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STRUCTURAL ELUCIDATION OF SOME NEW TITANACYCLES BY MEANS OF DEGRADATION AND ^{13}C NMR STUDIES

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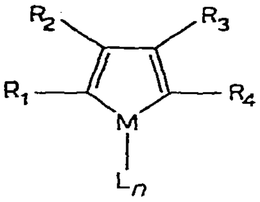
Summary

A reaction between diphenyltitanocene and phenyl(pentafluorophenyl)acetylene in refluxing benzene produces 1,1-bis(η^5-cyclopentadienyl)-2-phenyl-3-(pentafluorophenyl)benzotitanole in 44% yield. Degradation of the product with $HCl/CHCl_3$ affords titanocene dichloride and *Z*-1,2-diphenyl-1-(pentafluorophenyl)ethene. Reaction of diphenyltitanocene and phenyl(pentafluorophenyl)acetylene in benzene under photolytic conditions results in the exclusive formation of 1,1-bis(η^5-cyclopentadienyl)-2,5-diphenyl-3,4-di(pentafluorophenyl)titanole. The latter product can also be obtained in 77% yield from a reaction between titanocene dicarbonyl and phenyl(pentafluorophenyl)acetylene in hexane solution. Application of ^{13}C NMR spectroscopy to the structural elucidation of these and related metallacycles is discussed.

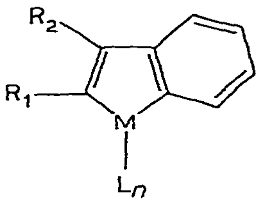
Introduction

Metallacyclic derivatives of the transition metals have been extensively investigated in recent years, since they are believed to serve as key intermediates in various homogeneous catalytic processes such as the cyclooligomerization of acetylenes [1] and the metathesis of olefins [2]. The potential aromaticity of certain unsaturated transition metal metallacycles has also been considered [3].

Two important classes of unsaturated metallacycles are the metallacyclopentadienes (metalloles) (I) and the metallaindenes (benzometalloles) (II), the latter being formally derivatives of I in which R_3 and R_4 represent a fused benzene ring system. In the titanium series, 1,1-bis(η^5-cyclopentadienyl)-2,3,4,5-tetraphenyltitanole (III) has been isolated by several groups of investigators [4—8], and its metallacyclic structure confirmed by an X-ray crystallo-

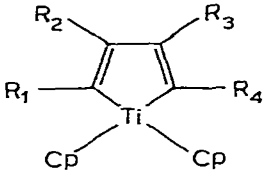


(I)

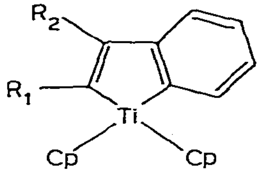


(II)

graphic study [9]. A variety of other titanoles in which R_1—R_4 = Mes, Me_3Si, etc., have also been prepared [10]. Benzotitanoles currently known include those where R_1 and R_2 = Ph (IV) [11], R_1 = Ph, R_2 = n-Bu (V) [12], R_1 and



(III, R_1 – R_4 = Ph)



(IV, R_1, R_2 = Ph;
V, R_1 = Ph; R_2 = n–Bu;
VI, R_1, R_2 = C_6F_5;
VII, R_1 = $SiMe_3$; R_2 = Ph)

R_2 = C_6F_5 (VI) [13], R_1 = $SiMe_3$, R_2 = Ph (VII) [13], as well as where R_1 and R_2 represent a variety of other organic substituents such as CF_3 and Me [14,15]. The metallacyclic structures of both VI and VII have likewise been confirmed by means of X-ray crystallographic studies [13].

In spite of the rapid growth of ^{13}C NMR investigations concerning organometallic compounds [16,17], no applications of this important spectral technique to the structural elucidation of unsaturated metallacyclic compounds such as I and II have been reported *. In the present paper, we discuss the formation of two new titanacycles, 1,1-bis-(η^5-cyclopentadienyl)-2-phenyl-3-pentafluorophenylbenzotitanole (VIII) and 1,1-bis-(η^5-cyclopentadienyl)-2,5-diphenyl-3,4-di-(pentafluorophenyl)titanole (XI), and the application of ^{13}C NMR spectroscopy to the elucidation of their structures. A structural verification of benzotitanole VIII by means of chemical degradation is also described.

