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ALKYL AND HYDRIDE-OLEFIN COMPLEXES OF NIOBOCENE

A.H. KLAZINGA and J.H. TEUBEN

Laboratorium voor Anorganische Chemie, Rijksuniversiteit, Nijenborgh 16,
9747 AG Groningen (The Netherlands)

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Summary

Reactions of Cp_2NbCl_2 with RMgCl (R = n-C_3H_7, i-C_3H_7, n-C_4H_9, s-C_4H_9 and n-C_5H_{11}) give niobocene hydride olefin complexes $Cp_2Nb(H)L$ (L = C_3H_6, C_4H_8 and C_5H_{10}). The last step of the reaction probably proceeds via a stereospecific β-H elimination from the monoalkyl species Cp_2NbR. Decomposition of n-alkyl products initially leads to *endo*-hydride olefin complexes exclusively, whereas iso-alkyls give predominantely the *exo*-isomers. The *endo*-hydride olefin complexes of niobocene are readily converted into alkylniobocenes by treatment with carbon monoxide or isocyanides. Carbonylation of the *exo*-isomers gives only $Cp_2Nb(CO)H$. It is not as easy to produce the *endo*- or *exo*-hydride olefin complexes, selectively as in the case of tantalum, but the conversion of niobocene hydride olefin complexes into alkylniobocenes proceeds much more easily than does the corresponding reaction for tantalum derivatives.

Introduction

Recently, we reported a novel, efficient and selective synthesis and some reactions of tantalocene hydride olefin complexes [1—3]. These complexes show interesting behaviour towards reagents such as carbon monoxide or isocyanides. Isomers with the olefin ligand in the *exo*-position do not react with isocyanides, but if heated with CO the olefin is displaced and the hydride carbonyl complex $Cp_2Ta(CO)H$ results. If the olefin is in the *endo*-position both CO and isocyanides induce insertion of the olefin into the Ta—H bond with formation of alkyltantalum complexes Cp_2TaRL (L = CO, R'NC). Attempts using an excess of CO and R'NC to induce insertion of the CO or R'NC ligand into the Ta—alkyl bond under mild conditions were not successful.

Since there are indications that the niobium compounds are more reactive than their tantalum analogues, probably due to the smaller stability of Nb—H than of Ta—H bonds, we decided to investigate the niobocene hydride olefin complexes $Cp_2Nb(H)L$. The only known example of this type is $Cp_2Nb(H)$-

C_2H_4, which was prepared from Cp_2NbH_3 and C_2H_4 [4]. This method is not successful for other hydride olefin complexes, so we decided to prepare these compounds by the Grignard method which gave the tantalum compounds [1].

In this paper we report the synthesis and properties of a number of niobocene hydride olefin complexes.

Results and discussion

Reaction of Cp_2NbCl_2 with two mol of RMgCl (R = n-C_3H_7, i-C_3H_7, n-C_4H_9, s-C_4H_9 and n-C_5H_{11}) in ether or pentane and subsequent extraction and crystallization form pentane yields the pale-yellow or pale-green products $Cp_2Nb(H)L$ (L = C_3H_6, C_4H_8 (1-butene) and C_5H_{10} (1-pentene)) in good yields. The niobocene hydride olefin complexes are monomeric, diamagnetic and very air-sensitive compounds.

The IR spectra of these complexes closely resemble those of the tantalum analogues (Fig. 1). The characteristic absorptions of the η^5-C_5H_5 groups are present and a rather broad absorption at 1600 cm^{-1} is assigned to ν(Nb—H). From the position and intensity of the absorption at 1195 cm^{-1} (a coupled C=C stretch, and CH_2 scissoring vibration [5]), it is concluded that the niobium—olefin bond is very strong, although probably not quite as strong as in the corresponding tantalum—olefin bond [6].

The ^1H NMR date of some niobocene hydride olefin complexes are given in Table 1. The interpretation is based on the arguments used for the tantalum compounds [1]. The assignment of *endo*- and *exo*-isomers is deduced from the position(s) of the substituent(s) on the double bond in the ^1H NMR spectra. In

