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DICYCLOPENTADIENYL-η^1- CYCLOOCTATRIENYLTITANIUM AND DICYCLOPENTADIENYL-η^3-CYCLOOCTATRIENYLNIOBIUM

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Summary

Dicyclopentadienyl-η^1-cyclooctatrienyltitanium and -η^3-cyclooctatrienylniobium are prepared from $(C_5H_5)_2MCl_2$ (M = Ti, Nb) and two equivalent amounts of i-PrMgCl in the presence of an excess of cyclooctatetraene For the preparation of $(C_5H_5)_2NbC_8H_9$ the presence of $NaBH_4$ is also necessary. The products obtained are characterized by IR, mass and ^{1}H NMR spectroscopy Reactions with HCl, thermal decomposition reactions, magnetic measurements and elemental analyses were performed to establish the structures

Introduction

Many organotransition metal compounds containing an eight-membered hydrocarbon ring are known [1] In most of these the metal is bound to the ring in a *di-*, *tetra-*, *hexa-* or *octa-hapto* fashion. A few compounds are known in which the metal-to-ring bond involves one or three carbon atoms, examples are $(C_8H_9)M(CO)_3X$ (X = halogen, M = Fe [2], Ru [3]) and $(C_8H_9)Co(CO)_3$ [4], all containing the η^3-cyclooctatrienyl ligand. Examples of σ-bonded eight-membered rings are even more scarce. Sharma et al reported the synthesis of di-η^1-cyclooctatetraenyldichlorometal compounds (M = Ti, Zr, Hf) [5], while Cooke et al. prepared an iron compound containing an η^1-cyclooctatetraenyl ligand viz $(C_5H_5)Fe(CO)_2(C_8H_7)$ [8]

In our search for sandwich- and pseudo-sandwich compounds of the early transition metals we encountered the new complex $(C_5H_5)_2NbC_8H_9$, which contains a η^3-cyclooctatrienyl ligand. As already shown by Martin et al [7], such a π-allylic ligand is unlikely for M = Ti. Indeed, the analoguous reaction starting from $(C_5H_5)_2TiCl_2$ led to $(C_5H_5)_2Ti(\eta^1\text{-}C_8H_9)$.

Experimental

General

All experiments were carried out under nitrogen, solvents were purified by standard methods. i-PrMgCl, $(C_5H_5)_2TiCl_2$ and $(C_5H_5)_2NbCl_2$ were prepared by established methods. C_8H_8 was obtained commercially and distilled before use Commercial $NaBH_4$ was used without purification. Elemental analyses were performed in the Analytical Department of the Chemical Laboratories of this University.

Preparation of $(C_5H_5)_2TiC_8H_9$

$(C_5H_5)_2TiCl_2$ (1 3 g, 5.1 mmol) was suspended in diethyl ether (150 ml) and about 10 mmol of C_8H_8 were added. The stirred suspension was cooled to −5°C and allowed to react with two equivalents of an i-PrMgCl solution in diethyl ether, which was slowly added from a syringe. The colour changed to dark green. After stirring for 1 h at room temperature the solution was filtered and cooled to −30°C. Dark green, very air-sensitive crystals of $(C_5H_5)_2TiC_8H_9$ were obtained (Yield 50%; Found: C, 74.80; H, 6 80; Ti 16.40 $C_{18}H_{19}Ti$ calcd.· C, 76 25; H, 6 77; Ti, 16.56%.)

Preparation of $(C_5H_5)_2NbC_8H_9$

Procedure 1. $(C_5H_5)_2NbCl_2$ (1.5 g, 5.1 mmol) was suspended in diethyl ether (150 ml) and C_8H_8 and $NaBH_4$ were added in slight excess. Two equivalents of i-PrMgCl in diethyl ether were added at room temperature. After stirring for 14 h the green mixture was extracted with diethyl ether, giving dark green, air-sensitive $(C_5H_5)_2NbC_8H_9$ in about 60% yield. These were recrystallized from pentane. (Found· C, 65.55; H, 5.97; Nb, 27 62. $C_{18}H_{19}Nb$ calcd : C, 65 85; H, 5.82; Nb, 28.33%.)

Procedure 2 A slight excess of C_8H_8 and $N(C_2H_5)_3$ was added at room temperature to $(C_5H_5)_2NbBH_4$ [8] (2 15 g, 9 mmol) in toluene (60 ml). After stirring for 12 h the green mixture was extracted with toluene Crystallization from pentane gave $(C_5H_5)_2NbC_8H_9$ (1.8 g, 60%).

