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Alkyl, Aryl, and Allyl Complexes of some Metallocenes*

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A survey is given of investigations carried out on compounds $(\pi\text{–}C_5H_5)_2MR_n$, where $M=Ti$, V, Zr, Nb and R is an alkyl, aryl, or allyl group. Many results not previously published are included.

Introduction

In this communication a survey is given of the investigations carried out at our laboratory on compounds Cp_2MR_n, where $Cp = \pi\text{–}C_5H_5$; $M = Ti, V, Zr, Nb$ and R is an alkyl, aryl, or allyl group. Prior to our study some complexes $Cp_2Ti^{IV}R_2$ with R = methyl[1,2] or aryl[3] had been reported, while the corresponding complexes $Cp_2V^{III}R$ were prepared by one of the present authors.[4,5,6] In general, these compounds were prepared according to:

$$Cp_2TiCl_2 \xrightarrow[\text{or } 2\,RMgX)]{2\,LiR\ (\text{or } 2\,NaR} Cp_2TiR_2 + 2LiCl$$

$$Cp_2VCl \xrightarrow[(\text{or } RMgX)]{LiR} Cp_2VR + LiCl$$

The melting points or decomposition temperatures of these compounds (including some recent results[7-14]) are given in Table I. Differential thermal analysis showed in several cases that an exothermic process takes place at the temperature previously regarded as the « melting point »; this indicates irreversible decomposition of the complex.[8] While the methyl complexes are stable at room temperature, the ethyl complexes could not be isolated,[5,15] nor were complexes of higher alkyls. The benzyl, phenyl, and p-tolyl complexes are stable again, but $Cp_2Ti^{IV}(o\text{–}CH_3C_6H_4)_2$ could not be prepared (nor could the α-naphthyl complex),[3] obviously due to steric hindrance. The stability of the complexes is considerably enhanced by the introduction of electronegative ligands, for instance in the complexes $Cp_2Ti^{IV}(R)Cl$ [16] or by replacing phenyl ligands by perfluorophenyl groups.[10,11,17]

Table I. Melting points (or decomposition temperatures) of complexes $Cp_2Ti^{IV}R_2$ and $Cp_2V^{III}R$

	$Cp_2Ti^{IV}R_2$		$Cp_2V^{III}R$	
R=	°C	Ref.	°C	Ref.
CH_3—	dec. 97	(1, 2)	100 (dec.)	(5)
$C_6H_5CH_2$—	dec. 100	(7)	109	(5)
C_6H_5—	dec. 120	(8)	92	(4)
p—$CH_3C_6H_4$—	dec. 130	(8)	90	(6)
m—$CH_3C_6H_4$—	137-139	(9)		
p—$(CH_3)_2NC_6H_4$—	137-139 (dec.)	(9)	108-111	(6)
C_6F_5—	228-230	(10)	208	(11)
C_5H_5—	128	(12)	98	(11)
$C_6H_5C{\equiv}C$—	141	(13)	135 (dec.)	(14)

Several attempts were undertaken to prepare complexes of composition $Cp_2V^{IV}R_2$ (with $R = C_6H_5$,[6,18] C_6F_5,[18] C_5H_5[12]) by reaction of vanadocene dichloride with organometallic reagents under conditions where the corresponding reaction with titanocene dichloride yields $Cp_2Ti^{IV}R_2$. However, in all cases reduction of vanadium took place and the complexes $Cp_2V^{III}R$ were formed instead of the compounds desired:

$$Cp_2VCl_2 \xrightarrow[(\text{or } 2\,NaR)]{2\,LiR} Cp_2VR + R^{\cdot} + 2LiCl$$

Similarly, reaction of vanadocene with methyl, ethyl or benzyl halides did not yield complexes $Cp_2V^{IV}(R)Cl$, but again complexes of trivalent vanadium:[5]

$$Cp_2V + RCl \longrightarrow Cp_2VCl + R^{\cdot}$$

$$2Cp_2V + RCl \longrightarrow Cp_2VCl + Cp_2VR$$

It was provisionally assumed that this difference in behaviour of titanium and vanadium is due to steric

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(7) H. A. Martin, Dissertation, Groningen (1967).

