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SOME COMPLEXES CONTAINING THE DICYCLOPENTADIENYL-NIOBIUM GROUP

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SUMMARY

The synthesis and properties of the complexes $(\pi\text{-}C_5H_5)_2NbCl_2$, $(\pi\text{-}C_5H_5)_2Nb(C_6H_5)_2$ and $(\pi\text{-}C_5H_5)_2Nb(\pi\text{-}C_3H_5)$ are described. The IR spectra of these complexes are analogous to those of the corresponding titanium complexes. The complex $(\pi\text{-}C_5H_5)_2NbCl_2$ has one unpaired electron per niobium atom; its mass spectrum is discussed. The complex $(\pi\text{-}C_5H_5)_2Nb(\pi\text{-}C_3H_5)$ is diamagnetic; its PMR spectrum indicates that the allyl group is π-bonded to niobium. These niobium complexes show a striking analogy with the corresponding complexes of titanium.

INTRODUCTION

Studies on the preparation and stability of complexes of general formula $(\pi\text{-}C_5H_5)_2MR_n$ (where M is a transition metal and R an alkyl or aryl group) led to the isolation of stable complexes of the type $(\pi\text{-}C_5H_5)_2TiR_2$ (ref. 1) and $(\pi\text{-}C_5H_5)_2VR$ (ref. 2). This difference in the behaviour of titanium and vanadium in their dicyclopentadienyl complexes may be due to the difference in the number of *d* electrons of the two elements, or to steric reasons since the atomic radius of Ti (1.32 Å) is considerably larger than that of V (1.22 Å). It seemed of interest, therefore, to study complexes containing the dicyclopentadienylniobium group, since niobium has the same number of *d* electrons as vanadium, but almost the same atomic radius (1.34 Å) as titanium. No complexes of composition $(\pi\text{-}C_5H_5)_2NbR$ had been described, while $(\pi\text{-}C_5H_5)_2Nb(\sigma\text{-}C_5H_5)_2$ was the only known[3] compound of the type $(\pi\text{-}C_5H_5)_2NbR_2$.

In a previous paper[4] we discussed the analogy of tetracyclopentadienylniobium and tetracyclopentadienyltitanium. In a preliminary communication[5] we reported the synthesis of the complexes $(\pi\text{-}C_5H_5)_2NbCl_2$ and $(\pi\text{-}C_5H_5)_2Nb(C_6H_5)_2$. The present paper gives detailed data of the preparation and the properties of the complexes $(\pi\text{-}C_5H_5)_2NbCl_2$, $(\pi\text{-}C_5H_5)_2Nb(C_6H_5)_2$ and $(\pi\text{-}C_5H_5)_2Nb(C_3H_5)$. It is found that these complexes also closely resemble the corresponding titanium complexes.

SYNTHESIS AND CHEMICAL PROPERTIES

Dicyclopentadienylniobium dichloride can be prepared from $NbCl_5$ in reasonable yield (40%); niobium is reduced to the tetravalent state by excess C_5H_5Na (ref. 3); treatment with hydrogen chloride leads to the final product:

$$NbCl_5+5\,C_5H_5Na \rightarrow (\pi\text{-}C_5H_5)_2Nb(\sigma\text{-}C_5H_5)_2+C_5H_5^{\cdot}+5\,NaCl$$

$$(\pi\text{-}C_5H_5)_2Nb(\sigma\text{-}C_5H_5)_2+2\,HCl \rightarrow (\pi\text{-}C_5H_5)_2NbCl_2+2\,C_5H_6$$

The chlorine atoms in dicyclopentadienylniobium dichloride can be replaced by organic groups as is the case with the analogous titanium complex[1,6]:

$$(\pi\text{-}C_5H_5)_2NbCl_2+2\,C_6H_5Li \rightarrow (\pi\text{-}C_5H_5)_2Nb(C_6H_5)_2+2\,LiCl$$

$$(\pi\text{-}C_5H_5)_2NbCl_2+2\,C_3H_5MgBr \rightarrow (\pi\text{-}C_5H_5)_2Nb(\pi\text{-}C_3H_5)+C_3H_5^{\cdot}+2\,MgBrCl$$

