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ORGANONIOBIUM COMPOUNDS CONTAINING CYCLOOCTATETRAENE AS A LIGAND

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Summary

The compound $C_8H_8NbCl_2 \cdot THF$ has been prepared from $NbCl_5$ and $K_2C_8H_8$ (mole ratio 2/3). In this compound the C_8H_8 ring is probably planar. Reaction of $C_8H_8NbCl_2 \cdot THF$ with C_5H_5Na (mole ratio 1/2) yields the complex $(\eta^5$-$C_5H_5)_2Nb(\eta^2$-$C_8H_8)$. Evidence is given for an unusual dihapto mode of bonding of the C_8H_8 ring in the latter complex. Reaction of the complex with $NaBH_4$ yields $(\eta^5$-$C_5H_5)_2Nb(\eta^3$-$C_8H_9)$. The mechanisms of the reactions are discussed.

Introduction

It has been suggested that similarities in the Cp_2ML_n ($Cp = \eta^5$-C_5H_5, n = 1,2) chemistry of titanium and niobium have their origin in the almost equal atomic radii of these metals (about 1.32 Å) [1]. For instance, the compounds $Cp_2M(C_6H_5)_2$ and $Cp_2M(\eta^3$-allyl) are readily prepared when M = Ti, Nb, but not when M = V. This was explained by steric arguments based on the smaller metal radius of V (1.22 Å). Recently we prepared the compounds $Cp_2MC_8H_9$ with M = Ti, Nb and found that these do not obey the above mentioned rule in that the C_8H_9 ligand is bonded differently (η^1 and η^3 respectively) [2]. Moreover, the mechanisms of the reactions leading to these compounds are obviously different, since the synthesis of $Cp_2NbC_8H_9$ required the addition of $NaBH_4$. We now report a more detailed investigation of the mechanism of the formation of $Cp_2Nb(\eta^3$-$C_8H_9)$. It is shown that $Cp_2Nb(\eta^2$-$C_8H_8)$ is an intermediate in this reaction. The latter compound was synthesized from the new complex $(\eta^8$-$C_8H_8)NbCl_2 \cdot THF$.

Results and discussion

The olive green, air-sensitive compound $C_8H_8NbCl_2 \cdot THF$ was prepared from $NbCl_5$ and $K_2C_8H_8$ (mole ratio 2/3) and characterized by elemental analyses and IR and mass spectroscopy. It is moderately soluble in THF, and slightly soluble or insoluble in other common organic solvents. The IR spectrum (Fig. 1) strongly

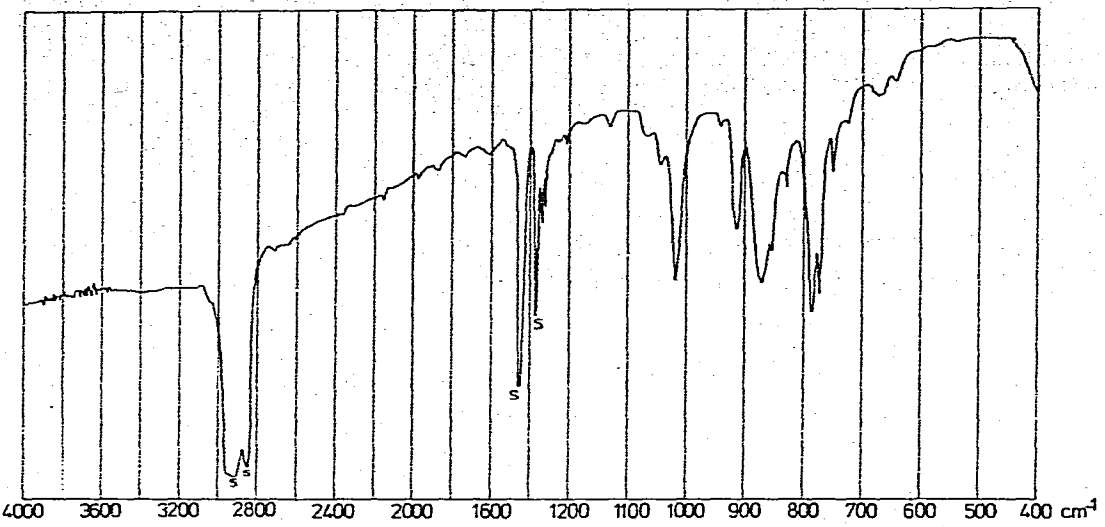

Fig. 1. IR spectrum of $C_8H_8NbCl_2 \cdot THF$. Absorptions of Nujol are indicated by s.

indicates the presence of a planar eight-membered ring, since it closely resembles the spectrum of (η^8-C_8H_8)$ZrCl_2 \cdot THF$ (prepared according to [7]). A crystal structure determination for this complex revealed the planarity of the eight-membered ring [3].

