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DICYCLOPENTADIENYL-η^3-CYCLONONATETRAENYLNIOBIUM

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Summary

The compound $(C_5H_5)_2NbC_9H_9$ was prepared from $(C_5H_5)_2NbCl_2$ and LiC_9H_9 (mole ratio 1/2), and characterized by IR and ^{1}H NMR spectroscopy and elemental analyses. Variable-temperature NMR spectroscopy revealed fluxional behaviour of the nine-membered ring, which is suggested to be bonded in an allylic fashion.

Introduction

Our interest in sandwich and pseudo-sandwich compounds of early transition metals, and particularly the behaviour of the eight-membered rings in $(C_5H_5)_2$-Ti-η^1-C_8H_9 and $(C_5H_5)_2$Nb-η^3-C_8H_9 [1], led us to extend our research to nine-membered hydrocarbon rings attached to Nb and Ti. Only very few organotransition metal compounds containing such rings are known. Deganello et al. [2] reported the synthesis of $C_9H_{10}Fe(CO)_3$; Verkouw and coworkers prepared C_5H_5Ti-η^7-C_9H_9 [3]. Work on several organotransition metal compounds containing nine-membered hydrocarbon rings is in progress in our laboratory. In this paper we report the synthesis and some properties of the complex $(C_5H_5)_2$-NbC_9H_9.

Experimental

General

All experiments were carried out under nitrogen. Solvents were distilled from $LiAlH_4$ before use. LiC_9H_9 was prepared from C_9H_9Cl and Li according to refs. 4 and 5.

Synthesis of $(C_5H_5)_2NbC_9H_9$

To a stirred suspension of $(C_5H_5)_2NbCl_2$ (0.8 g, 2.7 mmol) in diethyl ether (100 ml) a solution of C_9H_9Li (5.4 mmol) in THF (50 ml) was added at −10°C.

TABLE 1

THE MASS SPECTRUM OF $(C_5H_5)_2NbC_9H_9$ (recorded at 100°C)

m/e	Relative abundance (%)	Ion	Metastables
340	1	$C_{19}H_{19}Nb^+$	116.8
224	14	$C_{10}H_{11}Nb^+$	114.9
223	10	$C_{10}H_{10}Nb^+$	112.0
117	40	$C_9H_9^+$	90.5
116	100	$C_9H_8^+$	70.7
115	80	$C_9H_7^+$	68.8
91	18	$C_7H_7^+$	64.3
89	14	$C_7H_5^+$	57.3
66	16	$C_5H_6^+$	44.6
65	14	$C_5H_5^+$	
63	16	$C_5H_3^+$	

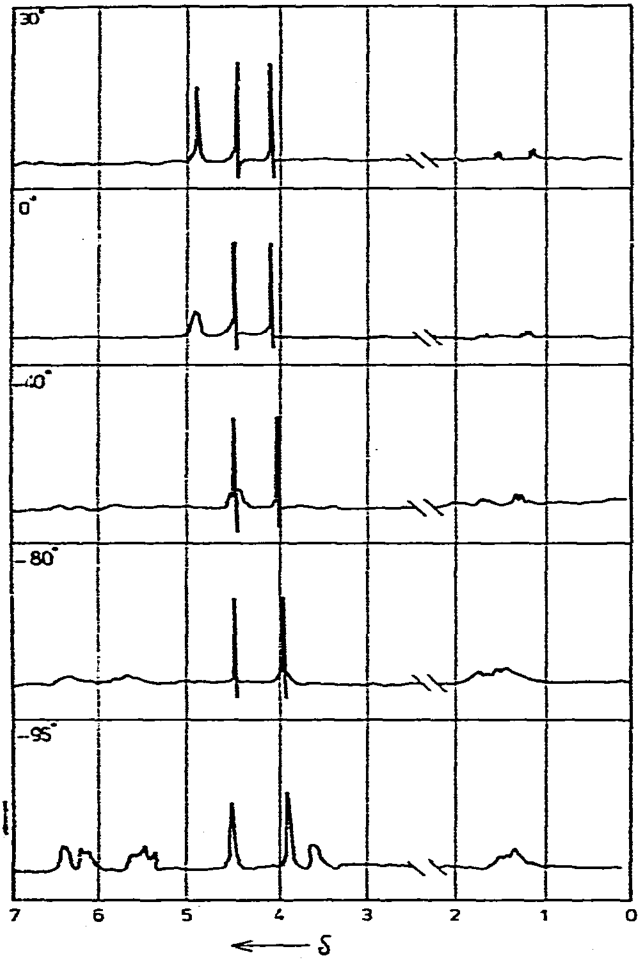

Fig. 1. Variable-temperature NMR spectra of $(C_5H_5)_2NbC_9H_9$ (resonances due to toluene and TMS are omitted).

During stirring at room temperature the colour changed from brown via violet to dark green. After filtration and cooling to —78°C, dark green crystals of $(C_5H_5)_2NbC_9H_9$ were obtained in about 40% yield. (Found: C, 66.23; H, 5.80; Nb, 26.83. $C_{19}H_{19}Nb$ calcd.: C, 67.06; H, 5.64; Nb, 27.30%). The compound is rather air-sensitive and unstable in solution (especially in CS_2, chlorinated solvents and THF) at room temperature.

Spectra

The IR spectrum of $(C_5H_5)_2NbC_9H_9$ was recorded on a Hitachi EPI-G spectrophotometer using a Nujoll mull between KBr plates. Absorptions were found at: 3120w, 3115w, 3090m, 3082m, 3070m, 1590m, 1420m, 1265m, 1135m, 1113w, 1065m, 1020m, 1000m, 980w, 965w, 952w, 933w, 912w, 898m, 860w, 843m, 835w, 830m, 802w, 790m, 780m, 760m, 718s, 682w, 623m, 589m cm^{-1}. The mass spectrum was recorded by Mr. A. Kiewiet with an AEI-MS9 instrument. The spectrum showed a parent peak at *m/e* 340 ($C_{19}H_{19}Nb^+$). Details are given in Table 1.