At low temperature (−45°), diphenyldicyclopentadienylniobium reacts with hydrogen chloride in ether with formation of dicyclopentadienylniobium dichloride and benzene; at room temperature, however, no detectable amounts of benzene or dicyclopentadienylniobium dichloride are formed. This is in contrast with the reaction of diphenyldicyclopentadienyltitanium with hydrogen chloride in ether, which proceeds both at −45° and at room temperature:

$$(\pi\text{-}C_5H_5)_2Ti(C_6H_5)_2+2\,HCl \xrightarrow{-45^\circ \text{ or } 23^\circ} (\pi\text{-}C_5H_5)_2TiCl_2+2\,C_6H_6$$

$$(\pi\text{-}C_5H_5)_2Nb(C_6H_5)_2+2\,HCl \xrightarrow{-45^\circ} (\pi\text{-}C_5H_5)_2NbCl_2+2\,C_6H_6$$

Reaction of allyldicyclopentadienylniobium with 4 *M* hydrochloric acid gives propene, as expected[6]. However, a slow further reaction takes place with formation of cyclopentadiene, as in the case of diallyldicyclopentadienylzirconium[9].

Diphenyldicyclopentadienylniobium and allyldicyclopentadienylniobium are very sensitive to air. When heated up to 200° no melting points are observed for the complexes $(\pi\text{-}C_5H_5)_2NbCl_2$, $(\pi\text{-}C_5H_5)_2Nb(C_6H_5)_2$ and $(\pi\text{-}C_5H_5)_2Nb(\pi\text{-}C_3H_5)$. In the case of $(\pi\text{-}C_5H_5)_2Nb(C_6H_5)_2$ a slow decomposition is observed above 150°.

SPECTRA

The IR spectra of the niobium complexes under discussion are analogous to those of the corresponding titanium complexes (Fig. 1). These spectra show the normal frequencies for π-bonded cyclopentadienyl groups[7]. In the spectra of the diphenyldicyclopentadienylmetal complexes the expected frequencies for phenyl groups are also present. The IR spectra of allyldicyclopentadienyl complexes of Ti and Zr have been discussed by Martin *et al.*[9]. They conclude that the C=C stretching frequency of σ-bonded allyl ligands is observed at about 1600 cm^{-1}, while for π-bonded allyl ligands this frequency is found at about 1500 cm^{-1}. Therefore, the C=C stretching frequency at 1480 cm^{-1} observed in the IR spectrum of allyldicyclopentadienylniobium indicates that the allyl group is π-bonded to the metal. In this configuration back-bonding by two electrons is possible; a diamagnetic complex is expected[9], as is actually observed. This configuration is also confirmed by the PMR spectrum of allyldicyclopentadienylniobium (Fig. 2). This shows two absorptions (with equal intensities) due to the cyclopentadienyl protons. Evidently the two rings show a different chemical shift. The allyl protons show the pattern expected for a π-bonded allyl group; all peaks show some secundary splitting as in the case of π-allylman-

