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SYNTHESIS AND PROPERTIES OF ARYLDICYCLOPENTADIENYLTITANIUM(III) COMPOUNDS

J. H. TEUBEN and H. J. DE LIEFDE MEIJER

Laboratorium voor Anorganische Chemie, Rijksuniversiteit, Zernikelaan, Groningen (The Netherlands)

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SUMMARY

The synthesis and properties of the compounds Cp_2TiR, with $R=C_6H_5$, *o*-, *m*-, *p*-$CH_3C_6H_4$, 2,6-$(CH_3)_2C_6H_3$, 2,4,6-$(CH_3)_3C_6H_2$, C_6F_5, $CH_2C_6H_5$, are described. Chemical and physical properties indicate that the R groups are σ-bonded to the titanium atom. The complexes are monomeric, with one unpaired electron per titanium atom. They are very air sensitive, and vary markedly in thermal stability; some of the compounds react with molecular nitrogen, to give complexes of the general formula $(Cp_2TiR)_2N_2$. Compounds Cp_2TiR with R=alkyl could not be isolated.

INTRODUCTION

Only few organotitanium(III) compounds of the general formula Cp_2TiR ($Cp=\pi$-C_5H_5) are known. Martin and Jellinek reported the synthesis and properties of Cp_2TiR (R=allylic group)[1]; the allylic group was found to be π-bonded to the titanium atom[2]. Some time ago we described[3] a phenylethynyl derivative $[Cp_2Ti(C{\equiv}CC_6H_5)]_2$. Although the structure of this diamagnetic complex is not fully known, it appears that the phenylethynyl groups are not simply σ-bonded to the metal atom. Only a small number of compounds Cp_2TiR in which R is a σ-bonded organic group have been reported. ESR spectroscopic evidence has been presented[4] for the existence of Cp_2TiR ($R=CH_3$, C_4H_7O) compounds in solution. Tricyclopentadienyltitanium, Cp_3Ti, described by Fischer and Löchner[5] as a complex with three π-bonded cyclopentadienyl rings was recently reformulated as $Cp_2Ti(\sigma$-$C_5H_5)$ on basis of its infrared spectrum[6]. In a review article, Coutts and Wailes[7] briefly mentioned the synthesis of a dimeric diamagnetic compound formulated as $(Cp_2TiC_6H_5)_2$, probably with bridging phenyl groups; no further information on this interesting compound has been published. We have published preliminary results on the synthesis of the compound $Cp_2TiC_6H_5$[8], which proved to be paramagnetic and monomeric. This compound reacts with molecular nitrogen with formation of a dinitrogen complex $(Cp_2TiC_6H_5)_2N_2$.

In the present paper we describe a more extensive study on compounds of the type Cp_2TiR with R=alkyl or aryl. Compounds with $R=C_6H_5$, *o*-, *m*-, *p*-

$CH_3C_6H_4$, 2,6-$(CH_3)_2C_6H_3$, 2,4,6-$(CH_3)_3C_6H_2$, C_6F_5, $CH_2C_6H_5$ were isolated and their properties studied; we did not succeed in isolating the compounds with R=alkyl.

EXPERIMENTAL

The compounds Cp_2TiR were prepared according to the reaction:

$$Cp_2TiCl+RMgX \rightarrow Cp_2TiR+MgXCl$$

All experiments were performed under pure argon[9], using Schlenk-type reaction vessels. Solvents were purified by conventional methods and carefully dried. Prior to use, they were freed from oxygen by repeated degassing and saturating with argon. Cp_2TiCl was prepared as described in the literature[10], and purified by sublimation (180°, 0.1 mm Hg) or recrystallization from toluene. Grignard reagents (about 0.7–1.0 *M*) were prepared in ether and stored under argon. C_6H_5Br and $C_6H_5CH_2Cl$ were distilled before use; the other organic halides were not purified. The Grignard reagents were syringed into the reaction vessels. At the same time, 1,4-dioxane, in an amount equimolar to the Grignard reagent, was added to precipitate the magnesium halide formed and to decrease the reducing action of the reagent[11].

