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# ON THE PROPERTIES OF BINUCLEAR CYCLOPENTADIENYL-FULVALENE-NITRENE COMPLEXES OF Nb

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## Summary

The properties of $(\eta^5.\eta^5\text{-}C_5H_4C_5H_4)(C_5H_5)_2Nb_2(\mu\text{-}NC_6H_5)_2$ (I) have been investigated. Reaction of I with acids (HCl, $H_2SO_4$ and $CX_3COOH$) includes diprotonation to form the dication, $[(\eta^5.\eta^5\text{-}C_5H_4C_5H_4)(C_5H_5)_2Nb_2(\mu\text{-}NC_6H_5)_2H_2]^{2+}$ (II). The process is reversible and the initial neutral compound I may be recovered under the action of a base. The protonated compound II may lose $NC_6H_5$ ligands as $C_6H_5NH_3^+$; the paramagnetic product of the dissociation $(C_5H_4C_5H_4)(C_5H_5)_2Nb_2Cl_4$ (III) has been isolated

## Results and discussion

In the earlier papers [1—3] we have described the synthesis and some properties of new types of binuclear fulvalene complexes of Nb with σ-bridging ligands $(\eta^5.\eta^5\text{-}C_5H_4C_5H_4)(C_5H_5)_2Nb_2(\mu\text{-}X)_{1-2}$. Further investigation of the properties of compounds of this type have been carried out. So far, reactions of the diamagnetic complexes with arylnitrene bridging ligands have been studied. A quite remarkable thermal stability distinguishes binuclear fulvalene niobium complexes with arylnitrene bridging ligands, $(\eta^5\ \eta^5\text{-}C_5H_4C_5H_4)(\eta^5\text{-}C_5H_5)_2Nb_2(\mu\text{-}NR)_2$. These complexes resist the action of atmospheric moisture and oxygen even at high temperatures. The stability of the complexes, and the fact that one-electron oxidation of them may proceed smoothly under appropriate conditions without destruction and even considerable distortion of the initial structure indicate that the $Nb_2N_2$ bonding electrons have rather low energies, and so these bonds are not very reactive chemically. We hoped therefore, that some other reactions would also not destroy the binuclear structures of these niobium complexes but give us interesting new compounds.

In our investigation we considered two possibilities: (i) Friedel-Crafts acylation of $(C_5H_4C_5H_4)(C_5H_5)_2Nb_2(\mu\text{-}NC_6H_5)_2$ (I) and (ii) protonation of I with

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strong acids. It was found that under mild conditions compound I reacts readily with reagents such as $CH_3COCl$, $CH_3COCl \cdot AlCl_3$ and $(CH_3CO)_2O$ $BF_3$ It is evident that there are four different sites liable to attack by electrophyls, i e carbon atoms of the phenyl, cyclopentadienyl and fulvalene ligands, and also the σ-Nb—N-bonds. Unfortunately, we could not isolate any product of substitution of an aromatic hydrogen. In all cases, even at low temperature (~—30°C), the reaction resulted in the destruction of the $Nb_2N_2$ fragment The extremely low solubility of the products made their separation impossible. However, it was established that at least some of these products were formed by the elimination of the nitrene ligands under the action of acids, HX, arising in the primary reaction of acylating agents with I and with traces of moisture. So the investigation of the interaction between I and protic acids, HX, is necessary for the study of the fulvalene-nitrene complexes I

We investigated the reaction of some proton donors, HCl, $H_2SO_4$, $CH_3COOH$ and $CF_3COOH$, with I. In experiments with HCl aqueous, alcoholic (EtOH and MeOH) solutions and solutions in ether and THF were used, the action of gaseous HCl on the solution of I in $CH_2Cl_2$ was also studied Compound I was found to dissolve readily in pure $CF_3COOH$, $H_2SO_4$ and concentrated solutions of HCl in water and alcohols, all the reagents being carefully purified to remove dissolved oxygen. On the other hand, compound I is practically insoluble in $CH_3COOH$ and in dilute aqueous solutions of HCl and $HBF_4$ (~5%). The reaction apparently result in the formation of a protonated ionic compound. The possibility of isolating I from these solutions is strong evidence for the absence of any deep structural changes during the protonation

The solid product of interaction between I and HCl (in $CH_2Cl_2$) was isolated, and the composition of this compound II as dicationic species was determined.

$$\underset{\text{(I)}}{(C_{10}H_8)(Cp)_2Nb_2(NPh)_2} \underset{NMe_3}{\overset{HCl}{\rightleftarrows}} \underset{\text{(II)}}{[(C_{10}H_8)(Cp)_2Nb_2(NPh)_2(H)_2]^{2+}(HCl_2^-)_2}$$

In contrast to the initial compound I which is readily soluble in $CH_2Cl_2$, $CHCl_3$, THF and benzene and insoluble in alcohols, the protonated complex II is readily soluble in alcohol and aqueous alcohol and insoluble in the other solvents mentioned.