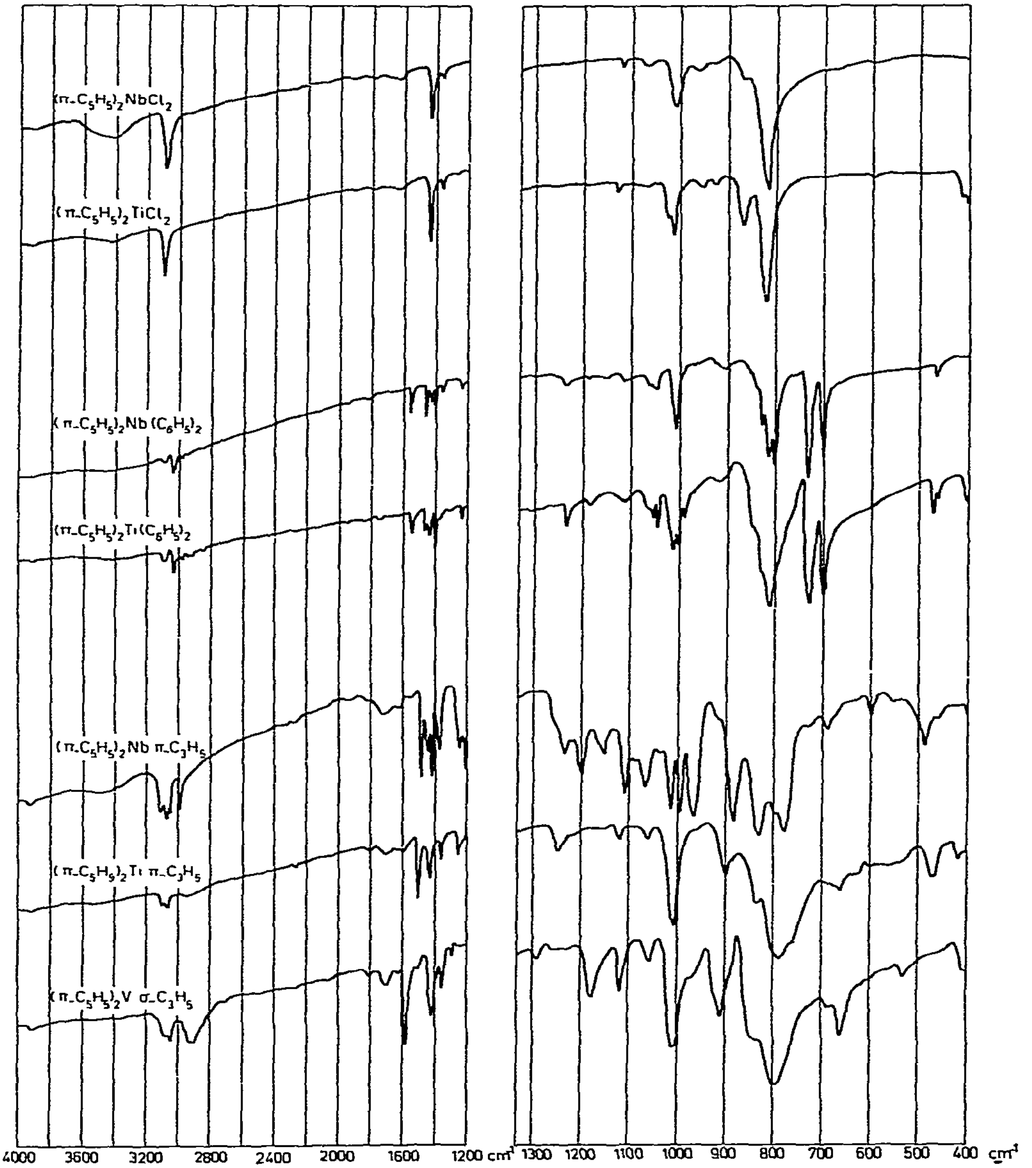

Fig. 1. IR spectra of $(\pi\text{-}C_5H_5)_2NbCl_2$, $(\pi\text{-}C_5H_5)_2TiCl_2$, $(\pi\text{-}C_5H_5)_2Nb(C_6H_5)_2$, $(\pi\text{-}C_5H_5)_2Ti(C_6H_5)_2$, $(\pi\text{-}C_5H_5)_2Nb(\pi\text{-}C_3H_5)$, $(\pi\text{-}C_5H_5)_2Ti(\pi\text{-}C_3H_5)$ and $(\pi\text{-}C_5H_5)_2V(\sigma\text{-}C_3H_5)$ in KBr discs.

ganese tetracarbonyl[10]. The observed chemical shifts and H–H coupling constants are given in the legend to Fig. 2.

The complex $(\pi\text{-}C_5H_5)_2NbCl_2$ is paramagnetic. In the temperature range 93–301°K a moment of 1.63 ± 0.01 B.M. is measured (corrected for induced diamagnetism). This corresponds with one unpaired electron per unit of $(\pi\text{-}C_5H_5)_2NbCl_2$ ($\mu_{\text{eff}} = 1.73$ B.M. calculated for spin only). The mass spectrum of $(\pi\text{-}C_5H_5)_2NbCl_2$ shows the fragmentation products consistent with the presence of a $\pi\text{-}C_5H_5M$ group