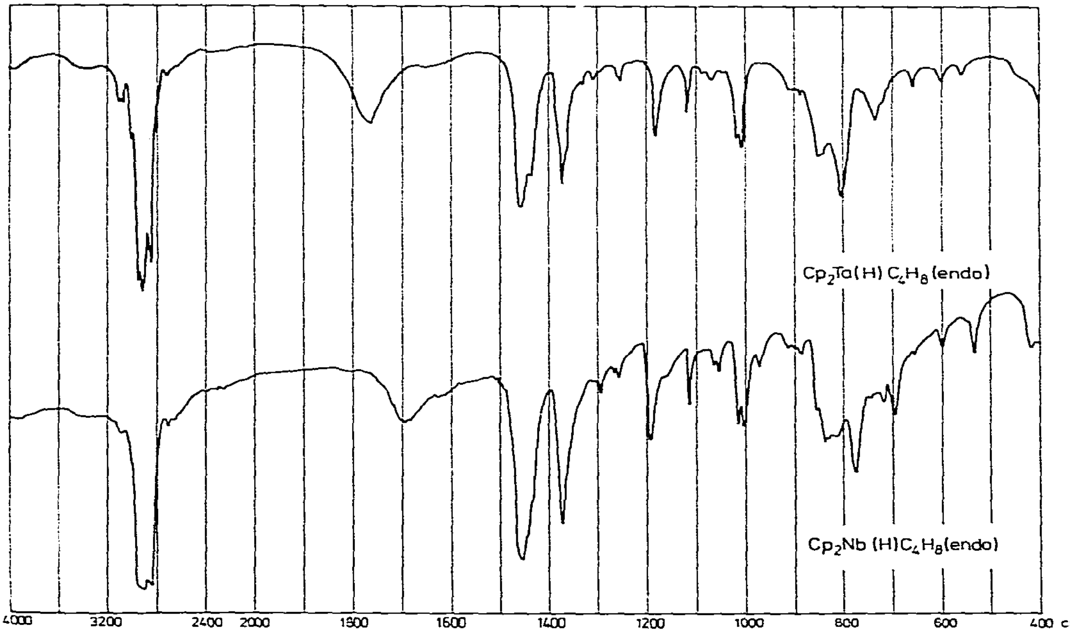


Fig. 1. IR spectra of $Cp_2Ta(H)C_4H_8$(*endo*) and $Cp_2Nb(H)C_4H_8$(*endo*).

TABLE 1

^1H NMR DATA OF $Cp_2Nb(H)L$ COMPOUNDS [a]

Compound	H_{Cp}	H_L	H
$Cp_2Nb(H)C_3H_6$ (*endo*)	4.50, 4.47	2.1—0.4	—2.84
$Cp_2Nb(H)C_3H_6$ (*exo*)	4.60, 4.50	1.8—0.4	—3.04
$Cp_2Nb(H)C_4H_8$ (*endo*)	4.52, 4.47	2.2—0.3	—2.79

[a] C_6D_6 solution, 35°C, internal standard TMS. Values are given in δ (ppm).

the mixture of products obtained from Cp_2NbCl_2 and i-C_3H_7MgCl the low-field CH_3 resonance at 1.98 ppm (broad unresolved singlet) is assigned to the *endo*-isomer. The resonance at 1.70 ppm (asymmetric doublet) arises from the *exo*-isomer.

The formation of hydride olefin complexes probably proceeds via a stereospecific β-H abstraction from the monoalkyl species (Scheme 1). Preferential formation of one isomer is expected: reaction with n-C_3H_7MgCl will lead to the *endo*-isomer, whereas i-C_3H_7MgCl is expected to give the *exo*-isomer. For tantalum the results agree with the proposed reaction mechanism. Only in the fast reactions (i-C_3H_7MgCl and s-C_4H_9MgCl) is the other isomer also formed. The ^1H NMR spectra of the products from the reactions of Cp_2NbCl_2 with RMgCl indicate that there are some remarkable differences in the isomer distribution between the niobium and tantalum compounds (Table 2). Whereas Cp_2TaCl_2 with n-C_3H_7MgCl yields only the *endo*-isomer, reaction of Cp_2NbCl_2 gives both isomers, although initially the *endo*-form predominates (Table 2).

The absence of the *exo*-isomer in the reaction of Cp_2NbCl_2 with s-C_4H_9MgCl is quite remarkable. In the reactions with either n-C_4H_9MgCl or s-C_4H_9MgCl, *endo*-$Cp_2Nb(H)C_4H_8$ is the only product, probably due to a lower thermal stability of the *exo*-conformation. Compared with Cp_2TaCl_2, the reactions of Cp_2NbCl_2 with RMgCl proceed much faster, probably due to an easier reduction of Cp_2NbCl_2 to Cp_2NbCl.