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(9) H. C. Beachell and S. A. Butter, *Inorg. Chem.*, *4*, 1133 (1965).

(10) M. A. Chaudhari, P. M. Treichel, and F. G. A. Stone, *J. Organometal. Chem.*, 2, 206 (1964).

(11) F. W. Siegert and H. J. de Liefde Meijer, *J. Organometal. Chem.*, *15*, 131 (1968).

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(13) H. Köpf and M. Schmidt, *J. Organometal. Chem.*, *10*, 383 (1967).

(14) J. H. Teuben and H. J de Liefde Meijer, *J. Organometal. Chem.*, *17*, 87 (1969).

(15) H. Sinn and F. Patat, *Angew. Chem.*, *75*, 805 (1963).

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reasons, the atomic radius of vanadium (1.22 Å) being smaller than that of titanium (1.32 Å). Since the cyclopentadienyl rings in Cp_2MR_n will not be parallel, this implies that considerably less space near the metal is available for ligands R if M=V than if M=Ti (Fig. 1). In order to check this hypothesis some series of experiments were undertaken:

(i) It was attempted to prepare a complex $Cp_2V^{IV}R_2$ with a ligand R having minimum steric requirements near its coordinating atom; the ligand $-C{\equiv}CC_6H_5$ was chosen for this purpose. Indeed, reaction of (phenylethynyl)sodium with vanadocene dichloride yielded $Cp_2V^{IV}(C_2C_6H_5)_2$ of m.p. 74-75° (dec.),[14] analogous to the bis(phenylethylnyl) complexes of titanocene[13] and zirconocene;[19] magnetic measurements confirmed the presence of tetravalent vanadium.[14]

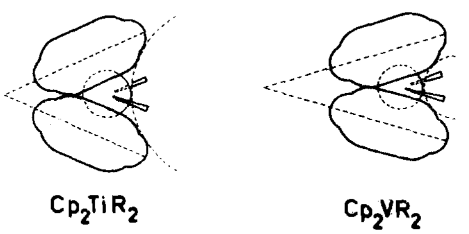
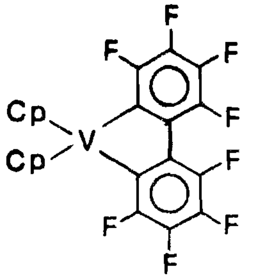


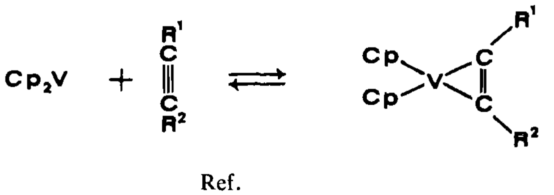
Figure 1. Schematic representation of complexes Cp_2TiR_2 and Cp_2VR_2.

(ii) It was attempted to prepare complexes $Cp_2V^{IV}R_2$ with bidentate ligands R_2. While experiments with R_2= 1,2,3,4-tetraphenylbutadienylene failed,[18] reaction of 2,2'dilithiooctafluorobiphenyl with vanadocene dichloride yielded the thermally stable, sublimable complex (A)[20] which is analogous to the corresponding titanium compound.[21]



(A)

In this connection our experiments on the reversible addition of acetylene derivatives at vanadocene may also be mentioned.[22] In view of the low CC stretching frequencies (1750-1825 cm^{-1}) which are comparable with the C=C stretching frequencies in substituted cyclopropenes, the adducts may be formulated as shown under (B). This description is consistent with the observed reduction of the number of unpaired electrons from three in vanadocene to one in the adducts.



