Journal of Organometallic Chemistry, 85 (1975) 193–197

ALLYLCYCLOOCTATETRAENETITANIUM AND RELATED COMPLEXES

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(Received August 13th, 1974)

Summary

The compounds $(C_8H_8\text{-}h_8)(R\text{-}h_3)Ti$ with R = allyl, 1- and 2-methylallyl have been prepared by treatment of $[(C_8H_8\text{-}h_8)TiCl{\cdot}THF]_2$ with RMgX (X = Cl, Br) in ether and the compounds $(C_8H_8\text{-}h_8)(R\text{-}h_3)Ti{\cdot}THF$ from the same reaction in THF. The green, paramagnetic compounds are sensitive to air and water. They decompose slowly at room temperature, but they can be stored at −30° without change. The IR spectra indicate that a $C_8H_8\text{-}h_8$ and an allylic-h_3 group are present in the molecule. Analogous compounds of vanadium could not be obtained.

Introduction

Allylic compounds of Ti and Zr were first described by Martin and Jellinek, viz. the compounds $(C_5H_5\text{-}h_5)_2(R\text{-}h_3)Ti$ [1] and $(C_5H_5\text{-}h_5)_2(R\text{-}h_3)_2Zr$ [2] with R = allyl and substituted allyl. Recently, Kablitz and Wilke reported the Zr compound $(C_8H_8\text{-}h_8)(R\text{-}h_3)_2Zr$, and we described the compound $(C_8H_8\text{-}h_8)$(1-methylallyl-h_3)Ti [4]. The present paper describes the synthesis and some properties of the compounds $(C_8H_8\text{-}h_8)(R\text{-}h_3)Ti$ and $(C_8H_8\text{-}h_8)(R\text{-}h_3)Ti{\cdot}THF$ with R = allyl, 1- and 2-methylallyl. The niobium analogues are under investigation. No similar vanadium compounds could be obtained.

Experimental

All experiments were carried out under purified nitrogen. Solvents were purified by conventional methods and were freed from oxygen by repeated degassing and saturation with nitrogen before use. Commercial allyl chloride, allyl bromide, crotyl bromide, 2-methylallyl chloride, cyclooctatetraene and $TiCl_3$ were used without purification. The Grignard reagents were prepared using a threefold excess of magnesium [5]; the solvents used were THF for the chlorides

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TABLE 1

ANALYTICAL DATA, YIELDS AND DECOMPOSITION TEMPERATURES FOR THE COMPLEXES $(C_8H_8\text{-}h_8)(R\text{-}h_3)Ti$

	Analysis found (calcd.) (%)			Yield (%)	Dec. temp. (°C)
	C	H	Ti		
Allyl	68.85, 68.08 (68.41)	7.05, 7.08 (6.79)	24.57, 24.53 (24.80)	57	43
1-Methylallyl	69.70, 70.18 (69.58)	7.53, 7.65 (7.30)	22.71, 22.88 (23.12)	70	113
2-Methylallyl	69.57, 69.36 (69.58)	7.83, 7.55 (7.30)	22.78, 22.95 (23.12)	40	113

and diethyl ether for the bromides. Analyses for C and H were carried out at the Microanalytical Department of this University under supervision by Mr. W.M. Hazenberg. Ti was determined in our Laboratory under the supervision of Mr. A.F. Hamminga. IR spectra were recorded using an Hitachi EPI-G spectrophotometer. The samples were examined as mulls in silicone oil (1500-1300 cm^{-1}) or Nujol (4000-400 cm^{-1}) between KBr discs.

The compounds $(C_8H_8\text{-}h_8)(R\text{-}h_3)Ti$ were prepared by a method described previously [4]. The THF complexes were prepared in a similar way with THF as the solvent. Yields, decomposition temperatures and analytical data are summarized in Tables 1 and 2.