Results and discussion

Synthetic and degradative studies

Hagihara and coworkers [11] demonstrated that the thermolysis of diphenyltitanocene and diphenylacetylene in refluxing benzene afforded the benzo-

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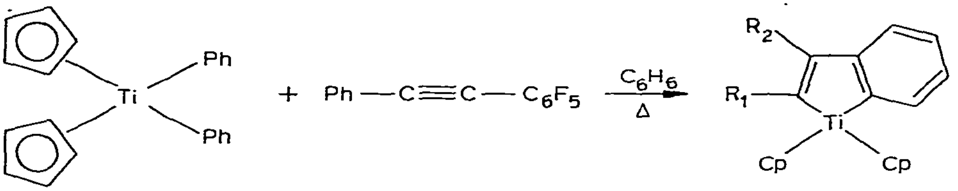
* ^{13}C NMR spectroscopy has been used in the characterization of certain saturated metallacycles [18—21].

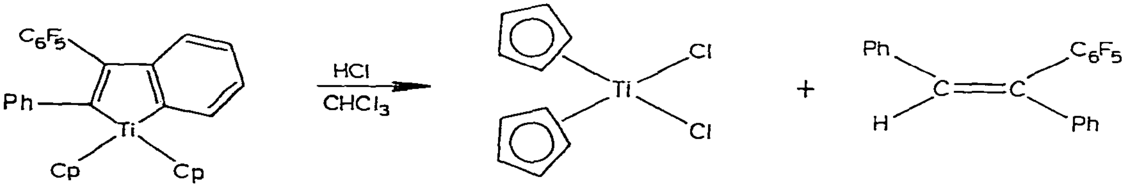
titanole IV in moderate yield. In view of the recent successful extension of this reaction to produce benzotitanole VI starting with di(pentafluorophenyl)-acetylene [13], it was also of interest to examine the reaction of diphenyltitanocene and phenyl(pentafluorophenyl)acetylene, since isomeric benzotitanoles might be anticipated in this case.

A thermal reaction between diphenyltitanocene and phenyl(pentafluorophenyl)acetylene in refluxing benzene in fact produced two benzotitanoles, VIII and IX, one in 44% yield and the other in less than 1% yield. The products could be separated by column chromatography on alumina.



(VIII, R_1 = Ph, R_2 = C_6F_5;
IX, R_1 = C_6F_5, R_2 = Ph)

The major product was identified as a benzotitanole by elemental analysis, IR, ^{1}H NMR and mass spectral studies. Degradation of this product by means of $HCl/CHCl_3$ afforded a 90% yield of titanocene dichloride and a 40% yield of Z-1,2-diphenyl-1-pentafluorophenylethene (X). The latter alkene was synthesized independently from a reaction between deoxybenzoin and pentafluorophenylmagnesium bromide, followed by hydrolysis and subsequent dehydration with 20% sulfuric acid. Alkene X prepared in this manner was shown to be identical in every respect to the alkene isolated by the degradation of the benzotitanole obtained in major amount, thus identifying the latter as VIII. Such a structural assignment is also in accord with ^{13}C NMR spectral studies (vide infra).

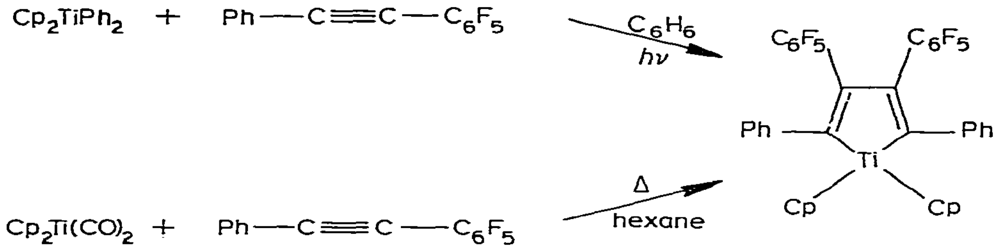


(VIII)

(X)

The minor product obtained from the thermolysis of diphenyltitanocene and phenyl(pentafluorophenyl)acetylene in benzene can be tentatively identified as a benzotitanole on the basis of its ^{1}H NMR and mass spectra, although it was produced in too low a yield to permit detailed structural studies. In view of the major product being identified as VIII, this minor product is most likely the isomeric benzotitanole IX.