(B)

	Ref.		Ref.
$R_1=R_2=COOCH_3$	(22, 23)	$R_1=R_2=p(t.butyl)C_6H_4$	(22)
$R_1=R_2=C_6H_5$	(22)	$R_1=p{-}CH_3C_6H_4$; $R_2=C_6H_5$	(22)
$R_1=R_2=C_6F_5$	(22)	$R_1=CH_3$; $R_2=C_6H_5$	(22)
$R_1=R_2=CF_3$	(23)	$R_1=CH_3$; $R_2=N(C_2H_5)_2$	(22)

(iii) Since the atomic radius of niobium (1.34 Å) is about the same as that of titanium, while its electron configuration is the same as that of vanadium, the reactions of $Cp_2Nb^{IV}Cl_2$ with organometallic reagents seemed of interest. It was found that the behaviour of niobium closely resembles that of titanium; the reaction of $Cp_2Nb^{IV}Cl_2$ with phenyllithium, for instance, yields $Cp_2Nb^{IV}(C_6H_5)_2$, stable up to 150°C.[24]

The allyl complexes $Cp_2M^{III}(C_3H_5)$ are of particular interest, as the allyl group can be either σ-bonded or π-bonded at the metal. The type of bonding can be recognized from the infrared spectra, since the C=C stretching band of σ-allyl ligands is observed around 1600 cm^{-1}, that of π-allyl ligands around 1500 cm^{-1}. Fig. 2 shows the infrared spectra of $Cp_2Ti^{III}(C_3H_5)$, $Cp_2V^{III}(C_3H_5)$, and $Cp_2Zr^{IV}(C_3H_5)_2$. It is seen that the allyl ligand is π-bonded in the titanium complex,[25] σ-bonded in the vanadium complex,[11] while the zirconium complex contains one σ-bonded and one π-bonded allyl group.[26] Again, niobium behaves in the same way as titanium (and different from vanadium), since the allyl ligand in $Cp_2Nb^{III}(C_3H_5)$ is π-bonded,[24] as is evident from the infrared spectrum and the NMR spectrum shown in Fig. 3.

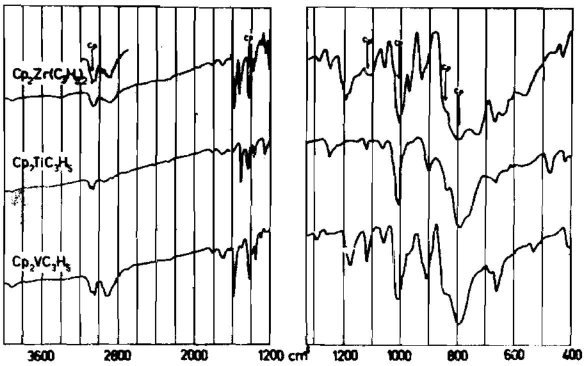


Figure 2. Infrared spectra of $Cp_2Zr(C_3H_5)_2$, $Cp_2Ti(C_3H_5)$, and $Cp_2V(C_3H_5)$ in KBr discs. The normal vibrations of the π—C_5H_5 ligands are indicated. The spectra show that the allyl ligand is σ-bonded in $Cp_2V(C_3H_5)$ (C=C stretch at 1588 cm^{-1}), π-bonded in $Cp_2Ti(C_3H_5)$ (1509 cm^{-1}), while one of the allyl groups in $Cp_2Zr(C_3H_5)_2$ is σ-bonded (1589 cm^{-1}), the other π-bonded (1533 cm^{-1}) to the metal.[26]

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(19) J. H. Teuben and H. J. de Liefde Meijer, unpublished results.

(20) T. M van der Huizen, F. W. Siegert, and H. J. de Liefde Meijer, unpublished results.

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(24) F. W. Siegert and H. J. de Liefde Meijer, *J. Organometal. Chem.*, *23*, 177 (1970).

(25) H. A. Martin and F. Jellinek, *J. Organometal. Chem.*, *8*, 115 (1967).

(26) H. A. Martin, P. J Lemaire, and F. Jellinek, *J. Organometal. Chem.*, *14*, 149 (1968).