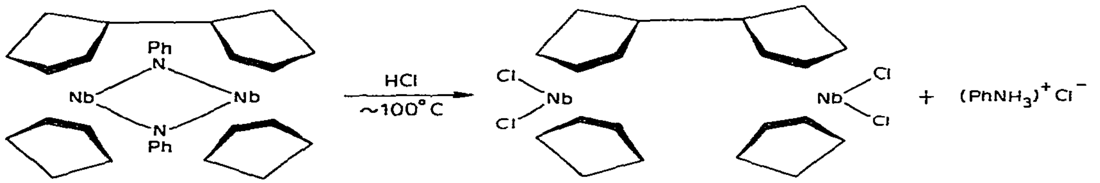
The reverse deprotonation reaction is the most important property of cation II. Thus the initial neutral compound I is regenerated when II is treated with a methanol solution of trimethylamine. Complex II is rather unstable in air and on heating. It undergoes slow decomposition in an inert atmosphere, even at room temperature. So the yield of I from the deprotonation reaction depends substantially on the period of time during which compound II was either kept under an inert atmosphere or exposed to the air. Similarly, the initial compound I may be isolated from its solutions in acids, e g. saturated solutions in HCl and $H_2SO_4$. The yiels are low, however.

We compared IR spectra of complexes I and II. The spectra differ from each other only insignificantly. the corresponding displacement of the main vibration frequencies is rather small. A noticeable divergence in the spectra may be seen only in the fingerprint region (500—900 $cm^{-1}$). Some lack of coincidence is also observed in the C—H vibration region (the band at 3030—3090 $cm^{-1}$ became broader for II). Besides, a new weak peak at 2315 $cm^{-1}$ appeared. Presumably, this band must be ascribed to the anion of salt II. So the protonation appears not to result in significant changes in the initial structure.

It is not clear which atoms are protonated. It is noteworthy that the protonation of the metal atoms is extremely unfavourable for steric reasons Accordingly, the spectrum of II lack peaks in the 1600—1700 $cm^{-1}$ region characteristic of Nb—H vibrations in various mono- and binuclear derivatives of niobocene hydrides [4—6] Protonation of nitrogen atoms of the bridging ligands thus seems to be most probable. The IR spectra cannot prove or reflute this suggestion definitively, since the frequency of N—H vibrations in cations obtained from tertiary substituted nitrogen derivatives is not characteristic and the corresponding band is not intense.

The PMR spectrum of I in concentrated $H_2SO_4$ is in agreement with this mode of protonation. No peaks are observed in the region of $\delta = 0$ to —20 ppm characteristic of M—H protons. A practically uniform shift of all C—H signals to low field is observed in spectra measured in $H_2SO_4$ compared with these measured in hexamethapole for I. This can hardly be accounted for if we suppose protonation of some individual carbon cycle. Broadening of the bands in both $H_2SO_4$ and $(Me_2N)_3P{=}O$ makes it difficult to attribute the signals to individual protons. The situation is aggrevated by the proximity of the chemical shifts of all the protons NMR spectra of substituted and deuterated fulvalene-nitrene complexes are now under extensive study, and the results will be reported.

It was noted above that solid HCl-protonated complex II is easily oxidized and decomposes on heating. In the absence of oxygen the slow process of nitrene ligands elimination takes place. This elimination reaction with HCl takes 5—10 hours at room temperature, the duration depends on the nature of the solvent. At 90—100°C the reaction takes only 15—30 minutes. The binuclear fulvalene complex $(C_{10}H_8)(C_5H_5)_2Nb_2Cl_4$ (III) and aniline hydrochloride are the products.



(I) (III)

Under the action of HCl, the paramagnetic fulvalene complex $(C_{10}H_8)$-$(C_5H_5)_2Nb_2(\mu\text{-}Cl)$ gives the same complex III and releases free hydrogen.

Complex III is a brownish-black finely-crystalline substance which is practically insoluble in organic solvents and water. The compound is stable in the air for several days. The structure of III was determined from the IR spectra Almost all frequencies observed are close to those of paramagnetic $(C_{10}H_8)$-$(C_5H_5)_2Nb_2(\mu\text{-}Cl)$ with a Cl bridge [2].