Elementary analyses for C and H were carried out at the Microanalytical Department of this University under supervision of Mr. W. M. Hazenberg; Ti was determined in our laboratory under supervision of Drs. B. P. Knol. Gas chromatographic analyses were performed with a F & M model 720 gas chromatograph. IR spectra were recorded with a Hitachi EPI-G spectrophotometer; air-sensitive compounds were suspended in Nujol, and the other compounds were embedded in KBr discs. Absorption spectra in the visible range were recorded with a Perkin–Elmer EPS-3T spectrophotometer. ESR spectra were recorded with a Varian E3 X-band EPR spectrometer. Magnetic susceptibilities were determined with a vibrating-sample magnetometer (PAR magnetometer type 150D), the measurements being performed at various temperatures between 4.2–100 K. The susceptibilities were corrected for induced diamagnetism. Melting points and decomposition temperatures were recorded using a low-temperature DTA apparatus[12]. Samples (ca. 20 mg) were sealed in evacuated (0.1 mm Hg) glass ampoules. The heating rate was 2–3 degree·min^{-1}. Molecular weights were determined cryoscopically in benzene.

Phenyldicyclopentadienyltitanium(III)

Phenylmagnesium bromide (7.4 ml of a 0.85 *M* solution) in ether was added dropwise during 30 min to a well-stirred suspension of 1.35 g (6.3 mmoles) of Cp_2TiCl in 50 ml of ether and an equimolar amount of 1,4-dioxane. Immediately afterwards, the solvent was removed in vacuum. All operations were performed at or below $-20°$. The reaction mixture was stirred with 150 ml of n-pentane. The green solution was filtered, and the filtrate was gradually cooled to $-78°$C. $Cp_2TiC_6H_5$ separated as green leaflets. The mother liquor was removed and the crystals were washed with n-pentane at $-78°$. After drying in vacuum at $-20°$ the crystals were isolated, sealed in ampoules under argon, and stored at $-78°$C. Yield 0.80 g (3.1 mmoles, 50%). Decompn. 29°. (Found: C, 75.45; H, 5.98; Ti, 18.33. $C_{16}H_{15}Ti$ calcd.: C, 75.30; H, 5.93; Ti, 18.77%.)

m-Tolyldicyclopentadienyltitanium(III) and p-Tolyldicyclopentadienyltitanium(III)

Under conditions which led to the isolation of phenyldicyclopentadienyltitanium(III), the *m*- and *p*-tolyl compounds could not be obtained in a pure form. Although the compounds were formed upon addition of the Grignard reagent to the Cp_2TiCl/ether mixture, they decomposed when the solvent was removed, giving a brown-purple solid and toluene (over 60% based on the Grignard reagent used). In the case of *p*-tolyldicyclopentadienyltitanium(III) a small amount (about 100 mg) of green crystalline material was obtained. From the IR-spectrum in Nujol, which shows π-cyclopentadienyl and *p*-tolyl absorptions, it was concluded that the green product consisted of $Cp_2Ti(p\text{-}CH_3C_6H_4)$.

o-Tolyldicyclopentadienyltitanium(III)

A mixture of 1.07 g (5.0 mmoles) of Cp_2TiCl, an equimolar amount of 1,4-dioxane and 50 ml of ether was stirred at −20°, and 4.4 ml of a 1.08 *M* solution of *o*-tolylmagnesium bromide in ether was added dropwise during 1 h. The solvent was then removed in vacuum at 0°, and the residue was stirred with 150 ml of n-pentane at 0°. The green solution was filtered and slowly cooled to −78°. $Cp_2Ti(o\text{-}CH_3C_6H_4)$ separated as long thin green needles. After washing with n-pentane at −78°, the crystals were dried in vacuum at 0° and isolated. The product was sealed in ampoules under Ar, and stored at −78°. Yield 0.71 g (2.6 mmoles, 55%). The compound was analyzed and characterized after recrystallization from n-pentane; m.p. 69°. (Found: C, 75.69, 75.57; H, 6.63, 6.67; Ti, 17.49, 17.38. Mol. wt., 270. $C_{17}H_{17}Ti$ calcd.: C, 75.84; H, 6.37; Ti, 17.79%. Mol. wt., 269.)