Table II. Allyl and methylallyl complexes of metallocenes

	m.p. (°C)	number of unpaired electrons	$\nu_{C=C}$ (cm^{-1}) π	$\nu_{C=C}$ (cm^{-1}) σ	Ref.
Allyl complexes					
$Cp_2Ti(C_3H_5)$	111-112 (dec.)	1	1509		(25)
$Cp_2Ti(CH_3)(C_3H_5)$		0		1597	(26)
$Cp_2Zr(C_3H_5)_2$	dec. 87	0	1533	1589	(26)
$Cp_2Zr(C_3H_5)Cl$		0		1598	(26)
$Cp_2V(C_3H_5)$	49	2		1588	(11)
$Cp_2Nb(C_3H_5)$	>200	0	1480		(24)
(2-methylallyl) complexes					
$Cp_2Ti(C_4H_7)$	dec. 114	1	1480		(25)
$Cp_2Ti(CH_3)(C_4H_7)$		0		1602	(26)
$Cp_2Zr(C_4H_7)_2$	−15	0	1520	1603	(26)
$Cp_2Zr(C_4H_7)Cl$		0		1606	(26)
$Cp_2V(C_4H_7)$	65	2		1598	(11)
2-butenyl complexes					
$Cp_2Ti(C_4H_7)$ *syn*	97 (dec.)	1	1533		(25)
$Cp_2V(C_4H_7)$ *cis* and *trans*	dec.			1610, 1625	(11)
other allylic complexes Cp_2TiR					
R = 1,1-dimethylallyl	dec. 51	1	1558		(25, 27)
1,2-dimethylallyl	71 (dec.)		1499		(28)
1,3-dimethylallyl	91 (dec.)	1	1546		(25)
1,2,3-trimethylallyl	73-75		1499		(28)

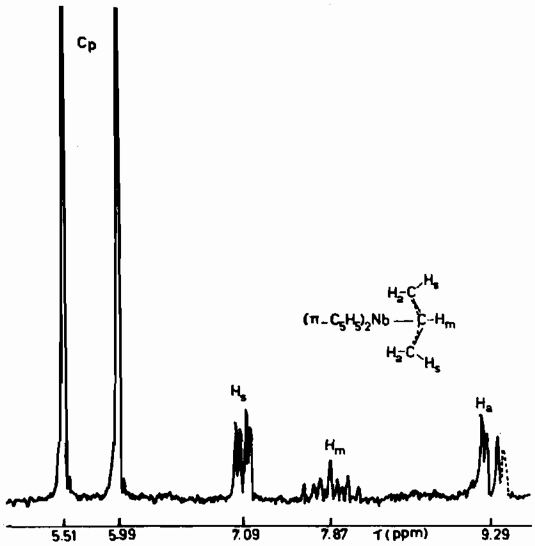

Figure 3. NMR spectrum of $Cp_2Nb(C_3H_5)$ in C_6D_6 at room temperature; internal standard TMS (τ 10 ppm).[24] The spectrum shows that the allyl ligand is π-bonded, and that the two cyclopentadienyl ligands in the molecule are not equivalent (cf. Fig. 5).

Some observations on allyl complexes of metallocenes are collected in Table II. The trend of the C=C stretching frequencies of the π-allyl ligands in the niobium, titanium, and zirconium complexes can be readily understood in terms of Ballhausen and Dahl's[29] treatment of the bonding in compounds Cp_2MR_n. The *n*d, (*n*+1)s, and (*n*+1)p orbitals of the transition metal M are combined to nine hybrid orbitals, six of which are used in binding the cyclopentadienyl ligands. Two of the remaining three hybrid orbitals combine with the (filled) bonding and non-bonding π-orbitals of the $\pi\text{–}C_3H_5^-$ ligand (regarded as anion). The empty antibonding π-orbital of the ligand combines with the third metal orbital (« backbonding ») which is occupied by two electrons in the case of $Cp_2Nb^{III}(\pi\text{–}C_3H_5)$ (Fig. 4). Thus, a very stable complex is achieved; the C–C–C π-bond of the ligand is considerably weakened by the backbonding, and its (asymmetric) C=C stretching frequency is low. In the case of $Cp_2Ti^{III}(\pi\text{–}C_3H_5)$ only one electron is available for back-bonding, while in $Cp_2Zr^{IV}(\sigma\text{–}C_3H_5)(\pi\text{–}C_3H_5)$ no back-bonding of the π-allyl ligand is possible, since the metal orbital in question binds the σ-allyl group. In $Cp_2V^{III}(C_3H_5)$ steric hindrance prevents π-bonding of the allyl group at the metal; the group is σ-bonded causing the compound to be much less stable than the niobium complex.

