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SYNTHESIS AND CHEMICAL PROPERTIES OF μ-HYDRIDO-μ-HALOGENODICYCLOPENTADIENYLFULVALENEDINIOBIUM *

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Summary

Bis-niobocene $(\eta^5:\eta^1\text{-}C_5H_4)_2(\eta^5\text{-}C_5H_5)_2Nb_2H_2$ when treated with organic halides, e.g. C_4H_9Cl, $C_6H_5CH_2Cl$, CCl_4, $CHCl_3$, CH_3I and C_2H_5Br gives quantitatively new fulvalene complexes $(\eta^5:\eta^5\text{-}C_{10}H_8)(C_5H_5)_2Nb_2(\mu\text{-}H)(\mu\text{-}Hal)$. The complex $(\eta^5:\eta^5\text{-}C_{10}H_8)(C_5H_5)_2Nb_2(\mu\text{-}H)(\mu\text{-}Cl)$ readily exchanges its bridging chlorine atom for methoxy and ethoxy groups or a hydride ligand. Reaction with water gives a diamagnetic compound, for which the structure $(\eta^5:\eta^5\text{-}C_{10}H_8)(C_5H_5)_2(Cl)_2Nb_2(\mu\text{-}O)$ is proposed.

A new method for the synthesis of bis-niobocene through interaction of $(C_5H_5)_2NbCl_2$ with NaH in THF was found. It is shown that in DME the same reaction between $(C_5H_5)_2NbCl_2$ and NaH gives an isomeric fulvalene complex $(\eta^5:\eta^5\text{-}C_{10}H_8)(C_5H_5)_2Nb_2(\mu\text{-}H)_2$ instead.

Introduction

In recent years, it has been clearly demonstrated that most low-valent dicyclopentadienyl species of early transition metals gave binuclear complexes. The "dimerisation process" results in electronic and coordinational saturation of the involved metal atoms. For each element of the series Ti, Zr, Nb, Ta, Mo and W different structural types of "dimers" exist. Their chemical reactions are complicated multicenter processes which include several stages. The investigation into details of these reactions began only recently.

Among binuclear metallocene complexes of the early transition metals with bridging $\eta^5:\eta^1\text{-}C_5H_4$ moieties [1–3], bis-niobocene $(\eta^5:\eta^1\text{-}C_5H_4)_2(C_5H_5)_2Nb_2H_2$ (I) is the only one not to rearrange spontaneously into the isomeric fulvalene complex $(\eta^5:\eta^5\text{-}C_{10}H_8)(C_5H_5)_2Nb_2(\mu\text{-}H)_2$ (II). Complete saturation of the coordi-

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* Dedicated to Professor Oleg Reutov on the occasion of his 65th birthday on September 5th, 1985.

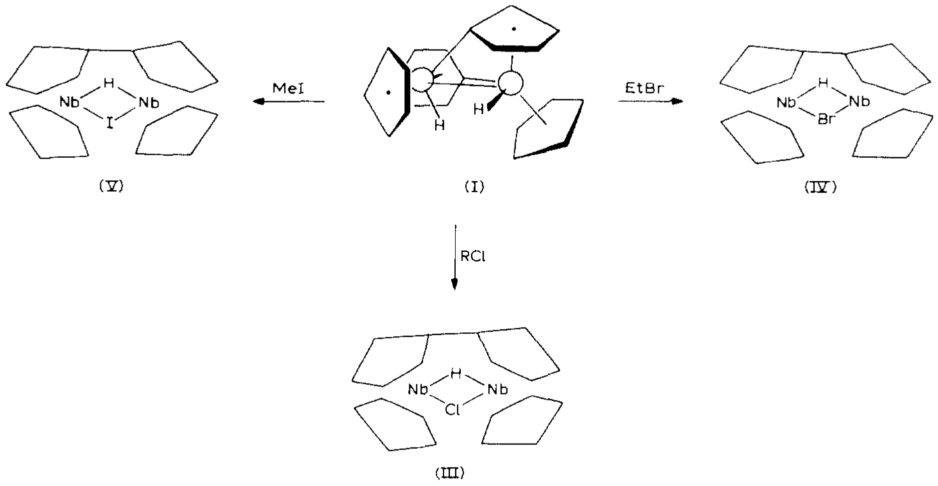
national sphere of both metal atoms involved and simultaneous exhaustion of coordinating abilities of all the ligands is a peculiar feature of structure I that is not shared by analogous complexes of other early transition metals [4]. This factor renders high kinetic stability to structure I. Nevertheless, we demonstrated earlier [5] that the reactions which involved both hydride ligands of complex I finally led to fulvalene complexes. Thus, reactions with aromatic azo compounds, aromatic amines and mercuric chloride resulted in substitution of both hydride bridges and the formation of a fulvalene ligand [5].