^1H NMR spectra were recorded on a Varian XL-100 instrument using toluene-d_8 as a solvent and TMS as an internal reference. At room temperature three singlets were observed at δ 4.08, 4.46 and 4.96 ppm (relative intensities 5/5/9). Upon cooling, the intensities and positions of the two cyclopentadienyl ring resonances (at δ 4.08 and 4.46 ppm) did not change significantly. The singal due to C_9H_9 protons (δ 4.96 ppm) collapsed and disappeared completely at —40°C. At about —95°C (the lowest temperature possible) new signals were observed as shown in Fig. 1.

Discussion

Elemental analyses and the mass spectrum (Table 1) are in agreement with the formula $C_{19}H_{19}Nb$. It is concluded from the IR, mass and NMR spectra that the two C_5H_5 ligands are π-bonded to the metal. The cyclononatetraenyl ligand in $C_{19}H_{19}Nb$ is fluxional as is clearly demonstrated by the NMR spectra at different temperatures. The selection of a solvent for the NMR measurements was limited, because of the high reactivity of the compound; of the more common organic solvents we found toluene-d_8 the most suitable for our purpose. The spectra recorded at 30, 0, —40, —80 and —95°C are shown in Fig. 1. The signal at 4.96 ppm, due to the nine-membered ring protons, broadens upon cooling. At —40°C, the signal has disappeared and new resonances between 5.3 and 6.5 ppm appear. At the lowest temperature possible (—95°C) three new resonances can be located on the low-field side of the original singlet. On the high-field side there is a new signal at 3.7 ppm; around 1.2 ppm another new signal appears, but the spectrum in this range also contains signals due to impurities, which make an assignment problematic.

One explanation for the observed fluxional character of the C_9H_9 ring may be that the ring is present as an η^1-bonded ligand. Known compounds involving such a ligand are $C_9H_9E(CH_3)_3$ (E = Si, Ge, Sn) [6]. Of these compounds, only that with E = Sn has a dynamic nine-membered ring system, the protons of which give rise to a singlet resonance signal at δ 5.30 ppm in the NMR spectrum. The complexes with E = Si, Ge have a non-fluxional C_9H_9 ligand. In their

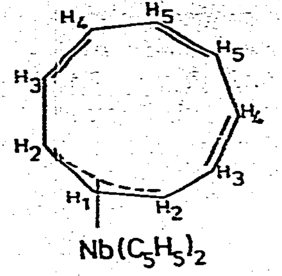

Fig. 2. Structure of $(C_5H_5)_2NbC_9H_9$.

spectra a multiplet resonance signal, due to eight protons of the C_9H_9 ring, is observed between 5.30 and 6.15 ppm, whereas the ninth proton gives a triplet at 3.42 ppm. If the C_9H_9 group in $(C_5H_5)_2NbC_9H_9$ were σ-bonded as in the tin compound, the ninth proton of the C_9H_9 ligand at low temperature should have its resonance signal at least a few ppm upfield of TMS (calculated from weighed averages); there would be no explanation for the resonance at δ 3.70 ppm.

Another possible explanation of the dynamic character of the nine-membered ring is that the ring behaves as an allylic ligand. By analogy with the assignment given for the low temperature NMR spectrum of the well-known compound $C_5H_5Mo(CO)_2(\eta^3\text{-}C_7H_7)$ [7], we assign the resonances at 6.48, 6.18 and 5.50 ppm to the protons H(3), H(4) and H(5), respectively (Fig. 2). The signal at 3.70 ppm originates from H(2). Then, the signal at 1.2 must be due to H(1). Such a δ-value corresponds quite well with that found for the allylic proton H(1) in the Mo compound [7], and with that calculated from weighed averages. We conclude that $C_{19}H_{19}Nb$ probably has the structure shown in Fig. 2, in which Nb has an eighteen-electron configuration.

In contrast to the compound $(C_5H_5)_2NbC_8H_9$, containing an allylic C_8H_9 group [1], $(C_5H_5)_2NbC_9H_9$ does not show an allylic C=C absorption in the region 1550—1450 cm^{-1} of the IR spectrum. However, such an absorption is also absent in the IR spectrum of $C_5H_5Mo(CO)_2C_7H_7$ [8]. The C_7H_7 ligand was assumed to be an η^3-cycloheptatrienyl group; later it was shown by low-temperature NMR measurements that the C_7H_7 ligand is bonded in an allylic fashion [7]. The observation that the C_5H_5 ring proton resonances are hardly affected by changes in temperature, indicates that there is a constant difference in chemical environment between the two five-membered rings. From this it may be concluded that the conformation of the nine-membered ring does not change significantly with temperature, indicating a non-planar structure of the ring at room temperature also.

As can be seen from the mass spectrum, the C_9H_9 group in $(C_5H_5)_2NbC_9H_9$ is very loosely bonded compared with the C_8H_9 group in $(C_5H_5)_2NbC_8H_9$ [1]. It is easily split off from $C_{19}H_{19}Nb^+$ as C_9H_9 or C_9H_8, leaving $C_{10}H_{10}Nb^+$ or $C_{10}H_{11}Nb^+$, respectively. $C_9H_9^+$ is converted into $C_9H_8^+$ (m^* 114.9) and $C_7H_7^+$ (m^* 70.8). $C_9H_8^+$ probably undergoes a rearrangement to an indene cation, which further breaks down via known routes [9,10].

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