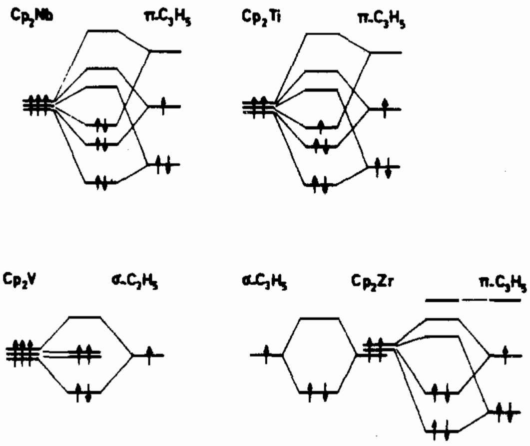

Figure 4. Schematic correlation diagrams representing the bonding of allylic ligands regarded as radicals at various metallocene groups.

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(27) R. B. Helmholdt, F. Jellinek, H. A. Martin, and A. Vos, *Rec. Trav. Chim. Pays Bas*, *86*, 1263 (1967).

(28) H. A. Martin and F. Jellinek, *J. Organometal. Chem.*, *12*, 149 (1968).

(29) G. J. Ballhausen and J. P. Dahl, *Acta Chem. Scand.*, *15*, 1333 (1961).

Table II includes data on complexes with methylallyl ligands. While in σ-allylic ligands introduction of a methyl group at either carbon 2 or 3 increases the C=C stretching frequency, the (asymmetric) C=C stretch of π-allylic ligands strongly depends on the position of the substituent:[27] the frequency decreases if the methyl group is introduced at the central carbon atom 2, but increases if it is at the outer carbons 1 or 3 of the π-allyl group. Similar observations have been made for allylic anions,[30] where the π-electrons are also delocalized. The electronic absorption spectra of the π-allylic complexes of titanocene are also strongly affected by the position of substituents in the allyl group.[28]

The stability of σ-allyl complexes of vanadocene decreases if substituents are introduced in the allylic ligands; attempted syntheses of $Cp_2V^{III}R$ with R=2-tert.butylallyl and R=3-methyl-2-butenyl did not yield these complexes, but vanadocene was obtained instead.[11] The stability of the π-allyl complexes of titanocene, on the other hand, is not greatly affected by substitution as long as the substituents at carbons 1 and 3 can occupy the syn-position[27] with respect to the hydrogen atom (or substituent) at the central carbon atom 2, while substituents at the latter atom must not be too bulky:[7] solutions of (2-phenylallyl)-titanocene are unstable.[27] The preference of substituents at carbons 1 and 3 for the syn-positions was confirmed by a determination of the crystal structure of (1,2-dimethylallyl)titanocene by X-ray diffraction (Fig. 5).[27] It is seen that substituents in the anti-position would come very close to one of the cyclopentadienyl rings. Indeed, (1,1-dimethylallyl)titanocene where one of the methyl groups must be in the anti-position, is an unstable complex.[25] This explains why π-allylic complexes of titanocene could not be obtained if the π-allylic system is part of a small or medium-sized ring;[28] in (π-cyclododecadienyl)titanocene, which could be prepared in low yields, the ring is large enough to allow ring closure to occur between the syn-positions of carbons 1 and 3 of the allyl group.[28]

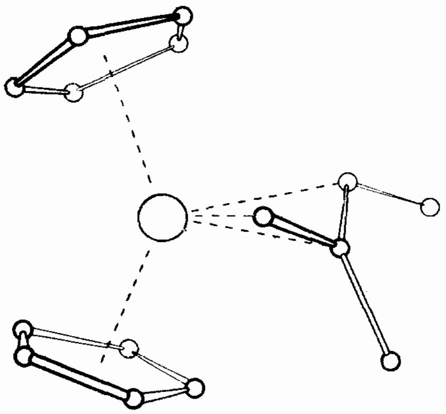

Figure 5. Molecular skeleton of (1,2-dimethylallyl)titanocene as determined by X-ray diffraction;[27] hydrogen atoms are not indicated.