It was interesting to study the substitution effect of only one hydride atom. In this present paper we describe the reactions of complex I with organic halides leading to the formation of new binuclear fulvalene complexes of niobium with hydride and halide bridges ($\eta^5:\eta^5$-$C_{10}H_8$)(C_5H_5)$_2$$Nb_2$($\mu$-H)($\mu$-Hal). We also present some substitution reactions of the bridging chlorine atom in one of these complexes.

Results and discussion

We studied the reactions of bis-niobocene I with organic halides. Various halides were used, among them C_4H_9Cl, $C_6H_5CH_2Cl$, CCl_4 $CHCl_3$, C_2H_5Br. CH_3I (as well as anhydrous HCl). The reactions were performed in toluene, bis-niobocene (1 mol) was treated with butyl chloride, benzyl chloride, ethyl bromide or methyl iodide (and HCl) (1 mol) with $CHCl_3$, (1/3 mol) or with CCl_4 (1/4 mol) *. The process began at room temperature and after heating quickly resulted in the formation of the new binuclear fulvalene complexes III–V, with bridging hydride and halide atoms. The yields were 70–80% (see Scheme 1).

SCHEME 1



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* The excess of halides led to the formation of an unidentifiable mixture of complexes.

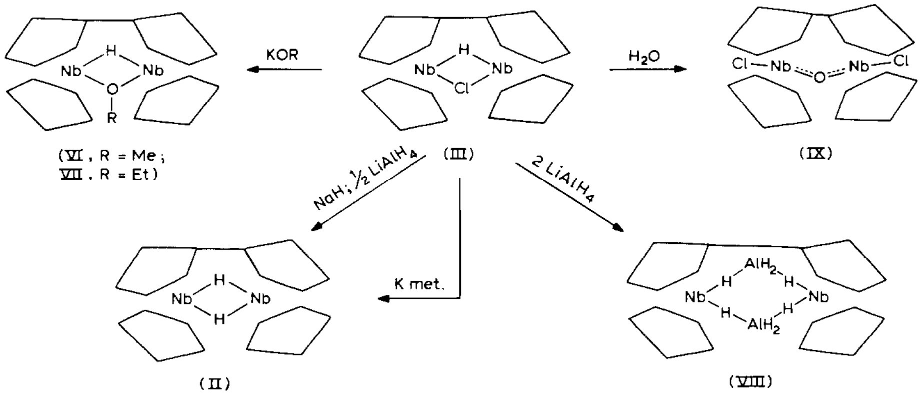
Thus the substitution of one hydride atom in the initial complex I for a halogen atom was accompanied by the formation of a fulvalene ligand and the rearrangement of the terminal hydride and halide atoms to a bridging position.

Compounds III, IV and V are diamagnetic dark brown solids readily soluble in aromatic hydrocarbons and ethers.

It is noteworthy that the reaction between RHal (1 mol) and complex I (1 mol) proceeds evidently in two steps. First, the reaction mixture turns from a pale greenish yellow to deep red and then, after heating to 100°C quickly turns brown. We were not able to identify the intermediate product. We can speculate that its structure may be similar to that of bis-niobocene I, viz. $(\eta^5:\eta^1\text{-}C_5H_4)_2(C_5H_5)_2Nb_2(H)(Cl)$, with terminal H and Cl atoms, or it may be an ionic compound with a bridging hydride ligand, viz. $[(\eta^5:\eta^1\text{-}C_5H_4)_2(C_5H_5)_2Nb_2(\mu\text{-}H)]^+Cl^-$. In both cases, the rearrangement of the structure of the type of bis-niobocene I into that of complexes III, IV and V is favoured because of the proximity of the two bridging $\eta^5:\eta^1\text{-}C_5H_4$ ligands and owing to the strong n-donating ability of halogene atoms.