2,6-Xylyldicyclopentadienyltitanium(III)

A mixture of 2.14 g (10.0 mmoles) of Cp_2TiCl, an equimolar amount of 1,4-dioxane, and 100 ml of ether, was stirred vigorously at 0°, and 11.1 ml of a 0.86 *M* solution of 2,6-xylylmagnesium bromide in ether was added dropwise, during 1 h. After additional stirring for 1 h the solvent was removed in vacuum at 0°. The residue was stirred for 2 h at room temperature with 200 ml of n-pentane. The green solution was filtered and slowly cooled to −78°. $Cp_2Ti[2,6\text{-}(CH_3)_2C_6H_3]$ separated as long thin green needles. The mother liquor was decanted, and the crystals were washed with n-pentane at −78°. The product was dried in vacuum at room temperature, sealed in ampoules under argon, and stored at −78°. Yield: 1.10 g (3.9 mmoles, 41%). The compound was obtained in pure form by sublimation (160°, 0.1 mm Hg); m.p. 180°. (Found: C, 76.37, 76.39; H, 6.94, 7.16; Ti, 16.83, 16.86. Mol.wt., 280. $C_{18}H_{19}Ti$ calcd.: C, 76.33; H, 6.76; Ti, 16.91%. Mol.wt., 283.)

Mesityldicyclopentadienyltitanium(III)

A mixture of 0.91 g (4.3 mmoles) of Cp_2TiCl, an equimolar amount of 1,4-dioxane, and 50 ml of ether, was stirred vigorously at 0° and 7.6 ml 0.52 *M* mesitylmagnesium bromide in ether was added dropwise. The reaction mixture was stirred for 2 h at room temperature after which time the solvent was removed in vacuum. The reaction products were extracted with 150 ml of n-pentane. After filtration the green extract was concentrated to 30 ml and cooled to −78°. Green crystals separated. The mother liquor was decanted and the crystals were washed with n-pentane (3 × 10 ml) at −78°. After drying in vacuum at room temperature the product was isolated, sealed in ampoules under argon, and stored at −78°. Yield: 0.76 g (2.6 mmoles, 65%) of $Cp_2Ti[2,4,6\text{-}(CH_3)_3C_6H_2]$. The compound was analyzed and characterized after recrystallization from n-pentane; m.p. 78°. (Found: C, 76.80, 76.51; H, 7.33, 7.42; Ti, 15.97, 16.15. Mol.wt., 287. $C_{19}H_{21}Ti$ calcd.: C, 76.77; H, 7.12; Ti, 16.11%. Mol.wt., 297.)

(Pentafluorophenyl)dicyclopentadienyltitanium(III)

A mixture of 1.82 g (8.5 mmoles) of Cp_2TiCl, an equimolar amount of 1,4-dioxane and 50 ml of ether was stirred at −20°, and 9.8 ml of a 0.87 *M* solution of (pentafluorophenyl)magnesium bromide in ether were added during 1 h dropwise. After additional stirring for 1 h at 0°, the solvent was removed in vacuum. The reaction products were stirred with 150 ml of n-pentane at 0°. The resulting solution was filtered and cooled to −78°. $Cp_2TiC_6F_5$ separated as thin brown-purple leaflets. Additional extraction of the residue with n-pentane and cooling gave more of the product. The crystals were washed at −78° with small portions of n-pentane. After drying in vacuum at room temperature the crystals were isolated in ampoules under argon, sealed, and stored at −78°. Yield 1.60 g (4.6 mmoles, 54%). A sample was analysed and characterised after recrystallization from n-pentane: decompn. 106°. (Found: C, 56.18, 56.36; H, 2.97, 2.92; Ti, 13.69, 13.60. Mol.wt., 335. $C_{16}H_{10}F_5Ti$ calcd.: C, 55.68; H, 2.92, Ti, 13.88%. Mol.wt., 345.)