Previous studies in our laboratory have shown that the photolysis of diphenyltitanocene and diphenylacetylene in benzene solution led to the formation of titanole III in moderate yield [8]. The same metallacycle had also been obtained earlier from a thermal reaction between titanocene dicarbonyl and diphenylacetylene [5]. In the present study, a photo-induced reaction between diphenyltitanocene and phenyl(pentafluorophenyl)acetylene in benzene led to the exclusive formation of a single titanole in 25% yield. This same metallacycle could be more readily obtained in 77% yield from a reaction between titanocene dicarbonyl and phenyl(pentafluorophenyl)acetylene in refluxing hexane solution.



(XI)

Degradation of the product by means of $HCl/CHCl_3$ likewise produced titanocene dichloride and a diphenyldi(pentafluorophenyl)butadiene, although in this case the structures of the latter organic product and therefore the titanole were not readily ascertained. On the basis of its ^{13}C NMR spectrum and a comparison with spectra of other metallacycles, however, the titanole can be assigned as XI.

^{13}C NMR spectral studies

Carbon-13 NMR was applied to the structure determinations of the benzotitanole and the titanole derivatives VIII and XI, respectively. To accomplish this, the quaternary carbon signals for both C(2, 3, 4, 5) (see Fig. 1 for the numbering used) as well as the four substituted carbons of the arene groups had to be located in the ^{13}C NMR spectra, and the structural assignments for some of the signals determined.

Selected ^{13}C NMR chemical shift data for a series of metallacyclic derivatives is presented in Table 1. Proton-decoupled and subsequently fluorine-decoupled ^{13}C NMR spectra of compound XI demonstrate that the signals at 210.3, 147.4, 117.4 and 116.4 ppm are due to the eight quaternary carbon atoms. Comparison of the quaternary carbon resonances for a number of other metallacyclic derivatives (i.e., III, XII, XV, and XVI in Table 1) indicates that the lowest field signal has the greatest variation and can be assigned to C(2, 5). This is supported by the observed doublets of doublets coupling (i.e., $J(^{103}Rh—^{13}C)$ and $J(^{31}P—^{13}C)$) on the lowest field quaternary carbon signal of XIV as well as the

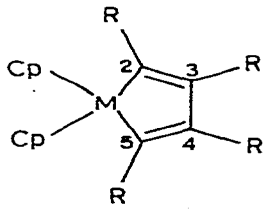
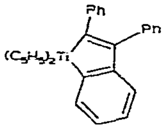
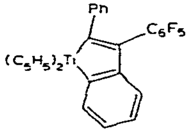
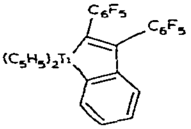
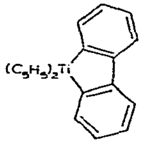


Fig. 1. Numbering scheme for the metallacyclic rings.

TABLE 1

^{13}C NMR DATA [e] OF 1,1-BIS(η^5-CYCLOPENTADIENYL)METALLACYCLE DERIVATIVES

Compound	C(2,5)	C(3,4)	Substituted carbons of arene groups		Ref.
$(C_5H_5)_2Ti(PhC_2Ph)_2$ (III)	202.1	147.2	141.1	135.4	6—8
 (IV)	2)202.7 5)195.1	3)146.9 4)143.1	140.8	137.9	11
$(PPh_3)(C_5H_5)Co(PhC_2Ph)_2$ (XII)	167.1 [a]	142.2	157.1	153.2	22
$(PPh_3)(C_5H_5)Co(C_6F_5C_2C_6F_5)_2$ (XIII)	163.5 [b]	114.0	— [d]	— [d]	23
$(PPh_3)(C_5H_5)Rh(C_6F_5C_2C_6F_5)_2$ (XIV)	161.9 [c]	113.2	— [d]	— [d]	24
$(C_5H_5)_2Ti(C_6H_5C_2C_6F_5)_2$ (XI)	210.3	117.4	147.5	116.4	this study
 (VIII)	2)209.9 5)195.5	3)117.0 4)147.7	141.6	— [d]	This study
 (VI)	2)187.4	3)115.4	128.3	122.4	13
$(C_5H_5)_2Zr(PhC_2Ph)_2$ (XV)	193.8	147.7	141.5	131.2	6
$(C_5H_5)_2Hf(PhC_2Ph)_2$ (XVI)	196.5	148.5	142.0	139.5	6
 (XVII)	196.2	142.6			12

[a] $J(^{31}P—^{13}C) = 30.1$ Hz. [b] $J(^{31}P—^{13}C) = 15.1$ Hz. [c] $J(^{31}P—^{13}C) = 11.9$ Hz; $J(^{103}Rh—^{13}C) = 36.7$ Hz. [d] Fluorine decoupling was not used for these ^{13}C NMR spectra. [e] Spectra were obtained in CH_2Cl_2 solvent.