Complex III easily enters substitution reactions in which the chlorine bridge is substituted under the action of nucleophilic agents. We have obtained methoxy- and ethoxy-bridged complexes VI and VII with structures analogous to III (see Scheme 2). It was found, however, that III did not interact with potassium isopropylate, t-butylate or cyclopentadienide. Also the chlorine bridge was easily substituted with another hydride atom when treated with strong hydride donating agents (e.g. sodium hydride or lithium tetrahydroalanate) or one-electron reducing agents (potassium). When treated with excess of lithium tetrahydroalanate complex III produces a tetrametallic adduct VIII with two AlH_3 Lewis acid moieties (see Scheme 2).

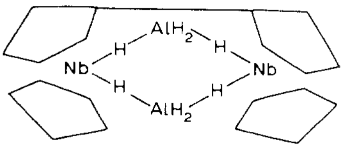
SCHEME 2



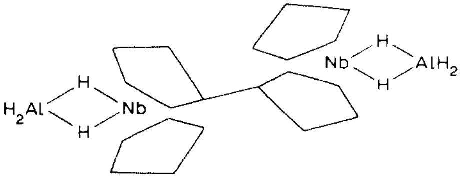
The structures of the complexes II–VIII were established after a ^1H NMR spectral study. Complexes III–VII have one mirror plane perpendicular to a straight line connecting the Nb atoms. There is a singlet of hydrogen atoms of free Cp rings in the spectra of III–VII. Besides, there are four well-resolved signals of the ABCD proton system of a fulvalene ligand, and a broad peak of a bridging H atom. The broadening is due to interaction with two Nb atoms (the nuclear spin value of which is 9/2). This signal is significantly shifted up-field compared to that of the terminal H atoms of both mononuclear and binuclear niobocene complexes [4].

The spectra of complexes II and VIII are simpler because the symmetry of their molecules is close to C_2, and the two-fold axis is present in both. The protons of their fulvalene ligands exhibit two triplet signals, characteristic of an AA'BB' system. The shapes of these signals are clearly different. This difference is due to a non equal contribution to line width from weak spin–spin interactions with Nb nuclei and also H bridges and other protons of the fulvalene ligand.

Two structures can be proposed for complex VIII, VIIIa and VIIIb, we prefer the closed structure VIIIa in view of clear resemblance of its spectrum with that of II.

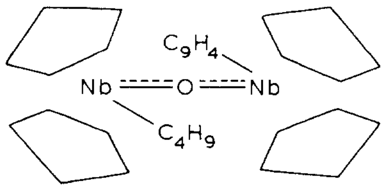


(VIII a)

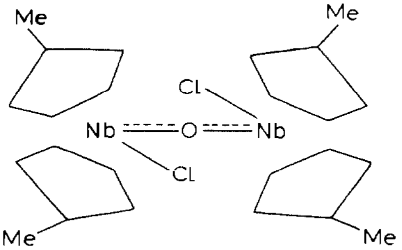


(VIII b)

The reaction between III (1 mol) and water (1 mol) seems to be more complicated than suggested above. It involves deep structural changes. The resulting complex IX contains two terminal chlorine atoms and one bridging O atom. Complex IX is thermally unstable and it is poorly soluble in every organic solvent. We studied its mass spectrum, which is typical of any binuclear fulvalene complex of niobium. The peak of a molecular ion (M^+) is the most powerful, fragmentation results mostly in loosing one Cp-ring (M^+ – Cp) and then a C_3H group (M^+ – Cp – C_3H). Besides IX, two complexes with similar structures, X and XI * with a linear fragment Nb–O–Nb and without a fulvalene bridging ligand were previously reported [7].