Results and discussion

The reaction of $[C_8H_8\text{-}h_8)TiCl\cdot THF]_2$ [6] with RMgX (X = Cl, Br; R = allyl, 1- and 2-methylallyl) in ether gives the green, paramagnetic complexes $(C_8H_8\text{-}h_8)(R\text{-}h_3)Ti$. With THF as a solvent, the green compounds $(C_8H_8\text{-}h_8)(R\text{-}h_3)Ti\cdot THF$ are formed. THF can be removed from the latter complexes by repeated washing with ether or pentane and crystallization from n-pentane. On reaction with a solution of HCl in ether, all the compounds give $[(C_8H_8\text{-}h_8)TiCl]_4$ [6]. The compounds are very sensitive to air and water. At room temperature they decompose

TABLE 2

ANALYTICAL DATA, YIELDS AND DECOMPOSITION TEMPERATURES FOR THE COMPLEXES $(C_8H_8\text{-}h_8)(R\text{-}h_3)Ti\cdot THF$

R	Analysis found (calcd.) (%)			Yield (%)	Dec. temp. (°C)
	C	H	Ti		
Allyl	68.64, 68.72 (67.93)	8.00, 8.15 (7.98)	18.08, 18.27 (18.06)	44	96
1-Methylallyl	68.04, 67.83 (68.82)	8.25, 8.28 (8.30)	17.36 (17.15)	34	91
2-Methylallyl	68.71, 68.36 (68.82)	8.40, 8.22 (8.30)	17.17 (17.15)	63	99

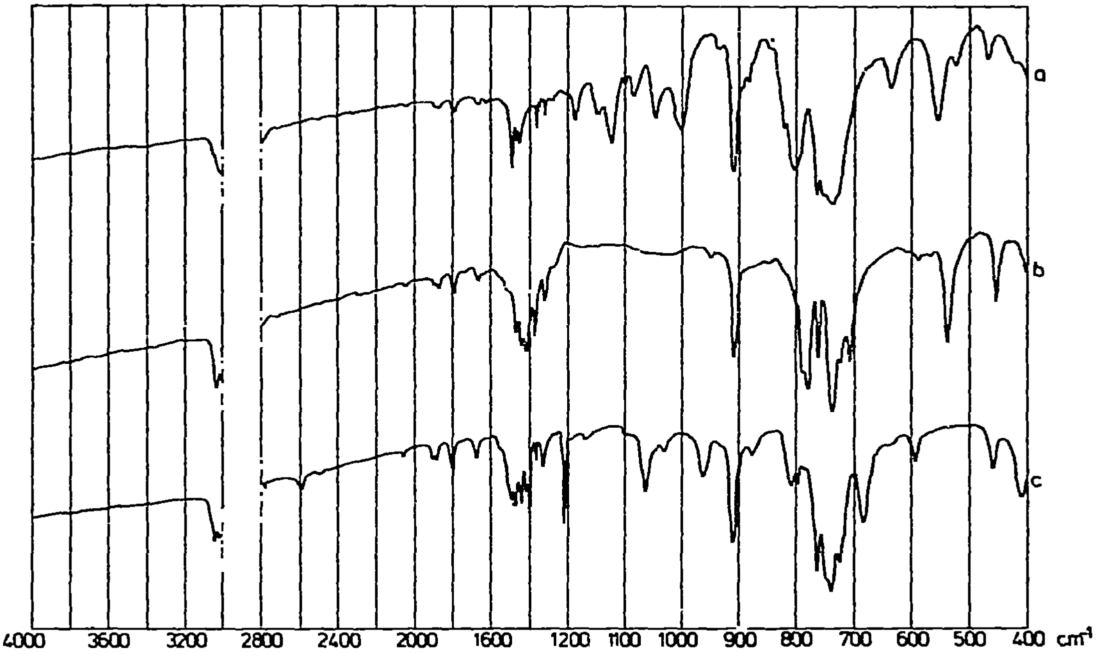

Fig. 1. IR spectra of: (a) $(C_8H_8\text{-}h_8)$ (allyl-h_3)Ti, (b) $(C_8H_8\text{-}h_8)$ (2-methylallyl-h_3)Ti, (c) $(C_8H_8\text{-}h_8)$-(1-methylallyl-h_3)Ti in silicone oil (1500-1300 cm^{-1}) and Nujol (4000-400 cm^{-1}).

slowly in solution or in the solid state. The pure compounds can be stored at —30° without change.