$J(^{31}P—^{13}C)$ coupling seen on the lowest field quaternary carbon signals of XII and XIII.

Assignments for the other quaternary carbon atoms are not as clearcut. The C(3, 4) signal of XVII is definitely at 142.6 ppm. We propose that the C(3, 4) signals for the other phenyl-substituted metallacycle derivatives are in the 142—147 ppm region. Substitution of a C_6F_5 group for a phenyl group on a metallacyclic ring causes the ring carbon signal to be more shielded. This change is clearly seen in the ^{13}C NMR data for compounds XII and XIII. Similar upfield shifts have been observed previously for other C_6F_5-substituted organic compounds [25] *. It should also be mentioned that without fluorine decoupling,

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* We have also measured the ^{13}C NMR spectrum of $C_6F_5CH{=}CH_2$ and find the olefinic CH signal at 123.8 ppm. The olefinic CH signal of $C_6H_5CH{=}CH_2$ is located at 135.8 ppm.

the substituted carbon atom of a C_6F_5 ring is not observed in the ^{13}C NMR spectrum, due to complex $J(^{19}F—^{13}C)$ coupling which broadens this signal.

Application of these findings to the ^{13}C NMR spectrum of VIII indicates that the quaternary carbon signals at 209.9, 195.5, 147.7 and 117.0 ppm are due to C(2), C(5), C(4) and C(3), respectively, and that the C_6F_5 group is attached to carbon C(3) in agreement with the chemical degradation study.

In the ^{13}C NMR spectrum of XI, the quaternary carbon signal at 116.4 ppm is assigned to the substituted carbon of the C_6F_5 group, since it is not observed without ^{19}F decoupling. The metallacycle carbon signals are at 210.3 and 117.4 ppm, which indicates that the C_6F_5 groups are attached to the C(3, 4) carbon atoms. No other ^{13}C signals were observed in the low field region (180—210 ppm), and therefore there were no detectable amounts of other isomers present in this sample.

Experimental

All operations were conducted under argon or nitrogen using standard Schlenk tube techniques. The argon or nitrogen was dried with P_2O_5 and H_2SO_4, and trace oxygen was removed by BTS catalyst (BASF). Hexane, heptane and benzene were dried over calcium hydride and freshly distilled under argon from calcium hydride. Ethyl ether was dried over sodium and freshly distilled under argon from sodium/benzophenone. ^1H NMR and IR spectra were obtained on Varian A-60 and Perkin-Elmer 237-B spectrometers, respectively. The ^{13}C NMR spectra were obtained with a Varian XL-100-15 spectrometer operating in the pulsed Fourier transform mode at 25.1 MHz. The instrument was equipped with a Transform Technology, Inc., pulse unit which delivers a 90° pulse in 15 μsec, and a 36K Nicholet 1089 Computer system with disc. The ^{13}C chemical shifts were measured relative to an internal standard peak and are reported relative to tetramethylsilane. The conversion factor used is $\delta(TMS) = \delta(CH_2Cl_2) + 53.89$ ppm. To aid in the relaxation of carbon nuclei, tris(acetylacetonato)chromium(III) (0.05 *M* concentration) was added to each NMR sample. Mass spectra were obtained on a Perkin-Elmer-Hitachi RMU 6L instrument. Melting points were determined in sealed capillaries under argon and are uncorrected. Microanalyses were performed by the Microanalytical Laboratory of the University of Massachusetts. Phenyl(pentafluorophenyl)-acetylene [26], diphenyltitanocene [27] and titanocene dicarbonyl [28] were prepared by literature procedures.

