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DICYCLOPENTADIENYL-NIOBIUM(III) AND -NIOBIUM(IV) COMPLEXES

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Summary

The reduction of $(\eta\text{-}C_5H_5)_2NbCl_2$ (I) under various conditions gives the dimer $(\eta\text{-}C_5H_5)_4Nb_2Cl_3$ (II) containing niobium(III) and niobium(IV). Reaction of II with $AgClO_4$ gives $[(\eta\text{-}C_5H_5)_4Nb_2Cl_2]^+ ClO_4^-$ (III). $FeCl_3$ and $(C_6F_5)_2TlBr$ displace I from II to give $(\eta\text{-}C_5H_5)_2Nb(\mu\text{-}Cl)(\mu\text{-}X)MY_2$, where M = Fe, X = Y = Cl(IV) and M = Tl, X = Br, Y = C_6F_5 (V). Reactions of I with metal halides MXY_2 give $(\eta\text{-}C_5H_5)_2ClNb(\mu\text{-}Cl)MXY_2$ where X = Y = Cl, M = Al (VI), Fe (VII), Tl (VIII) and X = Br, Y = C_6F_5, M = Tl (IX). The chemical behaviour of all these compounds is described.

Introduction

The reduction of I with sodium amalgam has been used to prepare niobium(III) halo derivatives [1—3] and other niobium(III) hydrides and alkyls have been extensively studied. We described here the isolation and structural identification of the first organo niobium(III)—niobium(IV) and its reactions with various metal halides which can be understood on the basis of the Lewis base character of I.

Results and discussion

$(\eta\text{-}C_5H_5)_2NbCl$ was previously prepared by reducing I with sodium amalgam in THF under nitrogen [1,2]. We have observed that this reaction takes place with the formation of an intermediate violet solution. Similar behaviour was observed when a toluene solution of $(\eta\text{-}C_5H_5)_2Nb(CH_3)Cl$ is treated with sodium amalgam in a molar ratio 1/1.2 under CO to give a final green solution with the intermediate formation of a blue solution [3]. In order to isolate the species responsible for this colour we used a shorter time of reaction; after stirring for 0.5 h the resulting violet solution was concentrated by evaporation

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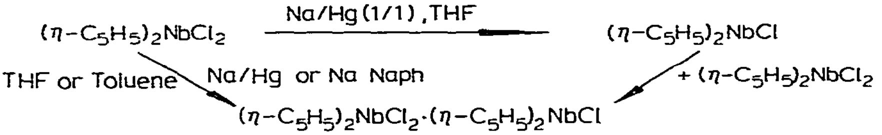
under vacuum and violet crystals analysing as $(\eta\text{-}C_5H_5)_2NbCl_2 \cdot (\eta\text{-}C_5H_5)_2NbCl$, were obtained. Analytical data are listed in Table 1. This formulation suggested that only half of the starting niobium(IV) complex had been reduced.

The same compound II can also be obtained as shown by eq. 1: (a) using a niobium(IV)/sodium amalgam mol ratio of 1/0.5 in THF, irrespective of the time of reaction, (b) by mixing solutions containing equimolar amounts of $(\eta\text{-}C_5H_5)_2NbCl$ and I (c) by reducing the niobium(IV) complex in toluene (again the result is independent of the molar ratio of the reactants and the reaction time, since II is insoluble in this solvent) and (d) by using sodium naphthalenide as the reducing agent instead of sodium amalgam.



(1)

Complex II is slightly soluble in non polar organic solvents and is air sensitive. Chlorine containing solvents such as chloroform, dichloromethane or carbon tetrachloride convert II into I. Complex II decomposes easily in polar organic solvents such as acetone, water and ethanol to give unidentified products. Violet solutions of II in THF in the presence of air immediately turn yellow, and $(\eta\text{-}C_5H_5)_2Nb(=O)Cl$ [1] can be isolated as a crystalline product.

Structural studies of II are limited by its lack of stability. Thus, molecular weight determinations in solution are prevented by its poor solubility and low stability in suitable organic solvents, and it was also not possible to obtain suitable crystals for X-ray diffraction.