The IR spectra of the compounds (Figs. 1 and 2) give evidence for the presence of a C_8H_8-h_8 and an allyl-h_3 or substituted allyl group in the molecule. The absorptions of the C_8H_8-h_8 ligand are observed at the usual wave numbers [7]. Evidence for π-bonding of the allyl ligands is found in the absorption band at ca. 1480 cm^{-1} (allyl: 1490 cm^{-1}; 1-methylallyl: 1495 and 1470 cm^{-1}; 2-methylallyl: 1468 cm^{-1}), which is assigned to the C=C stretching frequency, $\omega(C{=}C)_2$ of the allyl-h_3 langs (cf. Martin [1] and Siegert [8]).

In a 1-methylallyl moiety the methyl groups can occupy either the *syn* or the *anti* position with respect to the hydrogen atom at the central atom. This gives rise to two C=C stretching vibrations in the 1-methylallyl complexes. For 1-methylallylsodium Lanpher [9] found the absorptions of the *syn* and *anti* isomers at 1560 and 1525 cm^{-1} respectively. In the $(C_5H_5\text{-}h_5)_2$ (1-methylallyl-h_3)M complexes with M = Ti [1], Nb [8] and Ta [10] only one C=C stretching vibration has been observed for the allyl group. From a comparison of the IR data of these compounds with those of the corresponding allylic anions and from steric reasons it was concluded that the methyl group in the $(C_5H_5\text{-}h_5)_2$(1-methylallyl-h_3)M complexes (with M = Ti [1], Nb [8] and Ta [10]) occupies the *syn* position. This was confirmed by a crystal-structure determination in the case of the $(C_5H_5\text{-}h_5)_2$(1,2-dimethylallyl-h_3)Ti complex [11].

Replacement of the two C_5H_5 groups by one C_8H_8 group leaves more space for the allyl group. Thus, in the $(C_8H_8\text{-}h_8)$ (1-methylallyl-h_3)Ti complex both *syn* and *anti* isomers are possible. Taking into account Lanpher's results

