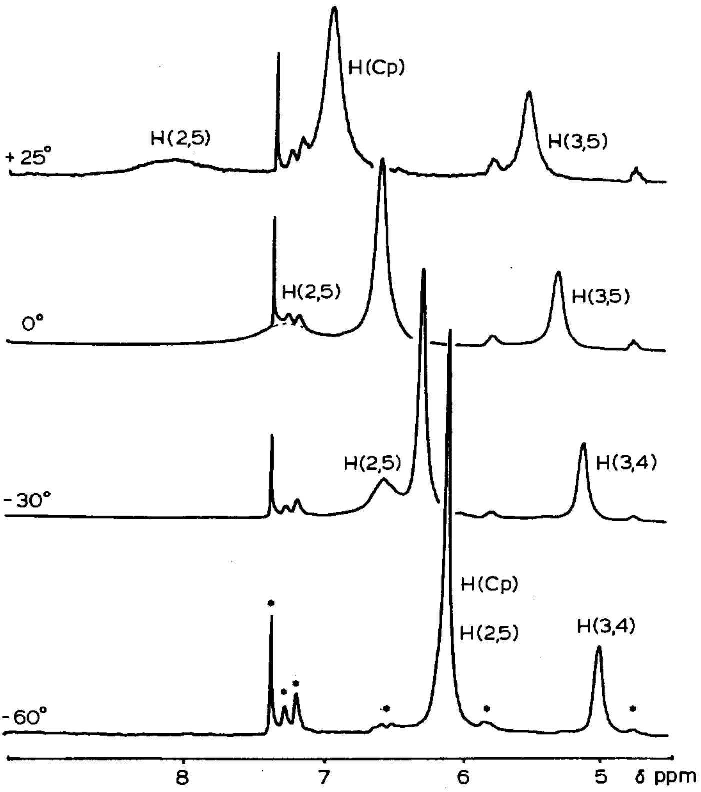


Fig. 1. ^1H NMR spectra of titanocene III at +25, 0, −30 and −60°C; * signals of the solvent (toluene-d_8) and unidentified impurities.

similarity of these complexes. Moreover, the ^1H NMR data are in agreement with other known physical and chemical evidence on the structure and composition of III [1,4–6].

The most reasonable explanation of temperature dependence of the spectrum of III proposes a thermal equilibrium between the singlet ground state of molecule III, and its excited triplet state. Comparison with known values of chemical shifts and line width of paramagnetic metallocene complexes, for which spin coupling is strictly impossible, demonstrates that in these cases paramagnetism affects NMR spectra much more significantly [15]. This fact indicates that the population of the triplet state of III at room temperature is insignificant, but it is sufficient to cause a visible downfield shift and broadening of ^1H nuclear magnetic resonance lines. A similar temperature effect was reported in a ^1H NMR study of difulvalenedichromium $(\eta^5:\eta^5\text{-}C_{10}H_8)_2Cr_2$ [16].

The strict diamagnetism reported for III in the solid state does not contradict with very weak paramagnetism for its solutions. It is noteworthy that there is much evidence for magnetic behaviour of crystalline binuclear dicyclopentadienyltitanium derivatives, $(\eta^5\text{-}C_5H_5)_2Ti\langle\overset{X}{\underset{X}{\ }}\rangle Ti(\eta^5\text{-}C_5H_5)_2$, containing no fulvalene ligand. Many of them have residual paramagnetism even at very low temperatures [17–19].

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