(X)



(XI)

All three complexes are deep blue and strictly diamagnetic. It was shown that X and XI are centrosymmetrical molecules, the fragments Nb–O–Nb being almost linear with very short Nb–O distances (about 2.0 Å). It indicates at least partial double bonding between Nb and O. Complex IX differes from X and XI in one significant structural detail: presence of one fulvalene ligand, instead of two free Cp rings, renders the molecule sterically strained. It is plausible that either the fragment Nb–O–Nb is obviously bent in IX or the two Cl atoms are situated in cisoid configuration with respect to the line connecting the Nb atoms.

Finally, we propose a new synthetic method to synthesize bis-niobocene I, which we found to be more convenient than the method applied earlier [8]. Bis-niobocene I

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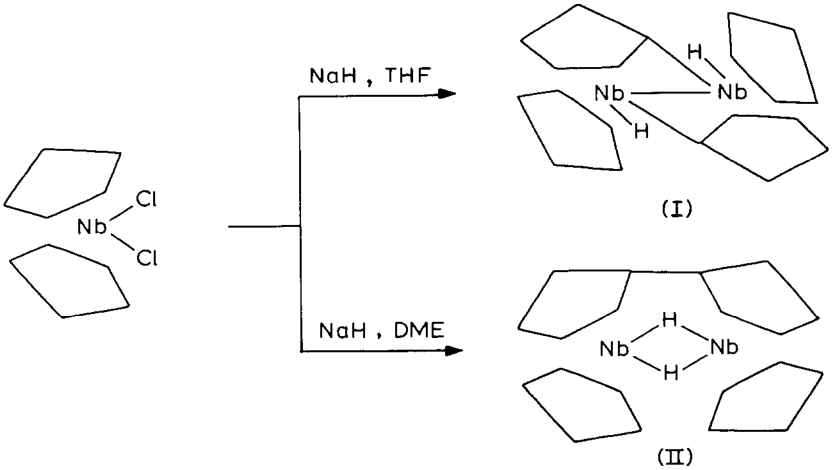
* Complex XI was synthetized by A.A. Pasynskii and coworkers. The structural data are in press (Koord. Khimiya, 1985 (U.S.S.R.)).

is obtained by treatment of Cp_2NbCl_2 with excess of NaH in THF first at room temperature and then on heating to 90–100°C. The yields are 80–90% and the product is easily isolated in a pure state.



It was found that treatment of Cp_2NbCl_2 with NaH in DME led to a quantitative yield of the isomeric complex II. We are interested in further investigation of this phenomenon.

Experimental

General procedure and materials. Schlenk vacuum techniques were applied in all cases. The solvents used were freed from oxygen and moisture by common methods. NMR samples sealed into 5-mm tubes were run on a Jeol FX-100 spectrometer. C_6D_6 was used as a solvent for all the samples. A value of 7.290 ppm was accepted for the chemical shift of the proton in C_6HD_5 and all other chemical shifts were correlated with that value (δ scale being used). The mass spectrum was registered on a MX 1303 instrument.

Preparation of complexes

$(\eta^5:\eta^1\text{-}C_5H_4)_2(C_5H_5)_2Nb_2H_2$ *(I).* In a standard run a mixture of Cp_2NbCl_2 (1.50 g, 5.1 mmol) and NaH (0.60 g, 25 mmol) in 20 ml THF was stirred for 24 h at room temperature. Then the reaction mixture was heated to 100°C for 2 h. The deep greenish brown solution was decanted, THF removed, and the residue was extracted with toluene (20 ml). After toluene evaporation 1.0 g (90%) of I was obtained.

The ^1H NMR spectrum of this sample is identical to that reported by Tebbe and Parshall [6].

$(\eta^5:\eta^5\text{-}C_{10}H_8)(C_5H_5)_2Nb_2(\mu\text{-}H)_2$ *(II).* A mixture of Cp_2NbCl_2 (1.50 g, 5.1 mmol) and NaH (0.60 g, 25 mmol) was stirred in 20 ml dimethoxyethane (DME) for 36 h at room temperature. The solution was decanted from excess of NaH, DME removed, and the evolved residue was extracted with toluene (20 ml). After toluene evaporation 1.0 g (90%) of II was obtained. Analytical and ^1H NMR characteristics of II are given below, where the exchange reactions of III are summarized.