Thermolysis of $(C_5H_5)_2TiC_8H_9$

A solution of $(C_5H_5)_2TiC_8H_9$ (310 mg, 1.1 mmol) in benzene-d_6 (2 ml) was stirred for 1 h at 75°C. Volatile materials were removed in vacuo and collected in a cold trap. ^1H NMR spectroscopy showed the presence of C_5H_6 and no C_5H_5D. After evaporation the residue was characterized as $C_5H_5TiC_8H_8$ by IR spectroscopy [9] (yield 220 mg, 90%).

Reaction of $(C_5H_5)_2TiC_8H_9$ with HCl

To a stirred solution of $(C_5H_5)_2TiC_8H_9$ (430 mg, 1.5 mmol) in pentane (40 ml) 5.0 ml of a 0.3 *N* HCl solution in diethyl ether was added at room temperature. A green-brown precipitate was formed immediately, and characterized as $(C_5H_5)_2TiCl$ by its IR spectrum (yield 91%). The yellow pentane solution was evaporated, leaving a yellow oil, which was characterized as a mixture of 1,3,6- and 1,3,5-cyclooctatriene by ^1H NMR and IR spectroscopy and by GLC. The ratio of the two isomers as determined by NMR and GLC was 1,3,6-C_8H_{10}/

1,3,5-C_8H_{10} = 9/2. The total yield of C_8H_{10} (about 50%) was determined by NMR spectroscopy using CCl_4 as a solvent and a weighed amount of benzene as internal reference (C_8H_{10} obtained from $Na_2C_8H_8$ and methanol was used for comparison)

Reaction of $(C_5H_5)_2NbC_8H_9$ *with HCl*

Treatment of $(C_5H_5)_2NbC_8H_9$ with HCl gave $(C_5H_5)_2NbCl_2$ (characterized by IR spectroscopy and chemical analysis), together with cyclooctatriene, which was characterized by GLC and by NMR and IR spectroscopy The isomer ratio found was 1,3,6-C_8H_{10}/1,3,5-C_8H_{10} = 5/2.

Spectra

The infrared spectra of the compounds were recorded on a Hitachi EPI-G spectrophotometer with nujol mulls between KBr windows

$(C_5H_5)_2TiC_8H_9$ 3080w, 3022w, 3002w, 1620m, 1435m, 1403m, 1365m, 1303w, 1135w, 1128w, 1058w, 1018s, 1005s, 962w, 912m, 900m, 892m, 845m, 840m, 815m, 798s, 760s, 750sh, 742m, 730s, 700m, 690s, 610w, 540m, 475w cm^{-1}.

$(C_5H_5)_2NbC_8H_9$. 3110w, 3082w, 3070m, 3012(sh), 3000m, 1605s, 1540m, 1420m, 1368m, 1300w, 1260w, 1230w, 1116s, 1068m, 1023(sh), 1018m, 998m, 896s, 842m, 830m, 802(sh), 792s, 752m, 738s, 700s, 610w, 592w, 540m, 475m cm^{-1}.

Mass spectra were recorded by Mr. A Kiewiet with an AEI-MS9 instrument. Due to the extreme air-sensitivity of $(C_6H_5)_2TiC_8H_9$ a reliable mass spectrum could not be obtained The mass spectrum of $(C_5H_5)_2NbC_8H_9$ showed a parent peak at *m/e* 328. Metastables and peaks with a relative abundance larger than 20 are listed in Table 1.

TABLE 1

MASS SPECTRUM OF $(C_5H_5)_2NbC_8H_9$ (recorded at 115°C)

m/e	Rel abundance (%)	Ion	Metastables
328	25	$C_{18}H_{19}Nb^+$	M^* 57 5
224	100	$C_{10}H_{11}Nb^+$	$C_8H_7^+ \xrightarrow{-C_2H_2} C_6H_5^+$
223	90	$C_{10}H_{10}Nb^+$	M^* 58 5
197	20	$C_8H_8Nb^+$	$C_8H_8 \xrightarrow{-C_2H_2} C_6H_6^+$
104	24	$C_8H_8^+$	M^* 59 5
93	24	Nb^+	$C_8H_9^+ \xrightarrow{-C_2H_2} C_6H_7^+$
91	48	$C_7H_7^+$	
79	36	$C_6H_7^+$	M^* 151 7
78	52	$C_6H_6^+$	$C_{18}H_{19}Nb^+ \xrightarrow{-C_8H_9} C_{10}H_{10}Nb^+$
77	40	$C_6H_5^+$	M^* 153 3
65	20	$C_5H_5^+$	$C_{18}H_{19}Nb^+ \xrightarrow{-C_8H_8} C_{10}H_{11}Nb^+$

The ^{1}H NMR spectrum of $(C_5H_5)_2NbC_8H_9$ was recorded on a Jeol C-60 HL instrument with toluene-d_8 as the solvent and TMS as internal standard. The signals observed are at τ (ppm) 3.8 (dd, 2H), 4.3—4.8 (m, 4H), 5.15 (s, 5H), 5.33 (t, 1H), 5.05 (3, 5H), and 7.2—7.6 (m, 2H).