Benzyldicyclopentadienyltitanium(III)

To a well-stirred mixture of 0.73 g (3.4 mmoles) of Cp_2TiCl, an equimolar amount of 1,4-dioxane and 50 ml of ether, 5.1 ml 0.64 *M* benzylmagnesium chloride in ether were added dropwise during 30 min. Stirring was continued for half an hour. After the solid products had settled, the brown solution was filtered, and the filtrate was cooled to −78°. Brown crystals separated. The residue was twice extracted with the mother liquor. Finally the crystals were washed at −78° with small portions of ether and dried in vacuum at −10°. The brown crystalline product was sealed in ampoules under argon and stored at −78°. All operations were performed at −20°. Yield 0.41 g (1.5 mmoles, 47%) of $Cp_2TiCH_2C_6H_5$. The compound was analyzed and characterized after recrystallization from n-pentane; decompn. 43°. (Found: C, 75.11, 75.47; H, 6.54, 6.56; Ti, 17.75, 17.74. Mol.wt., 255. $C_{17}H_{17}Ti$ calcd.: C, 75.84; H, 6.37; Ti, 17.79%. Mol.wt., 269.)

Reaction with bromine

Bromine (1.6–1.7 mmoles) was added to a mixture of 1 mmol of Cp_2TiR and 10 ml of n-pentane at −78°. The reaction mixture was allowed to warm slowly to room temperature, and stirred for about 2 h. Cp_2TiBr_2 was precipitated. The RBr was quantitatively determined by GLC, and identified by its retention time and by IR or mass spectrometry. The yield of Cp_2TiBr_2 was spectrometrically determined in 1,2-dichloroethane solution (λ_{max} 428 nm, ε 3.22×10^3 $l \cdot mol^{-1} \cdot cm^{-1}$). In a number of reactions we also found RH, probably due to reaction of Cp_2TiR with HBr which was formed by bromination of the solvent. The results are given in Table 1, and show that the stoichiometry is:

$$Cp_2TiR + 1.5\ Br_2 \rightarrow Cp_2TiBr_2 + RBr.$$

TABLE 1

REACTION OF Cp_2TiR WITH BROMINE

R	*RH* (%)	*RBr* (%)	*Cp_2TiBr_2* (%)
C_6H_5		88	96
o-$CH_3C_6H_4$		73	100
2,6-$(CH_3)_2C_6H_3$		98	102
2,4,6-$(CH_3)_3C_6H_2$	3	77	96
C_6F_5	15	50	85
$C_6H_5CH_2$	3	75	93

Reaction with hydrogen chloride

Hydrogen chloride gas was bubbled through a suspension of 1 mmole of Cp_2TiR in 10 ml of n-pentane at $-78°$. A reaction took place immediately, RH and a precipitate of green Cp_2TiCl being formed according to:

$$Cp_2TiR+HCl \rightarrow Cp_2TiCl+RH$$

After the mixture had warmed to room temperature, Cp_2TiCl was oxidized with an excess of hydrogen chloride:

$$Cp_2Ti^{III}Cl+HCl \rightarrow Cp_2Ti^{IV}Cl_2+\tfrac{1}{2}\,H_2$$

The RH products were quantitatively determined by GLC and identified by their retention times and IR and/or mass spectrometry. After washing with n-pentane, Cp_2TiCl_2 was identified by its infrared spectrum and quantitatively determined by visible spectrometry in 1,2-dichloroethane (λ_{max} 525 nm, ε 2.00×10^2 $l \cdot mol^{-1} \cdot cm^{-1}$; λ_{max} 392 nm, ε 2.39×10^3 $l \cdot mol^{-1} \cdot cm^{-1}$). The results are shown in Table 2.

TABLE 2

REACTION OF THE COMPOUNDS Cp_2TiR WITH HYDROGEN CHLORIDE

R	*RH* (%)	*Cp_2TiCl_2* (%)
C_6H_5	95	85
o-$CH_3C_6H_4$	96	86
2,6-$(CH_3)_2C_6H_3$	97	87
2,4,6-$(CH_3)_3C_6H_2$	101	70
C_6F_5	99	84
$C_6H_5CH_2$	96	61