Complex II has a μ_{eff} of 1.81 BM at 20°C which reveals the presence of one unpaired electron for each dimeric unit. This value is similar to that found for the analogous $(\eta\text{-}C_5H_5)_4Ta_2Cl_3$ [4]. The molecular ion is absent in the mass spectrum but other interesting peaks are observed, with the values and assignments shown in Table 2. The IR spectrum shows absorptions due to the $\eta\text{-}C_5H_5$ ring [5] and the Nb—Cl region under 400 cm^{-1} is closely related to that observed for I, as indicated in Table 3.

TABLE 1

ANALYTICAL DATA FOR CYCLOPENTADIENYLNIOBIUM COMPLEXES

Complex		Analysis (Found (calcd.) (%))		Colour
		C	H	
I.	$(\eta\text{-}C_5H_5)_2NbCl_2$	40.57(40.85)	3.56(3.42)	Brown
II.	$(\eta\text{-}C_5H_5)_2NbCl_2 \cdot (\eta\text{-}C_5H_5)_2NbCl$	43.27(43.47)	3.87(3.64)	Deep violet
III.	$[\eta\text{-}C_5H_5)_4Nb_2Cl_2]^+ ClO_4^-$	38.94(38.96)	4.07(3.27)	Orange-brown
IV.	$(\eta\text{-}C_5H_5)_2Nb(\mu Cl)(\mu Cl)FeCl_2$	28.33(28.52)	3.15(2.37)	Brown-yellowish
V.	$(\eta\text{-}C_5H_5)_2Nb(\mu Cl)(\mu Br)Tl(C_6F_5)_2$	30.56(30.13)	1.78(1.15)	Brown
VI.	$(\eta\text{-}C_5H_5)_2ClNb(\mu Cl)AlCl_3$	27.63(28.07)	2.55(2.34)	Pale brown
VII.	$(\eta\text{-}C_5H_5)_2ClNb(\mu Cl)FeCl_3$	26.74(26.32)	2.69(2.19)	Orange yellowish
VIII.	$(\eta\text{-}C_5H_5)_2ClNb(\mu Cl)TlCl_3$	20.43(19.85)	1.98(1.65)	Red-brown
IX.	$(\eta\text{-}C_5H_5)_2ClNb(\mu Cl)TlBr(C_6F_5)_2$	29.04(28.93)	1.52(1.10)	Brown

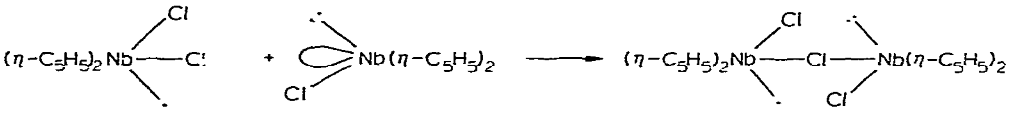
TABLE 2

MASS SPECTRUM OF $(\eta\text{-}C_5H_5)_2NbCl_2 \cdot (\eta\text{-}C_5H_5)_2NbCl$

m/e	Relative abundance (%)	Ion [a]
293	36.38	$Cp_2NbCl_2^+$
258	21.56	Cp_2NbCl^+
228	100	$CpNbCl_2^+$
193	20.92	$CpNbCl^+$
166	34.19	$NbCl_2^+$
129	18.96	Cp_2NbCl^{2+}
65	23	Cp^+
39	95	$C_3H_3^+$

[a] $Cp = C_5H_5$.

From these data we suggest that the most reasonable structure contains a single chlorine bridge as this places 18 and 17 electrons, respectively, on the niobium(III) and niobium(IV) atoms, although other structures cannot be excluded. In this case the formation of complex II is the consequence of the acidic character of $(\eta\text{-}C_5H_5)_2NbCl$, which achieves 18 electrons by accepting one pair from one of the chlorine atoms of I, as depicted in eq. 2



(2)

Complex II does not react with free ligands such as PPh_3 and CO. The reaction of II with $AgClO_4$ followed by addition of PPh_3 only lead to a precipitate corresponding to one of the chlorine atoms at room temperature even with an excess of the silver salt, and the cationic complex formed does not react further with PPh_3.

$$(\eta\text{-}C_5H_5)_4Nb_2Cl_3 + AgClO_4 \rightarrow [(\eta\text{-}C_5H_5)_4Nb_2Cl_2]^+[ClO_4]^- + AgCl \qquad (3)$$

Probably the cationic complex (III) contains a double chlorine bridge in order to retain 17 and 18 electrons respectively on the two Nb atoms [6].