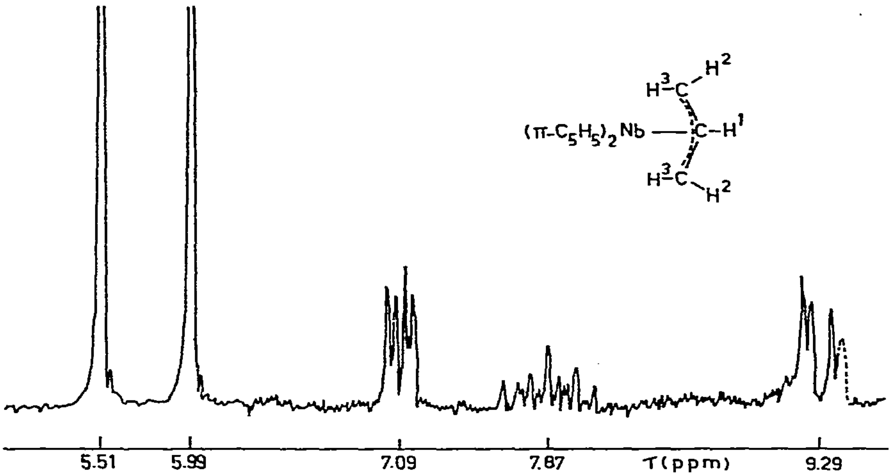

Fig. 2. PMR spectrum of $(\pi\text{-}C_5H_5)_2Nb(\pi\text{-}C_3H_5)$ in C_6D_6 at room temperature. The chemical shifts are given relative to TMS (τ 10.0 ppm) as internal standard. The shifts are assigned as follows: $\pi\text{-}C_5H_5$, τ 5.51 (5) and 5.99 (5); H_1, τ 7.87 (1); H_2, τ 7.09 (2); H_3, τ 9.29 (2). Relative intensities between parentheses. The splittings are indicative of the following coupling constants (Hz): J_{12} 9.5, J_{13} 15.0, J_{23} 5.0. The dotted peak is mutilated by the TMS lock.

TABLE 1

MASS SPECTRUM OF $(\pi\text{-}C_5H_5)_2NbCl_2$

The most characteristic ions are listed. Of ions containing chlorine only the peaks attributed to the ions containing ^{35}Cl isotopes are given.

m/e	Rel. abundance	Ion
293	100	$C_{10}H_{10}Cl_2Nb^+$
258	30	$C_{10}H_{10}ClNb^+$
228	96	$C_5H_5Cl_2Nb^+$
202	11	$C_3H_3Cl_2Nb^+$
193	8	$C_5H_5ClNb^+$
167	7	$C_3H_3ClNb^+$
146.5	2	$C_{10}H_{10}Cl_2Nb^{2+}$
93	0.3	Nb^+
66	0.8	$C_5H_6^+$
65	2	$C_5H_5^+$
35	0.3	Cl^-

in the molecule[8]. No peaks are observed above the value of *m/e* of the parent ion. The groups of peaks assigned to ions containing two chlorine atoms show the expected isotopic distribution pattern. Only peaks corresponding to ^{35}Cl are given in Table 1. Metastable peaks were observed at $m/e = 177.4$, 179.3 and 181.1 and at $m/e = 225.6$, 227.6 and 229.2. The first series of metastable peaks is due to loss of one C_5H_5 group from the parent ion, and the second series to loss of one chlorine atom from the parent ion.

DISCUSSION

The physical and chemical properties of the niobium complexes reported are in agreement with a di-π-cyclopentadienyl structure in these complexes: (π-C_5H_5)$_2$-$NbCl_2$, (π-C_5H_5)$_2$Nb(C_6H_5)$_2$ and (π-C_5H_5)$_2$Nb(C_3H_5).