The mass spectrum of $C_8H_8NbCl_2 \cdot THF$ (Table 1) shows a peak at *m/e* 267 due to the ion $C_8H_8Nb^{35}Cl_2^+$ *.

Reaction of $C_8H_8NbCl_2 \cdot THF$ with two equivalent amounts of CpNa in diethyl ether yields a red-brown paramagnetic compound, which is rather air-sensitive and moderately soluble in organic solvents except alkanes. The elemental analyses are in agreement with the composition $C_{18}H_{18}Nb$. The mass spectrum at temperatures lower than 120°C, shows only $C_8H_8^+$ and its fragmentation via $C_6H_6^+$ and $C_5H_6^+$. At higher temperatures a spectrum is obtained with a mass peak at *m/e* 328, corresponding with $C_{18}H_{19}Nb^+$. The spectrum as a whole closely resembles the mass spectrum of $Cp_2NbC_8H_9$ [2], the major difference being the absence of a metastable peak at m^* 59.5 for the decomposition $C_8H_9^+ \rightarrow C_6H_7^+$ in the spectrum of $C_{18}H_{18}Nb$.

$C_{18}H_{18}Nb$ reacts with HCl in diethyl ether with quantitative formation of Cp_2NbCl_2 (identified by its IR spectrum). The volatile materials formed contained 1,3,5- and 1,3,6-cyclooctatriene in a ratio of about 1/1 (GLC). No C_5H_6 was detected.

Reaction of $C_{18}H_{18}Nb$ with $NaBH_4$ in diethyl ether results in quantitative formation of $Cp_2NbC_8H_9$, which was characterized by its IR spectrum [2].

The above provides strong evidence for the presence of a Cp_2Nb group in the $C_{18}H_{18}Nb$ compound. Additional support for this is provided by the IR spectrum (Fig. 2), which shows the characteristic Cp absorptions near 3100, 1000 and 800 cm^{-1}. Since the compound is paramagnetic it is likely that the eight-mem-

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[*] $C_8H_8NbCl_2 \cdot THF$ looses its THF very readily in vacuum just above room temperature. The product is (η^8-C_8H_8)$NbCl_2$. The same product was obtained by Van Oven from the reaction of $(C_8H_8)_2Nb$ with HCl in diethyl ether [4].

TABLE 1

THE MASS SPECTRUM OF $C_8H_8NbCl_2 \cdot THF$ (RECORDED AT 170°C)

m/e	Relative abundance (%)	Ion	Metastables
267	20	$C_8H_8NbCl_2^+$	$m^* = 102$
241	35	$C_6H_6NbCl_2^+$	$C_8H_8^+ \rightarrow C_8H_7^+$
189	15	$C_2H_2NbCl_2^+$	$m^* = 76.5$
163	12	$NbCl_2^+$	$m^* = 58.5$
128	8	$NbCl^+$	$C_8H_8^+ \rightarrow C_6H_6^+$
103	58	$C_8H_7^+$	$m^* = 57.5$
104	100	$C_8H_8^+$	$C_8H_7^+ \rightarrow C_6H_5^+$
78	75	$C_6H_6^+$	
51	30	$C_4H_3^+$	

bered ring serves as a two-electron donating ligand, thus giving the metal a seventeen-electron configuration. Such an η^2-C_8H_8 ligand is quite unusual; $CpMn(CO)_2$-(η-C_8H_8) providing the only known example [5]. The occurrence of the larger ring as an η^2-C_8H_8 ligand is in good agreement with the IR spectrum. In the region 1500—1600 cm^{-1} two bands are observed, at 1520 and 1592 cm^{-1}, which can be attributed respectively, to the coordinated C=C and the uncoordinated C=C's of the C_8H_8 ligand. The postulated structure $Cp_2Nb(\eta^2$-$C_8H_8)$ suggested that a synthesis starting from Cp_2NbCl_2 might be possible, and reaction of the latter compound with i-PrMgCl and C_8H_8 in diethyl ether gave a product with the same spectral and chemical properties as that from $C_8H_8NbCl_2 \cdot THF$ and CpNa. Furthermore, reaction with $NaBH_4$ leads to $Cp_2NbC_8H_9$. Thus $Cp_2NbC_8H_8$ can be regarded as an intermediate in the synthesis of $Cp_2NbC_8H_9$.