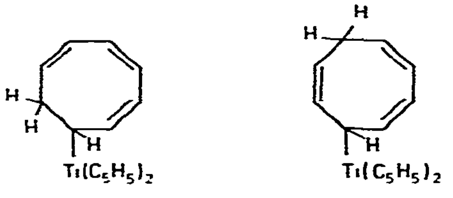
Discussion

The infrared spectrum and the reaction of $(C_5H_5)_2TiC_8H_9$ with HCl clearly demonstrate the presence of a $(\pi\text{-}C_5H_5)_2Ti$ group in the new compound. The Ti and H analyses are in keeping with the formula $C_{18}H_{19}Ti$. (The C analysis is less satisfactory, probably due to the formation of some titanium carbide during oxidation). A reliable mass spectrum could not be obtained due to the extreme air-sensitivity of $(C_5H_5)_2TiC_8H_9$. However, a peak at *m/e* 105 showed $C_8H_9^+$ (and its decay to $C_6H_7^+$ at *m/e* 79 [10]) in a higher abundance than $C_8H_8^+$ (at *m/e* 104). This is unusual for compounds containing C_8H_8 ligands (see e.g. [9]). Thermal decomposition of $(C_5H_5)_2TiC_8H_9$ in benzene-d_6 yields $C_5H_5TiC_8H_8$, quantitatively. ^{1}H NMR of the volatile products of this reaction showed the presence of C_5H_6; no C_5H_5D was found, indicating that the leaving C_5H_5 group had abstracted a proton from a C_8H_9 group and not from the solvent.

Reaction of $(C_5H_5)_2TiC_8H_9$ with HCl yields a mixture of 1,3,6- and 1,3,5-cyclooctatriene in a ratio of 9/2. Since both isomers are stable under the conditions involved [11], it seems possible that $(C_5H_5)_2TiC_8H_9$ is a mixture of the two isomers shown in Fig. 1; however, isomerization may occur during the acidolysis of the complex. In these structures titanium is in a formal oxidation state of +3. This is in keeping with magnetic susceptibility measurements, from which a μ_{eff} 1.7 BM (temperature range: 100—300 K) was found.

Chemical analyses and the mass spectrum of $(C_5H_5)_2NbC_8H_9$ are in agreement with the formula $C_{18}H_{19}Nb$. The two C_5H_5 groups are π-bonded to the metal as can be seen from the IR and ^{1}H NMR spectra. The difference in chemical shift of the protons of the two five-membered rings (singlets at τ 5.15 and 5.85 ppm, respectively) is somewhat larger than in $(C_5H_5)_2Nb(\pi\text{-allyl})$ [12] ($\Delta\tau$ 0.70 vs. $\Delta\tau$ 0.52 ppm) indicating a larger difference in the chemical environment of the two C_5H_5 rings in $(C_5H_5)_2NbC_8H_9$. The structure of the C_8H_9 ligand can also be elucidated from the IR and ^{1}H NMR spectra.

IR-spectrum. Absorptions at 3000 and 1540 cm^{-1} are strongly indicative for π-bonding between the central metal and an allylic system [13], thus giving the



(a) (b)

Fig. 1. Two possible forms of $(C_5H_5)_2TiC_8H_9$.

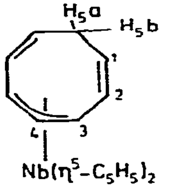


Fig 2 Structure of $(C_5H_5)_2NbC_8H_9$

metal an eighteen-electron configuration The CC stretching frequency at 1540 cm^{-1} is higher than that in $(C_5H_5)_2$Nb-allyl and -methyl homologues [14], indicating that the metal—allyl bond is weaker in the new compound This is in agreement with the results of Martin et al [7] on homologues of $(C_5H_5)_2Ti(\pi\text{-allyl})$, they found that substitution in the anti-position of the allyl group destabilizes the complexes and that no analogous Ti complexes could be made in which the allyl group is part of a small ring. The existence of carbon—carbon double bonds in $(C_5H_5)_2NbC_8H_9$ is indicated by the absorption at 1605 cm^{-1}. This value agrees with a C_8H_9 structure with two separated double bonds conjugated to the allylic system. From these IR spectral data we conclude that the complex contains an η^3-cyclooctatrienyl group as shown in Fig 2