TABLE 3

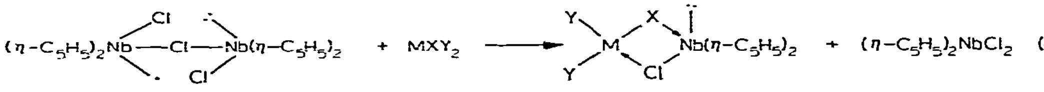
IR ABSORPTIONS OBSERVED FOR NIOBIUM COMPLEXES UNDER 400 cm^{-1}

I	II	III	IV	V	VI	VII	VIII	IX
			380vs(2) [a]		620s(1) [a]	380s(2) [a]		
380w	360—370w	—	—	—	375vw	370s	375w	380m
305s	300s	—	—	—	300m	300w	345s	350w
290vs	280vs	—	—	—	280vs	270m	320s	250—270s
270vs	265vs	—	—	—	260vs	230m	290vs	
							265s(3)	

[a] (1) ν(Al—Cl); (2) ν(Fe—Cl); (3) ν(Tl—Cl).

Complex III behaves as a conductor in acetone (Λ 135 ohm^{-1} cm^2 mol^{-1}) and is paramagnetic with μ_{eff} 1.6 BM at room temperature. The IR spectrum shows absorptions due to the η-C_5H_5 ring [5] and the T_d ClO_4^- [7], but there is no absorption assignable to terminal Nb—Cl bonds (see Tables 1 and 3).

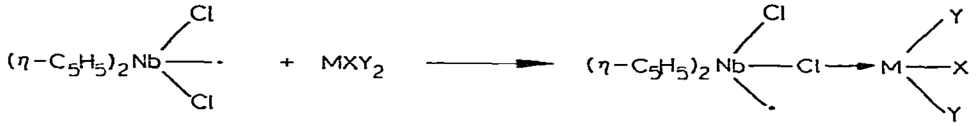
The niobium(III) in II behaves as a Lewis acid, and so other metal donors would be expected to play the same role as the remaining unreduced I. We found that II reacted with $FeCl_3$ and $(C_6F_5)_2TlBr$, with displacement of I to give the corresponding heterodinuclear compounds, as indicated in eq. 4:



(4)

$(X = Y = Cl, M = Fe$ (IV); $X = Br, Y = C_6F_5, M = Tl$ (V))

When these reactions are carried out using an excess of the metal halide a subsequent reaction with I takes place because the halides are strong Lewis acids and their acidity comes into action when opposed to the donor ability of the niobium(IV) complex. In order to confirm this behaviour we carried out separate reactions of I with the same and similar metal halides and observed the formation of heterodinuclear complexes, as indicated in eq. 5:



(5)

$(X = Y = Cl$ $M = Al$ (VI), Fe (VII), Tl (VIII) ; $X = Br$ $Y = C_6F_5$ $M = Tl$ (IX))

As expected, the niobium(III) unit is diamagnetic, so that complexes IV and V have the magnetic behaviour which corresponds to the other metal center in the dimer. Thus, V is diamagnetic and IV shows a μ_{eff} 5.7 BM at room temperature due to the tetrahedral iron(III) d^5 center. The ^{1}H NMR spectrum of V shows two peaks at 5.69 and 5.57 ppm from TMS (deuterobenzene as solvent) showing that the two (η-C_5H_5) rings are not equivalent, and thus that the tetrahedral environment of the thallium is asymmetric with respect to the reflection plane of the rings.

Both compounds are very air sensitive and rigorous precautions must be taken during their handling to avoid decomposition. The IR spectra show the absorptions of the (η-C_5H_5) ring [5], the C_6F_5 group [8] for V and the ν(Cl—Fe) [9] for IV, but there is no absorption assignable to terminal niobium—chlorine bonds (see Tables 1 and 3).

The niobium(IV) unit in complexes VI—IX is paramagnetic due to the presence of one unpaired electron, so that all the complexes are paramagnetic.

