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Sandwich compounds of titanium

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SUMMARY

In this thesis the synthesis and some properties of a number of sandwich compounds containing either a planar cyclooctatetraene-, ($\eta^8\text{-C}_8\text{H}_8$), or a planar cycloheptatrienyl-, ($\eta^7\text{-C}_7\text{H}_7$), ligand are described and discussed. The cyclooctatetraene complexes are compounds of titanium, the cycloheptatrienyl complexes are compounds of titanium, vanadium, zirconium or niobium.

A short introduction is presented in chapter 1; some general considerations are given which serve as a guide for this investigation.

Three new types of sandwich compounds are described in chapters 2, 3 and 4; in these compounds a $\eta^5\text{-C}_5\text{H}_5$, a $\eta^4\text{-C}_4(\text{C}_6\text{H}_5)_4$ and a $\eta^3\text{-C}_3\text{H}_4\text{CH}_3$ ligand respectively are bound to the ($\eta^8\text{-C}_8\text{H}_8$)Ti group.

The IR- and mass-spectra of the compound ($\eta^8\text{-C}_8\text{H}_8$)($\eta^5\text{-C}_5\text{H}_5$)Ti indicate that the rings are planar and that all carbon atoms are bound to the metal. This agrees with the observed paramagnetism of the compound (chapter 2). The supposed structure is confirmed by X-ray analysis: the planar rings are approximately parallel.

The IR-, NMR- and mass-spectra of the compound ($\eta^8\text{-C}_8\text{H}_8$)[$\eta^4\text{-C}_4(\text{C}_6\text{H}_5)_4$]Ti indicate the presence of a planar $\eta^8\text{-C}_8\text{H}_8$ ligand, while the second ligand is supposed to be a tetrahapto(tetraphenyl)-cyclobutadiene group (chapter 3).

The IR- and mass-spectra of ($\eta^8\text{-C}_8\text{H}_8$)($\eta^3\text{-C}_3\text{H}_4\text{CH}_3$)Ti show that a planar $\eta^8\text{-C}_8\text{H}_8$ ring is present and a trihapto-1-methylallyl ligand (chapter 4).

Compounds of the type ($\eta^7\text{-C}_7\text{H}_7$)($\eta^5\text{-C}_5\text{H}_5$)M with M = Ti, Zr or Nb are described in chapter 5. In view of the close resemblance of the IR- and mass-spectra of these compounds and the spectra of the corresponding vanadium compound, the structure of which is known, it is evident that in the Ti, Zr and Nb complexes also both rings are planar. X-ray analysis of the titanium compound confirms the supposed structure: the rings are planar and approximately parallel.

A surprising feature in this structure is the short distance of the titanium atom to the carbon atoms of the seven-membered ring, viz.: 2.19 Å. This is considerably less than the distance of c. 2.32 Å normally found for Ti-C bonds.

A remarkable phenomenon observed in the mass spectra of the compounds $(h^7-C_7H_7)(h^5-C_5H_5)M$ is the rearrangement to bisbenzene-metal ions, $(C_6H_6)_2M^+$. This is investigated more thoroughly with the aid of the mass spectra of the ring-substituted titanium compounds $(h^7-C_7H_6R)(h^5-C_5H_4R)Ti$, ($R = H, CH_3$). These mass spectra indicate that substantial proportions of the compounds rearrange to ions of bisbenzene-titanium derivatives upon electron impact (chapter 7).

The attempted synthesis of the compound $(h^7-C_7H_7)_2Ti$ leads to the formation of $(h^7-C_7H_7)(h^5-C_7H_9)Ti$; the compound is characterized by IR-, NMR- and mass-spectra. The corresponding vanadium compound was also prepared (chapter 6).

Chapter 8 briefly describes unsuccessful attempts to isolate V, Zr or Nb analogues of some titanium compounds described in previous chapters, and unsuccessful attempts to prepare some other sandwich compounds of titanium, particularly those containing a $h^6-C_6H_6Ti$ group.

In chapter 9 the results described in the previous chapters are discussed; explanations are offered for the short Ti-C distances in the $(h^7-C_7H_7)Ti$ group and for the failure to prepare $(h^7-C_7H_7)_2Ti$ and complexes containing a $(h^6-C_6H_6)Ti$ group.

Chapter 10 describes the experimental part of the investigations.