The magnetic susceptibility of III per metal atom was measured: $\mu_{eff}$ is 1.71 BM at 290 K and 1.41 BM at 80 K. The decrease of the effective magnetic moment corresponds to a weak exchange interaction through the fulvalene ligand This is also indicative of the absence of direct M—M interaction and also of halogen bridges, M—Cl—M, in molecule III. It is noteworthy that the observed experimental value for $\mu_{eff}$ is slightly higher than the value one would expect. Thus the value for $\mu_{eff}$ measured at room temperature should be somewhat lower than the spin only value due to exchange interactions, even if they are weak.

We note that the air stability and the ready availability of fulvalene-nitrene derivatives of Nb offer a good opportunity to synthesize new types of binuclear complexes of this metal.

## Experimental

All manipulations during the preparation, extraction and purification of compounds II and III were carried out in evacuated Schlenk-type glassware All solvents were carefully purified, dried and freed of dissolved gases. IR spectra of II, III and aniline hydrochloride were recorded as Nujol mulls on LOMO IRS-29 instrument and PMR spectra on a Varian XL-100 spectrometer. Measurements of effective magnetic moments were carried out using the Faraday technique.

### *Preparation of* $[(C_{10}H_8)(C_5H_5)_2Nb_2(NC_6H_5)_2H_2]^{2+}[HCl_2]^-_2$ *(II)*

a) A filtered solution of 0.044 g (0 07 mmol) of I in $CH_2Cl_2$ (15 ml) was kept in an atmosphere of dry purified HCl for 2 hours. An orange powder precipitated. The precipitate was decanted, washed repeatedly with $CH_2Cl_2$ and dried. The yield was 0.026 g (47%) of II. The compound decomposed above 100°C. Found: C, 50.35; H, 4.43, Nb, 23.51; Cl, 20.04 $C_{32}H_{32}Nb_2N_2Cl_4$ calcd.: C, 49.77; H, 4.18; Nb, 24.06; Cl, 18,36%. IR ($cm^{-1}$): 3030—3090s, 2315m, 1590s, 1160m, 1125m, 1030m, 1015m, 855s, 745s, 703w, 695m.

b) A moist vapour formed over concentrated hydrochloric acid was used instead of pure HCl. The mixture was kept in this atmosphere at room temperature for 10 hours. The precipitate was treated as described above. The yield was 0.029 g (53%) of II.

### *Deprotonation of II*

0.023 g (0.03 mmol) of II and 0.018 g (0 3 mmol) of $(CH_3)_3N$ were described in $CH_3OH$ (10 ml). A fine orange precipitate was formed. The solvent was evaporated in vacuo, and the dry precipitate was dissolved in hot THF. After filtration and slow evaporation of solvent in air, 0.015 g (80%) of I was isolated (decomposes without melting above 300°C [3]).

### *Destructive preparation of* $(C_{10}H_8)(C_5H_5)_2Nb_2Cl_4$ *(III) from I*

A solution of 0.063 g (0.10 mmol) of I in $CH_2Cl_2$ (20 ml) and a small amount (~0.1 g) of concentrated hydrochloric acid were heated in a sealed tube to 90—100°C for 3 hours. The solution gradually turned colourless and a finely crystalline precipitate was formed. The tube was opened and the precipitate was filtered off, washed thoroughly with $CH_2Cl_2$, $CH_3OH$, with $CH_2Cl_2$ again and dried in vacuo. 0.051 g (86%) of III with decomposition temperature

160°C was obtained. Due to its insolubility in all solvents tested, complex III was not purified by recrystallization. Found: C, 39.79, H, 3.10; Nb, 32 57. $C_{20}H_{18}Nb_2Cl_4$ calcd.: C, 40.99, H, 3.10; Nb, 31.71%. IR ($cm^{-1}$): 1321w, 1295m, 1115w, 1080s, 1030w, 1012w, 990m, 909m, 875m, 870m, 825s, 805m.

Aniline hydrochloride (0.1 g, 40%) was isolated from the $CH_3OH$ extract and then identified from its IR spectrum.

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## References

1 Yu T. Struchkov Yu L Slovchotov A I Yanovskii V P Fedin and D A Lemenovskii Izv Akad Nauk SSSR, Ser, Khim (1979) 1421

2 D A Lemenovskii V.P Fedin Yu L Slovohotov A I Yanovskii and Yu T Struchkov Koord Khimiya, 6 (1980) 882.

3 A N Nesmeyanov E G Perevalova V.P Fedin Yu L Slovohotov, Yu T Struchkov and D A Lemenovskii, Doklady Akad Nauk SSSR 252 (1980) 1141

4 F N Tebbe and G W Parshall J Amer Chem Soc 93 (1971) 3793

5 D.A Lemenovskii, V.P Fedin A V. Aleksandrov Yu L Slovohotov and Yu T Struchkov, J Organometal Chem 201 (1980) 257

6 C.R Lucas and M L H Green J Chem Soc Chem Commun , (1972) 1005