Niobocene hydride olefin complexes are thermally less stable than the tantalum analogues; e.g. $Cp_2Nb(H)C_4H_8$ decomposes at 66°C, $Cp_2Ta(H)C_4H_8$ (*endo*) at 110°C. Thermal decomposition of the tantalocene hydride olefin complexes gives both alkanes and the corresponding olefins (for ($Cp_2Ta(H)C_3H_6$ a propane/

SCHEME 1

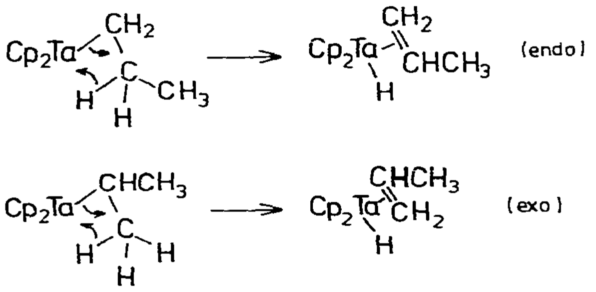


TABLE 2

$Cp_2Nb(H)L$ PRODUCTS FROM THE REACTION OF Cp_2NbCl_2 WITH RMgCl

Grignard reagent	Reaction time (h)	*endo*-Isomer (%)	*exo*-Isomer (%)	Total yield (%)
n-C_3H_7MgCl	0.5	65	35	[a]
n-C_3H_7MgCl	1.5	55	45	[a]
n-C_3H_7MgCl	2.0	50	50	55
i-C_3H_7MgCl	0.5	30	70	[a]
i-C_3H_7MgCl	2.0	50	50	50
n-C_4H_9MgCl	2.0	100	—	60
s-C_4H_9MgCl	2.0	100	—	20
n-$C_5H_{11}MgCl$	2.0	100	—	[a]

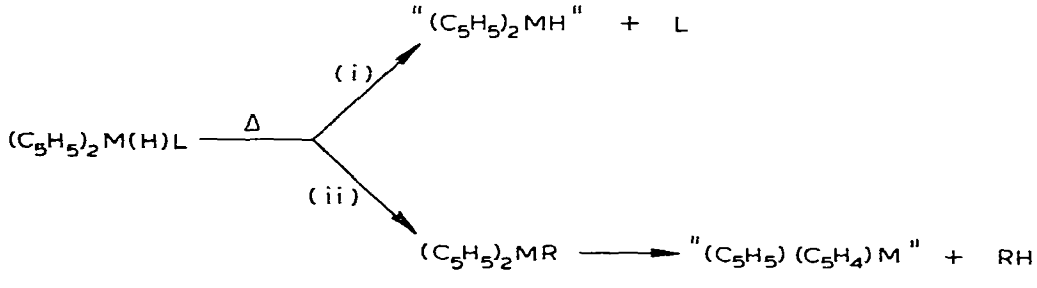
[a] Not determined.

propene ratio of about 4/1 is found). The formation of these products can be rationalized in terms of two different decomposition pathways; the first involves a direct cleavage of the metal—olefin bond to give the olefin and "Cp_2TaH", and the second an insertion of the olefin into the metal—hydride bond leading to Cp_2TaR, followed by Cp hydrogen abstraction by the alkyl group, leading to the alkane (Scheme 2), a process frequently observed for aryl- and alkyl-titanocene complexes [7,8]. Thermal decomposition of the niobocene hydride olefin complexes results in quantitative formation of alkanes, indicating that alkyl formation is much easier for niobium than for tantalum.

Carbonylation of niobium hydride olefin complexes

The nature of the reactions of niobocene hydride complexes with CO depends on the position of the olefin as has also been found for the tantalum compounds [2]. The *endo*-isomers give carbonyl alkyls $Cp_2Nb(CO)R$, whereas the *exo*-isomers give the carbonyl hydride complex $Cp_2Nb(CO)H$. Carbonylation of the pentane extract from the reaction of Cp_2NbCl_2 with *n*-C_3H_7MgCl or i-C_3H_7MgCl gives both $Cp_2Nb(CO)C_3H_7$ and $Cp_2Nb(CO)H$, whereas in the reactions with the products from n-C_4H_9MgCl, s-C_4H_9MgCl and n-$C_5H_{11}MgCl$ either $Cp_2Nb(CO)C_4H_9$ or $Cp_2Nb(CO)C_5H_{11}$ is formed, in keeping with the formation of only the *endo*-isomers.