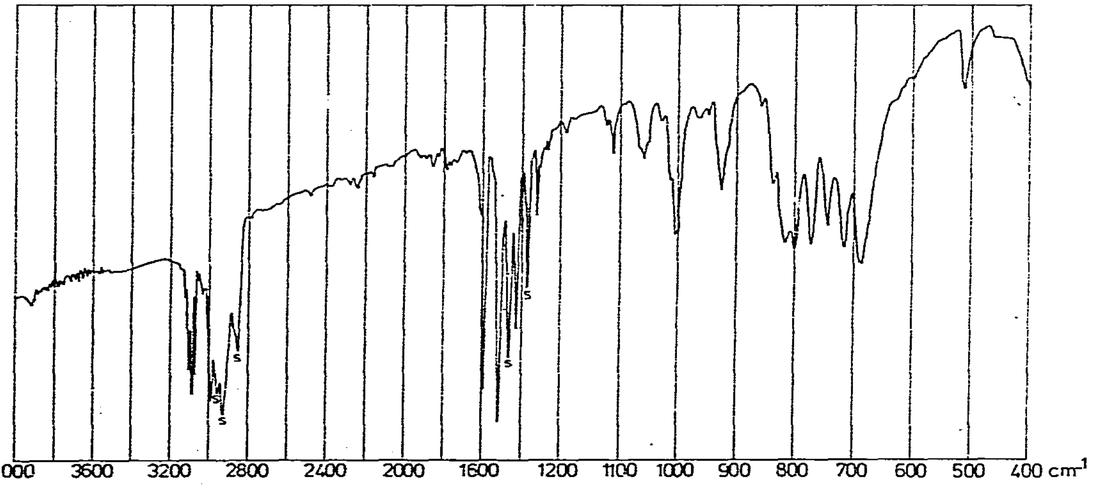


Fig. 2. IR spectrum of $Cp_2Nb(\eta^2$-$C_8H_8)$. Absorptions of Nujol are indicated by s.

Mechanistic considerations concerning the $Cp_2NbC_8H_9$ formation

Reaction of Cp_2NbCl_2 with i-PrMgCl leads to a diamagnetic niobium hydride species, probably $Cp_2Nb(H)C_3H_6$ [6]. Subsequent coordination of C_8H_8 gives $Cp_2NbC_8H_8$. Starting from $(\eta^8\text{-}C_8H_8)NbCl_2 \cdot THF$ and CpNa, the formation of $Cp_2NbC_8H_8$ involves a decrease of the hapticity of the C_8H_8 ligand. This contrasts the findings of Kablitz and Wilke who performed a similar reaction with $(\eta^8\text{-}C_8H_8)ZrCl_2 \cdot THF$ and obtained the product $(\eta^8\text{-}C_8H_8)CpZrCl$ [7]. They suggested that complete substitution was prevented by steric hindrance, but in view of our results on the niobium analogue this might well be a consequence of the more difficult reduction of the zirconium species, which is required for the formation of $Cp_2M(\eta^2\text{-}C_8H_8)$. The reaction of $Cp_2NbC_8H_8$ with $NaBH_4$, yielding $Cp_2NbC_8H_9$, probably proceeds via the intermediate $Cp_2Nb(H)C_8H_8$. Evidence for this is supplied by another method of preparation of $Cp_2NbC_8H_9$, viz. reaction of Cp_2NbBH_4 with $N(C_2H_5)_3$ in the presence of C_8H_8 to give $Cp_2NbC_8H_9$, via the intermediate Cp_2NbH [2]. The proposed reaction pathways are outlined in Scheme 1.