Thermolysis of diphenyltitanocene and phenyl(pentafluorophenyl)acetylene

A mixture of 500 mg (1.50 mmol) of diphenyltitanocene, 406 mg (1.50 mmol) of phenyl(pentafluorophenyl)acetylene and 15 ml of anhydrous benzene was refluxed for 1.5 h under argon with magnetic stirring. To the resultant dark red solution was added ca. 1.0 g of alumina and the solvent was removed with continuous stirring under vacuum. The residue was added to a column of alumina (2 × 35 cm) packed dry under argon. Elution with hexane followed by 1/1 hexane/benzene removed a colorless band which contained unreacted phenyl(pentafluorophenyl)acetylene (62 mg, 15% recovery). Further elution with 1/1 hexane/benzene produced an orange band. The solvent was removed under vacuum to give 342 mg (43.7%) of 1,1-bis-(η^5-cyclopentadienyl)-2-phenyl-3-(pentafluorophenyl)benzotitanole. An analytical sample, m.p. 231—232° C, was obtained by recrystallization from ethyl ether/heptane and subsequent drying in vacuo at room temperature. (Found: C, 69.24; H, 3.86. $C_{30}H_{19}F_5Ti$ calcd.: C, 68.96; H, 3.67%). IR (KBr) 1510m, 1475s, 1100m, 1020m, 990s, 975s, 865m, 812s, 750s, 715s, 705s cm^{-1}. ^{1}H NMR (C_6D_6) δ 5.84 (10 H, s, C_5H_5), 6.4—7.0 ppm (9 H, m, aromatic); mass spectrum *m/e* 522 (M^+).

Continued elution with 1/1 hexane/benzene developed an additional very small, yellow-colored band. The solvent was removed under vacuum, leaving an oily residue. The latter was washed with four 10-ml portions of hexane, leaving 2.0 mg (0.3%) of a product believed to be 1,1-bis-(η^5-cyclopentadienyl)-2-pentafluorophenyl-3-phenylbenzotitanole. Although this product could not be fully identified, due to the limited amount available, the ^{1}H NMR (C_6D_6) spectrum exhibited a singlet resonance at δ 5.74 ppm, assignable to η^5-C_5H_5 protons, as well as multiplet absorption in the aromatic region. It's mass spectrum showed a peak at *m/e* 522, assignable to the molecular ion of the benzotitanole.

Reaction of 1,1-bis-(η^5-cyclopentadienyl)-2-phenyl-3-(pentafluorophenyl)benzotitanole with HCl

1,1-Bis-(η^5-cyclopentadienyl)-2-phenyl-3-(pentafluorophenyl)benzotitanole (126 mg, 0.24 mmol) was dissolved in 15 ml of chloroform and treated with an excess of concentrated hydrochloric acid. The color of the chloroform layer turned to deep red. The organic layer was then separated, and the aqueous layer was extracted with four 10-ml portions of hexane. The organic portions were combined, the solvents removed, and the residue was extracted with hexane, leaving 53.3 mg (90%) of titanocene dichloride, m.p. 296—298° C, mixture m.p. 294—296° C. IR and ^{1}H NMR spectra of this product were identical to those of an authentic sample. The extracts were combined and purified by column chromatography (alumina, 1 × 15 cm). After evaporation of the solvent, white crystals were obtained which upon recrystallization from 95% ethanol gave 32.6 mg (40%) of *Z*-1,2-diphenyl-1-pentafluorophenylethene, m.p. 107° C. (Found: C, 69.35; H, 3.36. $C_{20}H_{11}F_5$ calcd.: C, 69.36; H, 3.20%). The ^{1}H NMR, IR and mass spectra, mixture m.p. and GC retention time of the product were identical to those of an authentic sample described below.

Synthesis of Z-1,2-diphenyl-1-pentafluorophenylethene

In a 500-ml 3-necked flask, equipped with a reflux condenser, a pressure-equalizing funnel and an inert gas inlet were placed 2.43 g (0.1 g-atom) of magnesium turnings, 50 ml of anhydrous ethyl ether and a few drops of deaerated bromopentafluorobenzene. After a reaction had begun, the remainder of the bromopentafluorobenzene (24.7 g, 0.10 mmol) was added with magnetic stirring over a period of 1.5 h. While stirring was continued, 19.6 g (0.10 mmol) of deoxybenzoin dissolved in 200 ml of anhydrous ether was then added over a period of 20 min, and the reaction mixture was allowed to stand overnight. The flask was placed in an ice bath, and 80 g of ice was added to the reaction mixture followed by 50 ml of cold 20% sulfuric acid. The ether layer was separated and the aqueous layer extracted with two 100-ml portions of ether. The ether was distilled from the combined extracts and the residue was refluxed for 2 h with 100 ml of 20% H_2SO_4 to dehydrate the resulting alcohol. The layers were separated and the product was vacuum distilled at 189—198°C/35 Torr. The distillate was taken up in 275 ml of hot 95% ethanol. Crystallization by cooling to 0°C gave 3.92 g (11%) of *Z*-1,2-diphenyl-1-pentafluorophenylethene, m.p. 107°C. (Found: C, 69.36, H, 3.09. $C_{20}H_{11}F_5$ calcd.: C, 69.36; H, 3.18%). IR (KBr) 1650w, 1600w, 1520m, 1490vs, 1450w, 1100m, 990vs, 970s, 930w, 850w, 750s, 680s cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.1—7.5 ppm (aromatic, vinyl), mass spectrum *m/e* 346 (M^+).