IR and PMR spectra of allyldicyclopentadienylniobium indicate that the allyl group is π-bonded to the metal. The bonding in the complexes (π-C_5H_5)$_2$MR_n (n = 1, 2 or 3) has been discussed by Ballhausen and Dahl[11]; three orbitals of the metal are available for combining with orbitals of the ligands R. In (π-C_5H_5)$_2$Nb(π-C_3H_5) two of these orbitals combine with the (filled) bonding and non-bonding π-orbitals of the $C_3H_5^-$ ligand. The empty anti-bonding π-orbital of the allyl ligand combines with the third metal orbital, which contains two electrons ("back-bonding"). In (π-C_5H_5)$_2$Ti-(π-C_3H_5) the metal orbital involved in back-bonding contains one electron; in (π-C_5H_5)$_2$Zr(π-C_3H_5)(σ-C_3H_5) no metal orbital is available for back-bonding with the π-allyl ligand. The effect of this back-bonding will be a weakening of the C–C–C π-bond of the ligand and, therefore, a decrease of its (asymmetric) C–C stretching frequency; indeed, the asymmetric stretching C–C frequency of (π-C_5H_5)$_2$Nb-(π-C_3H_5) is found at 1480 cm^{-1}, which is much lower than the corresponding frequencies[9] of (π-C_5H_5)$_2$Ti(π-C_3H_5) (1509 cm^{-1}) and (π-C_5H_5)$_2$Zr(σ-C_3H_5)(π-C_3H_5) (1533 cm^{-1}). The strong back-bonding in (π-C_5H_5)$_2$Nb(π-C_3H_5) achieves a thermally very stable complex; the compound can be sublimed at 135° (0.25 mm) without appreciable decomposition.

The dicyclopentadienylniobium complexes reported so far, *viz.* (π-C_5H_5)$_2$-$NbCl_2$, (π-C_5H_5)$_2$Nb(σ-C_5H_5)$_2$ (ref. 3), (π-C_5H_5)$_2$Nb(C_6H_5)$_2$ and (π-C_5H_5)$_2$Nb-(π-C_3H_5) show a striking analogy with the corresponding complexes of titanium.

Evidently, the deviating behaviour of vanadium in its dicyclopentadienyl complexes is to be ascribed to steric reasons (atomic radius Ti 1.32 Å, V 1.22 Å, Nb 1.34 Å, ref. 12); a more detailed discussion will be given elsewhere[14].

EXPERIMENTAL

All experiments were carried out in an atmosphere of purified nitrogen[13]. Solvents were purified by conventional methods; before use, they were freed from oxygen by repeated degassing and saturating with nitrogen. Elementary analysis of C, H and Nb (by combustion) were carried out in the Microanalytical Department of this University under supervision of Mr. W. M. Hazenberg. IR spectra were measured by means of a Hitachi EPI-G spectrophotometer. The samples were embedded in KBr discs excluding oxygen as described previously[6]. The mass spectrum of dicyclopentadienylniobium dichloride was recorded by Mrs. I. Rozema–Meijer by means of an AEI MS9 instrument. The PMR spectrum of allyldicyclopentadienylniobium was recorded by Drs. J. W. Marsman (Institute for Organic Chemistry TNO, Utrecht, The Netherlands) with a Varian Associates HR 100 A instrument. The magnetic susceptibility of dicyclopentadienylniobium dichloride was determined by Miss A. H. C. Bruining by the Faraday method.

Dicyclopentadienylniobium dichloride

Solid C_5H_5Na (22.4 g, 254.3 mmoles) was suspended in 200 ml of benzene at room temperature. Powdered $NbCl_5$ (12.4 g, 45.7 mmoles) was added to the mixture. The colour of the mixture immediately changed into blue. After stirring for 1 h the solvent was removed at reduced pressure and the residue evaporated to dryness.

216 ml of a solution of hydrogen chloride in ether (1.5 *M*) was added. The reaction mixture gradually turned grey. After stirring for 1 h the reaction mixture was evaporated to dryness. The residue was sublimed at 270° (0.25 mm). The sublimate consisted of 5.53 g (18.8 mmoles) of black crystals of dicyclopentadienylniobium dichloride; yield 41%. (Found: C, 40.76, 40.67; H, 3.52, 3.56. $C_{10}H_{10}Cl_2Nb$ calcd.: C, 40.85; H, 3.43%.)

Diphenyldicyclopentadienylniobium

Dicyclopentadienylniobium dichloride (1.39 g, 4.7 mmoles) was mixed with 50 ml of ether at 0°. A solution of phenyllithium in ether (13.9 ml, 0.68 *M*; 9.4 mmoles) was added dropwise. The colour of the reaction mixture changed into reddish brown. The reaction mixture was stirred during 1 h. The mixture was filtered, and the filtrate concentrated to about 30 ml. On cooling to −78°, diphenyldicyclopentadienylniobium separated as red-brown crystals. The mother liquor was removed and 0.44 g (1.2 mmoles) of diphenyldicyclopentadienylniobium were isolated; yield 37%. (Found: C, 69.26; H, 5.96; Nb, 24.53. $C_{22}H_{20}Nb$ calcd.: C, 70.03; H, 5.34; Nb, 24.62%.)