These arguments also explain that one of the ligands in tricyclopentadienyltitanium is σ-bonded to the metal, so that the complex is to be described as $(\pi\text{–}C_5H_5)_2Ti^{III}(\sigma\text{–}C_5H_5)$,[12] contrary to its original formulation.[31] The infrared spectrum of the complex[12] is almost identical with that of $(\pi\text{–}C_5H_5)_2V^{III}(\sigma\text{–}C_5H_5)$, the structure of which was established by wide-line NMR*. Similar infrared spectra (Fig. 6) were also observed for the mixed π,σ-cyclopentadienyl complexes $(\pi\text{–}C_5H_5)_3Zr^{IV}(\sigma\text{–}C_5H_5)$,[32,33] $(\pi\text{–}C_5H_5)_2Nb^{IV}(\sigma\text{–}C_5H_5)_2$[34] and $(\pi\text{–}C_5H_5)_2Ti^{IV}(\sigma\text{–}C_5H_5)_2$.[12] The structure of the latter complex is supported by its NMR spectrum at –40°C, which shows two signals of equal integrated intensity (Fig. 7), at lower temperatures the low-field signal (probably due to the $\sigma\text{–}C_5H_5$ protons) broadens, at +50°C the two signals collaps to one line indicating rapid interchange of the σ-bonded and π-bonded ligands.[35,36] Quite recently, the structure of $(\pi\text{–}C_5H_5)_2Ti(\sigma\text{–}C_5H_5)_2$ was also confirmed by X-ray analysis.[36] Thermal decomposition of tetracyclopentadienyltitanium(IV) gives tricyclopentadienyltitanium(III); similarly, vanadocene is obtained by thermal decomposition of tricyclopentadienylvanadium-(III).[12]

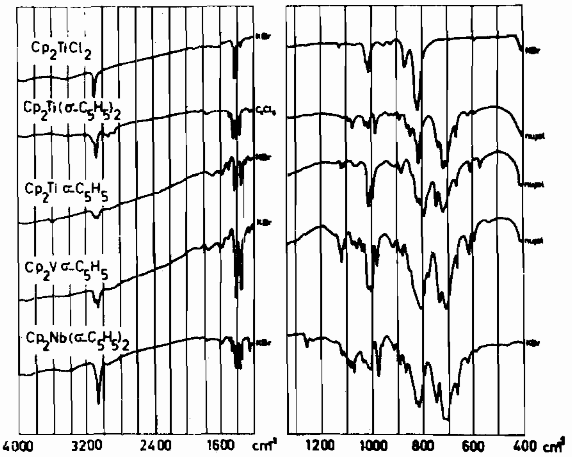

Figure 6. Infrared spectra of some mixed π,σ-cyclopentadienyl metal complexes;[12] for comparison, the spectrum of Cp_2TiCl_2 which shows the absorptions of $\pi\text{–}C_5H_5$ groups only, is also included.

In addition to tricyclopentadienyltitanium(III) a few more complexes of composition $Cp_2Ti^{III}R$ where R is σ-bonded to the metal, have recently been prepared by carrying out reactions

$$\tfrac{1}{2}\,[Cp_2TiCl]_2 \xrightarrow[\text{(or LiR)}]{\text{RMgX}} Cp_2TiR + MgXCl$$

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(30) E. J. Lanpher, *J. Amer. Chem. Soc.*, *79*, 5578 (1957).

(*) Some mistakes were made in the original report[11] on the NMR spectra: $(\pi\text{—}C_5H_5)_2V^{III}(\sigma\text{—}C_5H_5)$ gives two broad signals at 94 and 123 ppm (intensity ratio 1:2), $Cp_2V^{III}(\sigma\text{—}C_3H_5)$ two broad signals at 120 and 314 ppm (intensity ratio 2:1), all signals lying at lower fields than that of the solvent cyclohexane which served as an internal reference (0 ppm).

(31) E. O. Fischer and A. Löchner, *Z. Naturforschg.*, *15b*, 266 (1960).

(32) V. I. Kulishov, E. M. Brainina, N. G. Bokiy, and Yu.T. Struchkov, *Chem. Commun.*, 475 (1970).

(33) H. Feijth, F. W. Siegert, and H. J. de Liefde Meijer, unpublished results.

(34) E. O. Fischer and A. Treiber, *Chem. Ber.*, *94*, 2193 (1961).