^{1}H NMR. As far as the C_8H_9 proton resonances are concerned, the ^{1}H NMR spectrum of $(C_5H_5)_2NbC_8H_9$ closely resembles the spectra of compounds containing an η^3-cyclooctatrienyl ligand [2,3,4] By analogy with these compounds the NMR spectrum of the new complex can readily be explained in terms of the structure shown in Fig 2

The dd signal at τ 3 8 ppm arises from H_2 with coupling constants J_{21} 5 Hz and J_{23} 10 Hz The multiplet between τ 4 3 and 4 8 ppm is from H^1 and H^3. The triplet from H^4 at τ 5 33 ppm is partly overlapped by the resonance of one of the C_5H_5 rings· J_{43} 9 Hz The protons H^{5a} and H^{5b} give a complicated resonance signal indicating inequivalence of these two protons, just as in $C_8H_9Fe(CO)_3I$ [2]

Mass spectrum The relatively weak bonding between the metal and the eight-membered ring, indicated by the IR spectrum is in agreement with the small abundance of the parent ion $C_{18}H_{19}Nb^+$ in the mass spectrum compared with the relative abundance of $C_{13}H_{15}Nb^+$ in the mass spectrum of $(C_5H_5)_2Nb(\pi\text{-allyl})$ [14] The mass spectrum also shows preferential breakdown of the parent ion by elimination of C_8H_8 and formation of a hydride $C_{10}H_{10}NbH^+$

Mechanistic aspects of the formation of $(C_5H_5)_2MC_8H_9$ from $(C_5H_5)_2MCl_2$

$(C_5H_5)_2TiC_8H_9$. In Scheme 1 a proposed reaction mechanism is shown. The intermediates proposed in the formation of $(C_5H_5)_2TiC_8H_9$ are all known [15,16,

$$\begin{tikzcd}
(C_5H_5)_2TiCl_2 \arrow[r, "i\text{-}PrMgCl"] & (C_5H_5)_2TiCl \arrow[r, "i\text{-}PrMgCl"] & (C_5H_5)_2Ti\text{-}i\text{-}Pr \arrow[d, "-C_3H_6"] \\
& (C_5H_5)_2TiC_8H_9 & (C_5H_5)_2TiH \arrow[l, "C_8H_8"']
\end{tikzcd}$$

SCHEME 1. Proposed reaction mechanism for the formation of $(C_5H_5)_5TiC_8H_9$

17] The formation of $(C_5H_5)_2TiH$ dimer from $(C_5H_5)_2TiCl_2$ was previously demonstrated by Brintzinger [17]. The last step in the proposed reaction sequence involves addition of the metal hydride to a CC double bond of C_8H_8. Evidence for this addition reaction is obtained by treating C_8H_8 with $(C_5H_5)_2TiH_2MgX$ [18] which gives $(C_5H_5)_2TiC_8H_9$. Brintzinger [17] and James et al. [19] concluded that the Ti—H bond in $[(C_5H_5)_2TiH]_2$ is appreciably ionic, therefore, we regard the addition of $(C_5H_5)_2TiH$ to C_8H_8 as an electrophilic rather than as a free-radical reaction.

$(C_5H_5)_2NbC_8H_9$. Intermediate structures of the type proposed for the formation of $(C_5H_5)_2TiC_8H_9$ are not known for niobium. However, the occurrence of $(C_5H_5)_2NbH$ as an intermediate seems likely as is shown from the preparation of $(C_5H_5)_2NbC_8H_9$ by procedure 2 The reaction described is presumably initiated by the formation of $(C_5H_5)_2NbH$ and the Lewis acid—base adduct BH_3 $N(C_2H_5)_3$ The subsequent step then will be the insertion of C_8H_8 into the Nb—H bond. Procedure 2 was unsuccesful for the preparation of $(C_5H_5)_2TiC_8H_9$, because of the inability of $(C_5H_5)_2TiBH_4$ to split off a BH_3 fragment in the presence of a tertiary amine [19]. This observation argues in favour of the ionic character of the Ti—H bond in $[(C_5H_5)_2TiH]_2$. It seems probable that a Nb—H bond in $(C_5H_5)_2NbH$ is more covalent, and addition of such a bond to C_8H_8 may be a free-radical reaction.

Upon reaction of $(C_5H_5)_2NbC_8H_9$ with HCl one might expect only 1,3,6-cyclooctatriene if proton attack occurred only on the allylic fragment of the C_8H_9 group. The fact that also 1,3,5-cyclooctatriene was found suggests a mechanism in which the C_8H_9 ring rearranges after it is separated from the $(C_5H_5)_2Nb$ fragment and before proton attack. Probably the same holds for $(C_5H_5)_2TiC_8H_9$.

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