Allyldicyclopentadienylniobium

Dicyclopentadienylniobium dichloride (2.94 g, 10.0 mmoles) was mixed with 75 ml of ether at 0°. A solution of allylmagnesium bromide in ether (33.3 ml, 0.6 *M*; 20.0 mmoles) was added dropwise. The colour of the reaction mixture changed into green. The reaction mixture was stirred during 1 h. The solvent was removed under reduced pressure. Pentane (150 ml) was added; the mixture was refluxed, filtered and the filtrate cooled to −78°. Green-black crystals separated. The mother liquor was removed. The product was further purified by sublimation at 135° (0.25 mm). Isolation gave 0.75 g (0.29 mmole) of green-black crystals of allyldicyclopentadienylniobium; yield 29%. (Found: C, 59.13; H, 5.86. $C_{13}H_{15}Nb$ calcd.: C, 59.10; H, 5.73%.)

Analysis of the phenyl groups of diphenyldicyclopentadienylniobium and -titanium

Diphenyldicyclopentadienylniobium and -titanium reacted with hydrogen chloride in ether at −45° under formation of dicyclopentadienylmetal dichloride and benzene. (At room temperature no benzene or dicyclopentadienylniobium dichloride were formed from diphenyldicyclopentadienylniobium, contrary to the reaction starting from diphenyldicyclopentadienyltitanium). Benzene was quantitatively determined by gas chromatography; the dicyclopentadienylmetal dichlorides were weighed, and identified by IR spectroscopy. The following results were obtained:

Starting material	Temp. (°C)	Moles of product (per mole of starting material)	
		$(\pi\text{-}C_5H_5)_2MCl_2$	Benzene
$(\pi\text{-}C_5H_5)_2Ti(C_6H_5)_2$	−45 or 23	1.0	2.0
$(\pi\text{-}C_5H_5)_2Nb(C_6H_5)_2$	23	0.0	0.0
$(\pi\text{-}C_5H_5)_2Nb(C_6H_5)_2$	−45	0.9	1.7

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REFERENCES

1 L. Summers, R. H. Uloth and A. Holmes, *J. Amer. Chem. Soc.*, 77 (1955) 3604.
2 F. W. Siegert and H. J. de Liefde Meijer, *J. Organometal. Chem.*, 15 (1968) 131.
3 E. O. Fischer and A. Treiber, *Chem. Ber.*, 94 (1961) 2193.
4 F. W. Siegert and H. J. de Liefde Meijer, *J. Organometal. Chem.*, 20 (1969) 141.
5 F. W. Siegert and H. J. de Liefde Meijer, *Recl. Trav. Chim. Pays-Bas*, 87 (1968) 1445.
6 H. A. Martin and F. Jellinek, *J. Organometal. Chem.*, 8 (1967) 115.
7 H. P. Fritz, *Advan. Organometal. Chem.*, 1 (1964) 239.
8 R. B. King, *J. Amer. Chem. Soc.*, 90 (1968) 1417.
9 H. A. Martin, P. J. Lemaire and F. Jellinek, *J. Organometal. Chem.*, 14 (1968) 149.
10 F. A. Cotton, J. W. Faller and A. Musco, *Inorg. Chem.*, 6 (1967) 181.
11 G. J. Ballhausen and J. P. Dahl, *Acta Chem. Scand.*, 15 (1961) 1333.
12 C. F. Bell and K. A. K. Lott, *Modern Approach to Inorganic Chemistry*, Butterworths, London, 2nd ed., 1966, p. 87.
13 H. J. de Liefde Meijer, M. J. Janssen and G. J. M. van der Kerk, *Studies in the Organic Chemistry of Vanadium*, Inst. for Org. Chem. TNO, Utrecht, 1963.
14 F. W. Siegert and H. J. de Liefde Meijer, to be published.