SCHEME 2



The smooth reaction of the $Cp_2Nb(H)L$ complexes with CO contrasts with the corresponding reaction of the tantalum compounds, which requires higher temperatures. These observations again indicate an easier formation of the alkylniobium prior to or during the interaction with CO, as was indicated by the thermal decomposition.

The IR spectra of the alkylcarbonylniobocene complexes closely resemble those of $Cp_2Ta(CO)R$. As expected, the CO stretching vibrations are at higher wave-numbers (1895—1905 cm^{-1}) than for the tantalum analogues. Similar trends are observed for other 4*d* and 5*d* transition metal complexes (e.g. ref. 9). The ^1H NMR spectra of $Cp_2Nb(CO)R$ (in C_6D_6), where the Cp protons are found at δ 4.53 ppm, show exactly the same pattern as observed for the corresponding tantalum compounds [2].

The alkylniobium complexes are thermally less stable than their tantalum analogues, e.g. $Cp_2Nb(CO)C_4H_9$ decomposes at 130°C (m.p. 54°C) ($Cp_2Ta(CO)$-C_4H_9: m.p. 71°C, decomposition temperature 172°C). This may indicate a higher reactivity than for the tantalum compounds; however, under mild conditions the alkylniobium do not react with H_2, CO, or isocyanides, and behave in this respect quite like the tantalum complexes [2]. The formation of Cp_2Nb-$(CO)COC_2H_5$ from $Cp_2NbC_2H_5(C_2H_4)$ and CO at high temperatures and pressures [10] indicates that insertion of CO into a metal—alkyl bond can be expected under more forcing conditions.

Reaction with isocyanides

While the *exo*-isomer of $Cp_2Nb(H)C_3H_6$ does not react with isocyanides, reaction of equimolar amounts of *endo*-$Cp_2Nb(H)C_4H_8$ and R'NC (R' = 2,5-$(CH_3)_2C_6H_3$, cyclo-C_6H_{11}, CH_3 and t-C_4H_9) yields the isocyanide adducts Cp_2-$NbC_4H_9 \cdot$ R'NC in good yields. Again the reactions proceed much faster than with the corresponding tantalum compounds. With t-C_4H_9NC the reaction is complete within 0.5 h without formation of by-products; in contrast, with the corresponding tantalum compound it is possible to isolate pure $Cp_2NbC_4H_9 \cdot$ t-C_4H_9NC. The elemental analyses of the products (Table 3) are as expected.

The IR spectra of the niobocene isocyanide adducts are nearly identical with those of the corresponding tantalum compounds [3]. In line with the results obtained for hydride olefin and alkyl carbonyl complexes, the ν(NC) band for

TABLE 3

ANALYTICAL DATA OF THE COMPOUNDS $Cp_2NbC_4H_9 \cdot$ R'NC

Compound R' =	Yield (%)	Analysis (found (calc.) (%))			
		C	H	Nb	N
2,6-$(CH_3)_2C_6H_3$	39	67.18 (67.15)	7.03 (6.86)	22.36 (22.58)	3.50 (3.40)
C_6H_{11}	42	64.53 (64.78)	7.76 (7.77)	23.71 (23.86)	3.62 (3.60)
CH_3	35	59.53 (59.82)	6.88 (6.90)	29.35 (28.92)	4.32 (4.36)
t-C_4H_9	51	62.46 (62.81)	7.72 (7.77)	25.66 (25.57)	4.02 (3.85)

TABLE 4

SPECTROSCOPIC DATA OF $Cp_2NbC_4H_9 \cdot R'NC$

Compound R' =	IR ν(NC) (cm^{-1})	^{1}H NMR [b]		
		δ(Cp)	$\delta(C_4H_9)$	δ(R')
$2,6\text{-}(CH_3)_2C_6H_3$	1850 [a]	4.78	0.5—1.8	CH_3: 2.32, C_6H_3: 6.8
C_6H_{11}	1793	4.79	0.5—2.5	
CH_3	1796	4.76	0.5—1.8	2.93
$t\text{-}C_4H_9$	1803	4.78	0.5—1.9	1.31

[a] Broad absorption. [b] Internal standard TMS, 35°C, C_6D_6.