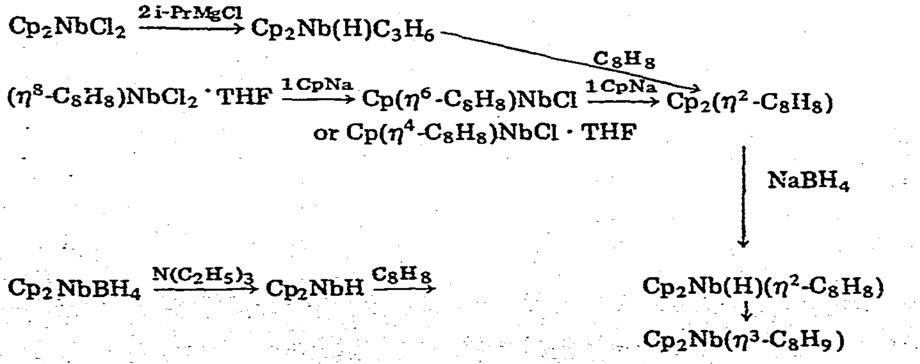
A compound, analoguous to the postulated $Cp_2Nb(H)(\eta^2\text{-}C_8H_8)$, is $Cp_2Nb(H)C_2H_4$, reported by Tebbe and Parshall [8]. This complex, however, is stable towards C=C insertion into the Nb—H bond, whereas $Cp_2Nb(H)C_8H_8$ is not. The stability of the ethylene complex has been explained by Lauher and Hoffmann, using MO bonding models [9]. Insertion of ethylene would result in $Cp_2NbC_2H_5$, which is expected to have a highest occupied molecular orbital (HOMO), destabilized relative to the HOMO of $Cp_2Nb(H)C_2H_4$. In the latter compound, there is stabilization of the HOMO because of π^*-interaction with anti-bonding ethylene orbitals. In our case, the product of insertion of C_8H_8 into the Nb—H bond is $Cp_2Nb(\eta^3\text{-}C_8H_9)$. In this complex, the HOMO is again stabilized by π^*-interaction with antibonding orbitals from the allylic fragment of the C_8H_9 ligand.

Experimental

All experiments were performed under nitrogen. Solvents were distilled over $LiAlH_4$. IR spectra were recorded on a Hitachi EPI-G spectrophotometer with

SCHEME 1

PROPOSED REACTION SEQUENCIES FOR THE FORMATION OF $Cp_2Nb(\eta^3\text{-}C_8H_9)$



Nujol mulls of the sample between KBr plates. The mass spectra were recorded by Mr. A Kiewiet with an AEI-MS9 instrument. Elemental analyses were performed at the Analytical Department of this University

Preparation of (η^8-C_8H_8)$NbCl_2$ · THF

To a well stirred suspension of $NbCl_5$ (3.0 mmol) in toluene (200 ml), 4.5 mmol of $K_2C_8H_8$ in THF (100 ml) were added slowly at —20°C. After stirring for 2 h at 10°C the brownish green solution was filtered. Upon cooling to —78°C olive green crystals of $C_8H_8NbCl_2$ · THF separated. (Found: C, 41.73; H, 4.92; Cl, 21.28; Nb, 27.84. $C_{12}H_{16}Cl_2ONb$ calcd.: C, 42.37; H, 4.75; Cl, 20.85; Nb, 27.32%.) Yield: 15%.

Preparation of $Cp_2Nb(\eta^2$-$C_8H_8)$

Procedure 1: Cp_2NbCl_2 (2.0 mmol), suspended in diethyl ether (100 ml) was allowed to react with i-PrMgCl (4.0 mmol) in diethyl ether in the presence of a slight excess of C_8H_8, at room temperature. After stirring for one hour the brown solution was filtered and cooled to —78°C. Reddish brown crystals of $Cp_2NbC_8H_8$ were isolated in 40% yield.

Procedure 2: $C_8H_8NbCl_2$ · THF (1.0 mmol), suspended in diethyl ether (100 ml), reacted with CpNa (2.0 mmol) at 0°C to form a brown solution, which was stirred for 1 h. Filtration and crystallization at —78°C yielded reddish brown crystals of $Cp_2NbC_8H_8$ in 50% yield. (Found: C, 65.49; H, 5.82; Nb, 28.06. $C_{18}H_{18}Nb$ calcd.: C, 66.07; H, 5.56; Nb, 28.39%.)

Reaction with $NaBH_4$

To a solution of $Cp_2NbC_8H_8$ (0.5 mmol) in diethyl ether (20 ml) was added an excess of finely ground $NaBH_4$. After stirring for 12 h the green solution was filtered and cooled to —78°C. $Cp_2NbC_8H_9$ [2], characterized by IR spectroscopy, was isolated in high yield (about 80%).

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