Attempted syntheses of alkyldicyclopentadienyltitanium(III) compounds

The method for synthesizing the aryl and benzyl compounds Cp_2TiR was not successful for the corresponding alkyl derivatives. Upon addition of RMgX ($R=CH_3$, C_2H_5, i-C_3H_7, t-C_4H_9; $X=Cl$ or Br) in ether to suspensions of Cp_2TiCl in the same solvent, complex brown reaction mixtures were obtained. Toluene extraction yielded dark brown products of irreproducible composition. The (partial) retention of the Cp_2Ti structure was demonstrated by the IR spectrum of the products, together with the results of the reactions with HCl or Br_2, which gave Cp_2TiCl_2 or Cp_2TiBr_2. Elementary analysis (of toluene extracts) showed the presence of Ti, Mg and halogen. In solution the brown products decomposed under gas evolution and loss of the Cp_2Ti structure; reaction of these decomposition products with hydrogen chloride in ether did not yield Cp_2TiCl or Cp_2TiCl_2, but gave a purple solution from which a purple compound was isolated. IR and visible spectroscopy showed this compound to be $[Cp(C_5H_4)TiCl]_2$. It reacted with HCl in excess with formation of green, probably polymeric, $[Cp(C_5H_4)TiCl_2]_n$. The same purple compound is obtained by reaction of "titanocene", $[Cp(C_5H_4)TiH]_2$, with HCl[13,14]. The reaction of Cp_2TiCl with alkyl Grignard reagents is still under investigation.

RESULTS AND DISCUSSION

The well-known method for the formation of transition metal–carbon σ-bonds by treatment of a metal halide with a Grignard reagent proved to be a convenient route for the preparation of compounds of the type Cp_2TiR with R=aryl or benzyl, (but not for R=alkyl). Under the conditions used the reaction of Cp_2TiCl and RMgX (X=Cl, Br) in ether proceeded according to:

$$Cp_2TiCl + RMgX \rightarrow Cp_2TiR + MgClX$$

After removal of the solvent in vacuum, extraction of the reaction products with n-pentane and cooling of the extracts, the new compounds were obtained as crystalline solids. After recrystallization the complexes with $R = C_6H_5$, $o\text{-}CH_3C_6H_4$, $2,6\text{-}(CH_3)_2C_6H_3$, $2,4,6\text{-}(CH_3)_3C_6H_2$, C_6F_5, $CH_2C_6H_5$ were obtained analytically pure. The complexes with $R = m\text{-}CH_3C_6H_4$ and $p\text{-}CH_3C_6H_4$ could not be isolated in a pure form, probably because of thermal decomposition of the compounds, and were studied in solution. Chemical analyses and molecular weights show the Cp_2TiR compounds to be monomeric. The physical and chemical properties indicate that the cyclopentadienyl group is π-bonded while the R groups are σ-bonded to the metal.

The halogens X_2 (X=Cl, Br, I) cleave the metal–carbon σ-bond:

$$Cp_2TiR + 3/2\,X_2 \xrightarrow{\text{n-pentane}} Cp_2TiX_2 + RX$$

For X=Br (Table 1) and X=I the reaction is almost quantitative; for X=Cl a quantitative study was not possible because of the high reactivity of chlorine towards the solvent and the reaction products. Hydrogen chloride also cleaves the titanium–carbon σ-bond:

$$Cp_2TiR + HCl \xrightarrow{\text{n-pentane}} Cp_2TiCl + RH$$

An excess of hydrogen chloride oxidizes the initially formed Cp_2TiCl:

$$Cp_2TiCl + HCl \xrightarrow{\text{n-pentane}} Cp_2TiCl_2 + \tfrac{1}{2}H_2$$

Again, the yields of RH and Cp_2TiCl_2 are almost quantitative (Table 2). These cleavages of the Ti–R bonds by halogens or HCl, with formation of RX or RH and the metal halides Cp_2TiX_2, is normal for σ-bonded organic derivatives of transition metals[15].