TABLE 5

DTA DATA OF $Cp_2NbC_4H_9 \cdot R'NC$ COMPLEXES

Compound	M.p. (°C)	Decomposition temperature (°C)
$Cp_2NbC_4H_9 \cdot 2,6\text{-}(CH_3)_2C_6H_3NC$	104	112
$Cp_2NbC_4H_9 \cdot C_6H_{11}NC$	64	72
$Cp_2NbC_4H_9 \cdot CH_3NC$	73	78
$Cp_2NbC_4H_9 \cdot t\text{-}C_4H_9NC$	60	63

the niobium adducts is found at higher wave-numbers than for their tantalum analogues (Table 4), demonstrating that Cp_2NbR is a weaker π-donor than the tantalocene derivative. The ^{1}H NMR spectra (Table 4) are as expected for these adducts.

Alkylniobium isocyanide complexes are rather inert, like their tantalum analogues. Attempts to force insertion of the isocyanide group into the Nb—alkyl bond with the aid of phosphines or excess of isocyanides failed, even at higher temperatures.

Summarizing it is clear that the chemistry of the niobocene hydride olefin complexes corresponds closely to that of the tantalum analogues, but the niobium complexes are thermally less stable (Table 5). The niobium hydride olefin complexes react faster with various substrates than their tantalum counterparts, indicating that for reactions starting from hydride olefin complexes and related compounds e.g. insertions into the metal—alkyl bond, niobium chemistry affords better prospects than tantalum chemistry. However, the reactions of the tantalum compounds are more stereospecific, and so the tantalum compounds remain good model compounds for investigating the chemistry of hydride olefin and related complexes.

Experimental

All experiments were performed under nitrogen. Solvents were distilled from benzophenoneketylsodium. Cp_2NbCl_2 was prepared according to ref. 11. The aryl and alkyl isocyanides were prepared by published procedures [11,12]. IR spectra were recorded on a Jasco-IRA-2 spectrophotometer with Nujol mulls of the sample between KBr discs. ^1H NMR spectra were run on a Perkin—Elmer R-24B (60 MHz) instrument. Decomposition temperatures and melting points were determined using a low-temperature DTA apparatus; heating rate 2—3° C/min. Elemental analyses were performed at the Microanalytical Department of this University under supervision of Mr. A.F. Hamminga.

Preparation of endo-$Cp_2Nb(H)C_4H_8$

To a well-stirred suspension of Cp_2NbCl_2 (650 mg, 2.2 mmol) in 50 ml of ether 4.3 ml of n-C_4H_9MgCl in ether (1.04 *M*) was added at room temperature. After 2 h the colour of the suspension had changed from brown to yellow. The solvent was removed under reduced pressure and the residue extracted with 100 ml of n-pentane. The pentane solution was concentrated to 50 ml and slowly cooled to —78° C. After decanting the mother liquor and washing with n-pentane at —20° C, the pale-yellow crystals were dried in vacuo and isolated. Yield: 365 mg *endo*-$Cp_2Nb(H)C_4H_8$ (60%). Analyses of *endo*-$Cp_2Nb(H)C_4H_8$: Found: C, 59.97; H, 6.89; Nb, 33.32. $C_{14}H_{12}Nb$ calcd.: C, 50.01; H, 6.83; Nb, 33.16%.

Other products $Cp_2Nb(H)L$ were prepared using the same procedure.

Preparation of $Cp_2Nb(CO)C_4H_9$

A solution of *endo*-$Cp_2Nb(H)C_4H_8$ (340 mg, 1.2 mmol) in 8 ml of toluene was stirred at 25° C under 1 atm of carbon monoxide. Within 1 h the colour of the solution had changed from yellow to blue-green. After evaporation, the residue was extracted with 60 ml of pentane. Concentration of the pentane solution and cooling to —78° C gave blue-green crystals. Yield: 240 mg $Cp_2Nb(CO)C_4H_9$ (65%, IR, ^1H NMR).

Preparation of $Cp_2NbC_4H_9 \cdot 2,6\text{-}(CH_3)_2C_6H_3NC$

A solution of *endo*-$Cp_2Nb(H)C_4H_8$ (310 mg, 1.1 mmol) and 2,6-$(CH_3)_2C_6H_3NC$ (145 mg, 1.1 mmol) in 6 ml of toluene was stirred for 1 h at room temperature. The dark green mixture was evaporated and the residue extracted with 40 ml of n-pentane. The pentane solution was slowly cooled to —78° C and dark green crystals separated. After decanting the mother liquor and washing with n-pentane at —20° C, crystals were isolated. Yield: 180 mg $Cp_2NbC_4H_9 \cdot 2,6\text{-}(CH_3)_2C_6H_3NC$ (39%).

The preparations of other isocyanide adducts of $Cp_2NbC_4H_9$ were carried out analogously.

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