$(\eta^5:\eta^5\text{-}C_{10}H_8)(C_5H_5)_2Nb_2(\mu\text{-}H)(\mu\text{-}Cl)$ *(III).* A solution of bis-niobocene I (obtained by the above method from 1.50 g Cp_2NbCl_2) in 20 ml toluene was mixed with a solution of 5 ml toluene containing CCl_4 (0.095 g, 0.62 mmol). The reaction mixture turned bright red. After short heating the colour of the mixture became brown. It was heated further at 100°C for 2 h. The solution was separated from the residue and then 1.10 g (90%) of crystalline III was obtained on slow evaporation of the toluene. The complex sublimes in vacuo at 270°C, with partial decomposition. Found: C, 49.33; H, 3.56; Cl, 7.39; Nb, 38.75. $C_{20}H_{19}ClNb_2$ calcd.: C, 48.89; H, 3.98; Cl, 7.38; Nb, 38.66%. ^1H NMR spectrum (δ ppm): 4.80(10 H); 2.60(2 H); 4.52(2 H); 4.89(2 H); 5.35(2 H); −11.97(1 H). Complex III was obtained also by the reactions of bis-niobocene I with HCl, n-C_4H_9Cl and $C_6H_5CH_2Cl$ (molar ratio 1/1); or I with CH_2Cl_2 (molar ratio 2/1); or I with $CHCl_3$ (molar ratio 3/1).

$(\eta^5:\eta^5\text{-}C_{10}H_8)(C_5H_5)_2Nb_2(\mu\text{-}H)(\mu\text{-}Br)$ (IV). The synthesis of IV was performed by the method described for III. 1.1 g (90%) of IV was obtained from 1 g of bis-niobocene I and C_2H_5Br (0.270 g, 2.48 mmol). The compound slowly decomposes at temperatures above 100°C. Found: C, 47.13; H, 3.81; Br, 15.60; Nb, 35.50. $C_{20}H_{19}BrNb_2$ calcd.: C, 46.75; H, 3.65; Br, 15.22; Nb, 35.39%. ^1H NMR spectrum (δ ppm): 4.82(10 H); 2.63(2 H); 4.40(2 H); 5.03(2 H); 5.27(2 H); −13.88(1 H).

$(\eta^5:\eta^5\text{-}C_{10}H_8)(C_5H_5)_2Nb_2(\mu\text{-}H)(\mu\text{-}I)$ (V). The synthesis of V was performed by the method described for III. 1.0 g (80%) of V was obtained from bis-niobocene I (1 g) and CH_3I (0.352 g, 2.48 mmol). The compound slowly decomposes at temperatures above 100°C. Found: C, 43.00; H, 3.49; Nb, 32.13. $C_{20}H_{19}Nb_2I$ calcd.: C, 41.96; H, 3.32; Nb, 32.51%. ^1H NMR spectrum (δ ppm): 4.82 (10 H); 2.76(2 H); 4.25(2 H); 5.12(2 H); 5.24(2 H); −14.11(1 H).

Exchange reactions of III

$(\eta^5:\eta^5\text{-}C_{10}H_8)(C_5H_5)_2Nb_2(\mu\text{-}H)_2$ (II). (a) A mixture of 1.0 g (2.08 mmol) of III and NaH (0.50 g, 20 mmol) was heated in 20 ml THF at 100°C for 20 h. The solvent was removed and the residue was extracted with toluene (20 ml). The solution was separated from the residue and then 0.8 g (80%) of crystalline II was obtained on slow evaporation of the toluene. The light green crystals of the complex contained co-crystallized THF. The compound decomposes without melting at 250–255°C. Found: C, 56.05; H, 6.06; Nb, 33.62. $C_{20}H_{20}Nb_2 \cdot 1.4\ C_4H_8O$ calcd.: C, 55.91; H, 6.23; Nb, 33.79%. ^1H NMR spectrum (δ ppm): 4.90(10 H); 3.61(4 H); 5.49(4 H); −20.85(2 H); 3.65(5.6 H THF); 1.80(5.6 H THF).

(b) A mixture of 1.0 g (2.08 mmol) of III and $LiAlH_4$ (0.038 g, 1.0 mmol) was heated in 10 ml THF for 5 h. After the THF was removed, the precipitate was extracted with 20 ml toluene. 0.85 g (85%) of II was obtained from this solution.