The physical properties of the compounds are also in agreement with the structure Cp_2TiR. The IR spectra (Fig. 1) show the absorption bands at 3100 w–m, 1135 vw, 1010 m–s and 800 s cm^{-1} characteristic for π-bonded cyclopentadienyl groups[16]. The bands at 1430 and 1370 cm^{-1} are also present, but they coincide with absorptions of Nujol. In the spectra of the compounds with R = phenyl or substituted phenyl, the characteristic group frequencies of the aryl moiety are found, suggesting σ-bonded aryl groups. No significant shifts as compared with normal organic aromatics are observed[17]. The same is true of the spectrum of $Cp_2TiC_6F_5$. Apart from the π-cyclopentadienyl absorptions, the characteristic C_6F_5 frequencies are found at 1630 m, 1495 s, 1072 m, 1057 m, 1038 s and 938 s cm^{-1} [18]. In the benzyl compound $Cp_2TiCH_2C_6H_5$ the organic group may be simply σ-bonded to the metal, or π-bonded, as is the allyl group in Cp_2Ti(allyl) derivatives. The same problem is presented by tetrabenzyltitanium, $(C_6H_5CH_2)_4Ti$. Brüser *et al.*[19] investigated the IR spectrum of the latter and favoured the σ-bonded conformation. In addition to π-cyclopentadienyl bands the spectrum of $Cp_2TiCH_2C_6H_5$ shows absorptions characteristic of a monosubstituted phenyl group. Other bands, in particular a strong CH_2 wag

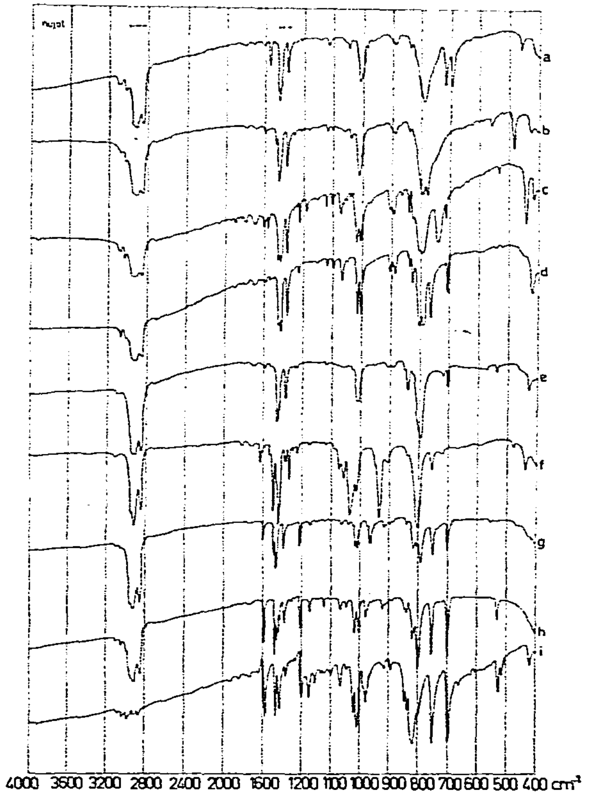

Fig. 1. IR spectra of: (a) $Cp_2TiC_6H_5$, (b) $Cp_2Ti(p\text{-}CH_3C_6H_4)$, (c) $Cp_2Ti(o\text{-}CH_3C_6H_4)$, (d) $Cp_2Ti[2,6\text{-}(CH_3)_2C_6H_3]$, (e) $Cp_2Ti[2,4,6\text{-}(CH_3)_3C_6H_2]$, (f) $Cp_2TiC_6F_5$, (g) $Cp_2Ti(CH_2C_6H_5)$, (h) $Cp_2V(CH_2C_6H_5)$ in nujol; (i) $Cp_2Ti(CH_2C_6H_5)_2$ in KBr. The nujol absorptions are indicated at the top of the figure.

at 1210 cm^{-1}, are in close agreement with the spectrum of $(C_6H_5CH_2)_4Ti$. This evidence together with the very close resemblance of the spectrum with that of $Cp_2Ti(CH_2C_6H_5)_2$ (Fig. 1) (in which the benzyl groups are expected to be σ-bonded for steric reasons) and $Cp_2VCH_2C_6H_5$ indicates that the benzyl group is σ-bonded in $Cp_2TiCH_2C_6H_5$. A noteworthy aspect of the IR spectra of the compounds described here is the close similarity to those of related organometallics such as $CpTiR_2$[18,20] and Cp_2VR[20,21] ($R=C_6H_5$, p-$CH_3C_6H_4$, $CH_2C_6H_5$, C_6F_5); in particular, the spectra of Cp_2TiR and Cp_2VR are almost identical (Fig. 1), suggesting a close similarity in bonding and structure.