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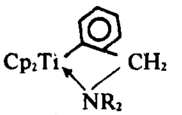
Table III. Complexes of composition Cp_2TiR

	m.p. (°C)	unpaired electrons	Ref.
$Cp_2Ti(\pi\text{—allyl})$		1	Table II
$Cp_2Ti(\sigma\text{—}C_5H_5)$	138-140 (dec.)	1	(12)
$Cp_2Ti(\sigma\text{—}C_6H_5)$	dec. 20-25	1	(37)
$Cp_2Ti(\sigma\text{—}C_6F_5)$	dec. 130	1	(8)
$Cp_2Ti(\sigma\text{—}CH_2C_6H_5)$	dec. 40	1	(8)
	169 ($R{=}CH_3$)	1	(38)
$Cp_2Ti(CH_3)$	not isolated	1	(39)
$[Cp_2TiH]_2$	dec. 70	0	(40)
$[(Cp_2Ti)_2C_4(C_6H_5)_2]$	>200	0	(14)

at low temperatures. These complexes (Table III) are less stable than the corresponding complexes $Cp_2Ti^{IV}R_2$ or $Cp_2V^{III}R$ (*cf.* Table I). $Cp_2Ti^{III}(CH_2C_6H_5)$[8] and $Cp_2Ti^{III}(C_6H_5)$[37] decompose when stored at room temperature; more stable complexes are obtained if the phenyl ligand of the latter complex is replaced by perfluorophenyl,[8] or if it carries (at an *ortho*-position) a group $\text{—}CH_2\text{—}NR_2$ that can coordinate at the metal[38] (Table III). The complexes $Cp_2Ti^{III}R$ mentioned are paramagnetic, in contrast to diamagnetic $[Cp_2Ti^{III}H]_2$[40] and the very stable complex of composition $[Cp_2Ti(C_2C_6H_5)]_2$[14] whose structure is yet unknown.

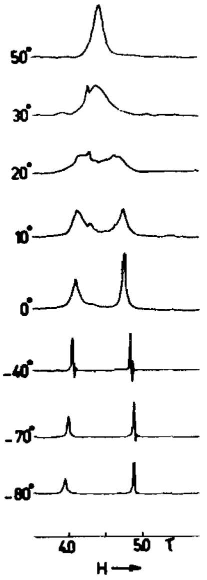


Figure 7. NMR spectra of $(C_5H_5)_4Ti$ (in deuterotoluene) at various temperatures; standard TMS (τ 10 ppm).[35]

Solutions of the paramagnetic complexes $[Cp_2Ti^{III}H_2]^-$,[28,39] $[Cp_2Ti^{III}(CH_3)_2]^-$, and $Cp_2Ti^{III}(CH_3)$[39] in ether or THF are stable at room temperature, but the corresponding ethyl and isopropyl complexes are either unstable or even non-existent.[39] (An early report on $Cp_2Ti^{III}(C_2H_5)$[41] is most probably incorrect[8]).

Reaction mixtures of titanocene monochloride (or dichloride) with an excess of ethyl or isopropyl Grignard reagent in THF or ether react with diolefins yielding π-allylic complexes of titanocene.[28] The same reaction mixtures are able to react with molecular nitrogen to produce ammonia after alcoholysis. Although this nitrogen-fixation reaction has received considerable attention,[42] no nitrogen-bearing complex of titanocene has been isolated until recently. We succeeded in isolating a blue crystalline complex of composition $[Cp_2Ti(C_6H_5)N]_n$ by reaction of solutions of $Cp_2Ti(C_6H_5)$ with nitrogen (1 atm.) at low temperatures; the reaction is reversible.[37] Similar reversible addition of nitrogen was also observed for several other complexes $Cp_2Ti^{III}R$.[8] On solvolysis $[Cp_2Ti(C_6H_5)N]_n$ does not yield ammonia, but N_2 is liberated again,[37] in contrast with the reaction mixtures mentioned above.

In view of the stereochemical differences between titanocene and vanadocene complexes it is comprehensible that complexes $Cp_2V^{III}R$ do not react with nitrogen. In the same way it can be understood that vanadocene complexes are far less active as co-catalysts in Ziegler-Natta polymerizations than are titanocene complexes.[43]

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