(c) The solution of 2.0 g (4.15 mmol) of III in toluene (15 ml) was vigorously stirred with potassium sand (0.178 g, 4.5 mg-atom) at room temperature for 10 h. The transparent light green solution was separated and the toluene removed. 1.3 g (70%) of II was obtained. These examples of II are free from co-crystallized solvent. ^1H NMR data are identical with those mentioned in (a).

$(\eta^5:\eta^5\text{-}C_{10}H_8)(C_5H_5)_2Nb_2(\mu\text{-}OCH_3)(\mu\text{-}H)$ (VI). A solution of 1.08 g (2.08 mmol) of III in toluene (20 ml) was heated with potassium methylate (0.14 g, 2.08 mmol) at 100°C for 5 h. The reaction mixture turned from brown to dark brown. The solvent was then removed and the residue was extracted with ether (20 ml). On slow evaporation of the solvent 1.0 g (quantitative yield) of crystalline VI was obtained (decomposition temperature > 270°C). Found: C, 52.75; H, 4.72; Nb, 39.37. $C_{21}H_{22}Nb_2O$ calcd.: C, 52.97; H, 4.66; Nb, 39.02%. ^1H NMR spectrum (δ ppm):

4.77(10 H); 2.61(2 H); 4.94(2 H); 5.01(2 H); 5.33(2 H); 2.83(3 H); −11.90(1 H).

$(\eta^5:\eta^5$-$C_{10}H_8)(C_5H_5)_2Nb_2(\mu$-$OC_2H_5)(\mu$-$H)$ (VII). A solution of 1.08 g (2.08 mmol) of III in toluene (20 ml) was heated with potassium ethylate (0.168 g, 2.08 mmol). The reaction mixture turned dark brown. The solvent was then removed and the residue was extracted with ether (20 ml). From this solution 1.0 g (quantitative yield) of VII was obtained (decomposition temperature > 250°C). Found: C, 53.37; H, 4.90; Nb, 37.86. $C_{22}H_{24}Nb_2O$ calcd.: C, 53.90 H, 4.93; Nb, 37.90%. ^{1}H NMR spectrum (δ ppm): 4.75(10 H); 2.57(2 H); 4.75(2 H); 4.85(2 H); 5.37(2 H); 0.39(3 H (Et)); 2.68(2 H (Et)); −12.00(1 H).

$(\eta^5:\eta^5$-$C_{10}H_8)(C_5H_5)_2Nb_2(\mu$-$AlH_4)_2$ (VIII). A mixture of 1.0 g (2.08 mmol) of III with $LiAlH_4$ (0.152 g, 4.0 mmol) in THF (20 ml) was heated at 100°C for 5 h. After removal of THF the residue was extracted with toluene (10 ml). From this solution 1.1 g (95%) of VIII was obtained as bright red crystals. Found: C, 47.50; H, 4.97. $C_{20}H_{26}Nb_2Al_2$ calcd.: C, 47.45; H, 5.18%. ^{1}H NMR spectrum (δ ppm): 4.80(10 H); 4.10(4 H); 5.88(4 H); −9.60(4 H). The signals of the terminal Al–H protons are not observed in the spectrum.

$(\eta^5:\eta^5$-$C_{10}H_8)(C_5H_5)_2Nb_2Cl_2(\mu$-$0)$ (IX). A solution of 2.0 g (4.15 mmol) of III in THF (30 ml) was heated with H_2O (0.075 g, 4.15 mmol) at 100°C for 40 h. A blue solution with a considerable brown precipitate resulted. The solution was decanted and the precipitate extracted with several portions of 20 ml THF. All the portions were mixed and the solvent removed. 1.0 g (45%) of IX was obtained. The complex sublimes in vacuo (5×10^{-2} mmHg) at 270°C but large amounts of it decomposed at this temperature. Mass spectrum: m/e 530(100%); m/e 465(50%); m/e 428(35%); the mass numbers are given for ^{35}Cl containing species. The spectrum is quite typical of binuclear fulvaleneniobium complexes [5].

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