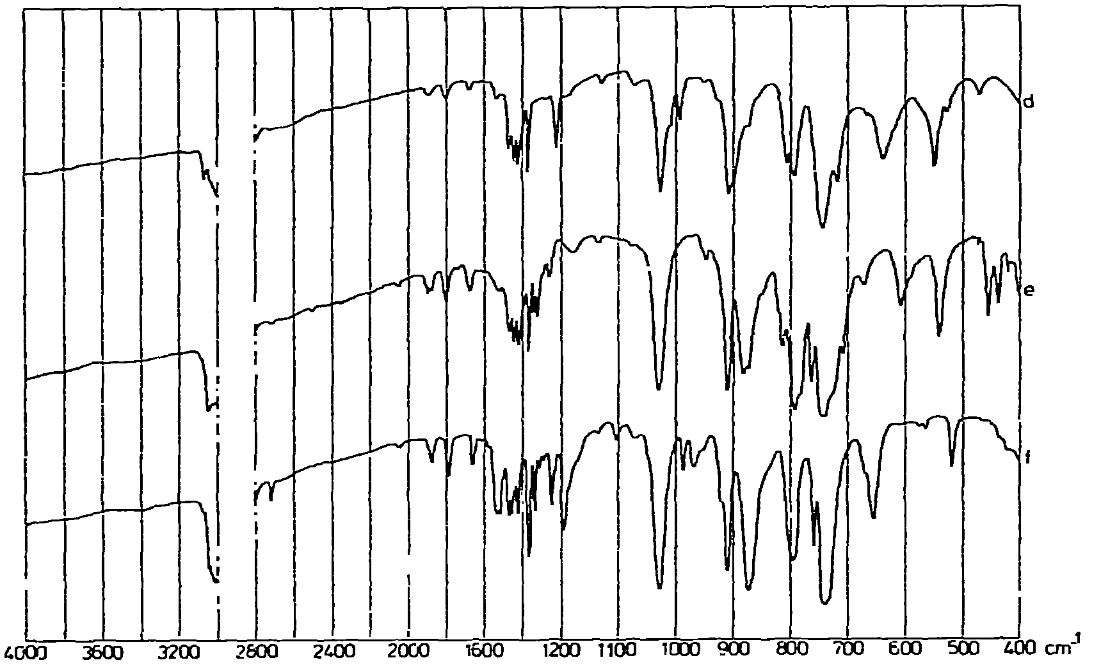

Fig. 2. IR spectra of: (d) (C_8H_8-h_8) (allyl-h_3)Ti·THF, (e) (C_8H_8-h_8) (2-methylallyl-h_3)Ti·THF, (f) (C_8H_8-h_8) (1-methylallyl-h_3)Ti·THF in silicone oil (1500-1300 cm^{-1}) and Nujol (4000-400 cm^{-1}).

[9], the C=C stretching vibration at 1495 cm^{-1} is assigned to the *syn* isomer, and the absorption at 1470 cm^{-1} to the *anti* isomer.

Complexes with a (C_8H_8-h_8)Ti moiety probably have enough space to accommodate two allyl groups. We attempted to prepare compounds of the type (C_8H_8-h_8) (C_3H_5-h_3)$_2$Ti or (C_8H_8-h_8) (C_3H_5-h_3) (C_3H_5-h_1)Ti. These attempts were not successful, because of reduction of tetravalent titanium in the starting compounds to trivalent titanium, either by $K_2C_8H_8$ or by the Grignard reagent. Tetravalent zirconium is much more stable towards these reducing agents and so the zirconium compounds (C_8H_8-h_8) (C_3H_5-h_3)$_2$Zr could be prepared [3].

In connection with Siegert's [8, 12] studies on allyldicyclopentadienyl complexes of Ti, V and Nb it seemed of interest to investigate the compound (C_8H_8-h_8) (C_3H_5)V. Siegert found that the allyl group in (C_5H_5-h_5)$_2$(C_3H_5-h_1)V acts as a one-electron ligand and ascribed this to steric reasons: the space left between the two C_5H_5-h_5 groups is not sufficient for a three-electron allylic ligand. This steric effect is removed if the two C_5H_5-h_5 groups are replaced by one C_8H_8-h_8 ligand and (C_8H_8-h_8) (C_3H_5-h_3)V might exist. However, we have been unable to prepare this and we did not find any evidence for the existence of compounds containing a (C_8H_8-h_8)V group. We assume that the orbitals of vanadium, which are less extended than those of titanium, would not overlap sufficiently with the orbitals of a C_8H_8-h_8 ligand, to stabilize the (C_8H_8-h_8)V moiety.

In the IR spectra of the THF complexes (C_8H_8-h_8) (R-h_3)Ti·THF (Fig. 2) the bands at 1028 and 880 cm^{-1} arise from the THF ligand. The latter band indicates that the THF molecule is coordinated to titanium via the oxygen atom, as in the compound $[(C_8H_8\text{-}h_8)TiCl\cdot THF]_2$ [6]. In the THF complexes the allyl group can occur in several orientations with respect to the THF ligand. This can give rise to more C=C stretching vibrations of the allyl group. In the compound $(C_8H_8\text{-}h_8)$ (1-methylallyl-h_3)Ti·THF there are three different absorption bands but no reliable assignment of these bands to the various isomers can yet be made.

The evidence indicates that the C_8H_8 group and the allyl ligand act as eight- and three-electron ligands, respectively. The titanium atom thus achieves a 15-electron configuration (17-electrons in the THF complexes), which is compatible with the observed paramagnetism of the complexes.

Acknowledgements

The authors are much indebted to Prof. Dr. F. Jellinek for his stimulating interest. This investigation was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

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