The compounds Cp_2TiR all have characteristic absorption spectra in the visible range. The complexes with $R=C_6H_5$, o-, m-, p-$CH_3C_6H_4$, 2,6-$(CH_3)_2C_6H_3$, 2,4,6-$(CH_3)_3C_6H_2$ are yellowish-green in toluene, and show absorption maxima at 440 nm (ε about 200 l·mol^{-1}·cm^{-1}) and at 620-640 nm (ε about 25 l·mol^{-1}·cm^{-1}). The effect of substitution of the phenyl group is very small. $Cp_2TiC_6F_5$ (purple) exhibits a maximum at 490 nm (ε 160 l·mol^{-1}·cm^{-1}) and a shoulder at about 600 nm (ε 42 l·mol^{-1}·cm^{-1}). $Cp_2TiCH_2C_6H_5$ (brown) only shows one intense broad band (ε 1050 l·mol^{-1}·cm^{-1}) at 440 nm.

The ESR spectra of the complexes with $R=C_6H_5$, o-, m-, p-$CH_3C_6H_4$, 2,6-$(CH_3)_2C_6H_3$, 2,4,6-$(CH_3)_3C_6H_2$ in toluene solution (10^{-3}–10^{-4} M) show a singlet signal at g 1.95; again, the spectra of $Cp_2TiC_6F_5$ (g 1.93) and $Cp_2TiCH_2C_6H_5$ (g 1.97) are slightly different. Magnetic susceptibility measurements of the solid compounds Cp_2TiR confirm the paramagnetic behaviour observed in solution.

TABLE 3

MAGNETIC MOMENTS OF THE COMPOUNDS Cp_2TiR

R	μ(B.M.)
C_6H_5	1.58
o-$CH_3C_6H_4$	1.81
2,6-$(CH_3)_2C_6H_3$	1.66
2,4,6-$(CH_3)_3C_6H_2$	1.72
C_6F_5	1.92*

The observed magnetic moments (Table 3) are close to the spin-only value for one unpaired electron per titanium atom. This suggests that the solid compounds Cp_2TiR are monomeric, as do molecular-weight determinations of benzene solutions of the compounds. This is in contrast with the diamagnetic dimer $(Cp_2TiC_6H_5)_2$ reported by Coutts and Wailes[7]. Unfortunately, little information on this complex is available, and it is not possible to compare it with our compounds.

As expected for organometallic compounds of low-valent titanium, the complexes Cp_2TiR are very reactive. They are extremely air-sensitive and have to be handled in an argon atmosphere. The reaction with air gives yellow to brown products of somewhat variable composition; evidently these products are mixtures. Their IR spectra indicate that π-bonded cyclopentadienyl groups are still present; broad intense bands in the 720–560 cm^{-1} range show the presence of Ti–O–Ti bridges[22].

The compounds Cp_2TiR decompose in solution under argon, the rate being dependent on R and on the solvent. With chlorine-containing solvents a violent reaction takes place. In other solvents, *e.g.*, n-pentane, ether, toluene or benzene, thermal decomposition is observed; RH is formed and the Cp_2Ti structure is lost. The same decomposition products are obtained by thermolysis of solid complexes. The thermal stabilities of the solid compounds vary strongly with the nature of the group R, the stability increasing in the sequence $R = p\text{-}CH_3C_6H_4 \sim m\text{-}CH_3C_6H_4 < C_6H_5 < CH_2C_6H_5 < o\text{-}CH_3C_6H_4 < C_6F_5 < 2,6\text{-}(CH_3)_2C_6H_3 \sim 2,4,6\text{-}(CH_3)_3C_6H_2$. The relation between the thermal stability and the nature of the group R will be discussed in a separate paper.

Another aspect of the high reactivity of the compounds under discussion is their reaction with molecular nitrogen. On exposure of the compounds Cp_2TiR to molecular nitrogen bimolecular complexes $(Cp_2TiR)_2N_2$ are formed. Detailed information on the synthesis and properties of these complexes and their relation with the so-called nitrogen-fixation systems will be given in a forthcoming paper. Preliminary results have been published[8].

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