While complexes VI,VIII and IX have μ_{eff} between 1.43 and 1.49 BM, complex VII has μ_{eff} 6.32 BM, as expected for a system with six unpaired electrons, one for the niobium(IV) atom and five for the tetrahedral iron(III) d^5 center. Complexes VI—IX are also air sensitive but less so than the niobium(III) derivatives, and can be easily manipulated under nitrogen. They are insoluble in alkanes, diethyl ether, and benzene, and scarcely soluble in THF and other polar organic solvents. Their IR spectra show characteristic absorptions of the (η-C_5H_5) ring [5] and the C_6F_5 group [8] for IX. Absorptions quite close to those observed for complex I are present under 400 cm^{-1} and besides other absorptions due to ν(Cl—Al) [10] for VI, ν(Cl—Fe) [9] for VII and ν(Cl—Tl) [11] for VIII. (Tables 1 and 3).

Experimental

All operations were performed under vacuum or in an inert atmosphere using Schlenk-type glassware. IR spectra were recorded on a Perkin—Elmer spectrophotometer (over the range 4000—200 cm^{-1}) using Nujol between CsI plates. Magnetic measurements were carried out by the Faraday method with a Bruker magnet system. ^1H NMR spectrum was determined on a Varian FT 80A spectrometer. C,H analysis were made with a Perkin—Elmer 204 B microanalyzer. Solvents were dried and distilled before use.

(η-C_5H_5)$_2$$NbCl_2$ was prepared according [12].

(η-C_5H_5)$_2$$NbCl_2$ · (η-C_5H_5)$_2$NbCl(II)

Method A. Sodium amalgam (1.68 mmol of Na) was added to a suspension of I (1.000 g, 3.40 mmol) in THF (100 ml). After 0.5 h of stirring at room temperature a violet solution and a precipitate were obtained. The solution was filtered and then concentrated under reduced pressure to give deep violet crystals of II, which were filtered off, washed with pentane and dried under vacuum. Yield 60%. The yield was better when the initial residue was extracted several times with THF.

The same result was obtained with toluene as solvent and Na Naph as reducing agent.

Method B. Sodium amalgam (1.7 mmol of Na) was added to a suspension of I (0.500 g, 1.70 mmol) in THF (50 ml). After 1 h of stirring at room temperature a brown solution and a precipitate were obtained. The solution was filtered and I (0.500 g, 1.70 mmol) was then added, to give a violet solution immediately. The solution was filtered and then concentrated under reduced pressure to give deep violet crystals of II, which were washed with pentane and dried under vacuum. Yield 90%.

$[(\eta\text{-}C_5H_5)_4Nb_2Cl_2]^+$ ClO_4^- (III)

$AgClO_4$ (0.037 g, 0.18 mmol) was added to a solution of II (0.100 g, 0.18 mmol) in THF (50 ml). After 5 min of stirring at room temperature a large precipitate was formed and the solution became pale brown. The solid was filtered off and dried under vacuum. The resulting brown solid was extracted with acetone (three times) to yield a brown solution. This solution yielded complex III as orange-brown crystals after concentration and cooling at −70°C. Yield 60%.

$(\eta\text{-}C_5H_5)_2Nb(\mu\text{-}Cl)(\mu\text{-}X)MY_2$ (M = Fe, $X = Y$ = Cl (IV); M = Tl, X = Br, $Y = C_6F_5$ (V))

When a solution of $FeCl_3$ (14 ml, 0.075 N) in diethyl ether was added to a solution of II (0.469 g, 0.085 mmol) in THF (70 ml), the original violet solution rapidly became brown-yellowish. After stirring at room temperature for 0.5 h the solution was concentrated to 30 ml then was cooled overnight to yield brown crystals of I. The mother liquid was concentrated to 15 ml and pentane added, to give brown-yellowish crystals of IV. The crystals were washed with cold pentane and dried under vacuum. Yield 40% (based on niobium).

Compound V was prepared similarly.

$(\eta\text{-}C_5H_5)_2NbCl(\mu\text{-}Cl)MY_2X$ (M = Al, $X = Y$ = Cl (VI) M = Fe, $X = Y$ = Cl (VII), M = Tl, $X = Y$ = Cl (VIII), M = Tl, X = Br, $Y = C_6F_5$ (IX)

A solution of $FeCl_3$ (22.67 ml, 0.075 N) in diethyl ether was added to a suspension of I (0.500 g, 1.70 mmol) in diethyl ether. After 0.5 h of stirring at room temperature the original brown solid became orange-yellow. The solid was filtered off and repeatedly washed with pentane then dried under vacuum, and was identified as complex VII. Yield 90%.

Compounds VI, VIII and IX were obtained similarly.

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