Photolysis of diphenyltitanocene and phenyl(pentafluorophenyl)acetylene

Diphenyltitanocene (500 mg, 1.50 mmol) and phenyl(pentafluorophenyl)-acetylene (813 mg, 3.00 mmol) were dissolved in 250 ml of anhydrous benzene in a Pyrex Schlenk tube under argon. The solution was then irradiated (Hanovia 450 W lamp, 15°C) with magnetic stirring for 3 h at room temperature, during which time the original golden orange solution turned dark green. The reaction mixture was concentrated to 10 ml under reduced pressure, ca. 2.0 g of alumina was added, and the remainder of the solvent was removed with continuous stirring at 10^{-3} Torr. The residue was added to a column of alumina (2 × 35 cm) packed dry under argon. The column was first eluted with hexane, then with 5/1 hexane/benzene and finally with 3/1 hexane/benzene to bring down a colourless band. Upon evaporation of the solvent, 400 mg of a solid was obtained. The composition of this material was determined by gas chromatography (15% OV-101) and by GC/MS. It was found to contain biphenyl [126.6 mg, 56% (based on Cp_2TiPh_2)], 1-phenyl-2-pentafluorophenylethene (35 mg, 4.3%) phenyl(pentafluorophenyl)acetylene (195 mg, 24% recovery), and diphenyl(pentafluorophenyl)ethene, (43.3 mg, 4.3%).

Further elution of the column with 2/1 hexane/benzene produced a green band. The solvent was removed at 10^{-3} Torr, leaving 270 mg (25.2%) of a green solid, 1,1-bis-(η^5-cyclopentadienyl)-2,5-diphenyl-3,4-di(pentafluorophenyl)-titanole. (Found: C, 63.88; H, 2.82. $C_{38}H_{20}F_{10}Ti$ calcd.: C, 64.04; H, 2.96%). IR (KBr) 1650w, 1600m, 1515m, 1475m, 1440m, 1110w, 1075m, 1010w, 975s, 865m, 800s, 750m, 700m cm^{-1}. ^1H NMR (acetone-d_6) δ 6.55 (10 H, s, C_5H_5), 6.7—7.4 ppm (10 H, m, aromatic); mass spectrum *m/e* 714 (M^+). Continued elution with benzene produced no other bands.

Thermolysis of titanocene dicarbonyl and phenyl(pentafluorophenyl)acetylene

Into a 50-ml, 3-necked flask round bottom flask equipped with a gas inlet valve was placed 140 mg (0.59 mmol) of titanocene dicarbonyl and 320 mg (1.19 mmol) of phenyl(pentafluorophenyl)acetylene along with 25 ml of hexane. The mixture was refluxed for 5 h after which time it was green in color. The solvent was removed in vacuo leaving a green residue. Approximately 10 ml of benzene was added to the residue together with ca. 1 g of 5% deactivated alumina. The benzene was removed under reduced pressure and the remaining solid added to a dry-packed column (1.5 × 35 cm) of 5% deactivated alumina. Elution with a 2/1 hexane/benzene mixture brought down a green band. Removal of the solvent left 330 mg (77%) of 1,1-bis(η^5-cyclopentadienyl)-2,5-diphenyl-3,4-di(pentafluorophenyl)titanole. IR, ^1H NMR and mass spectra were identical to those of the titanole isolated from the photolysis of diphenyltitanocene and phenyl(pentafluorophenyl)acetylene.

Reaction of 1,1-bis-(η^5-cyclopentadienyl)-2,5-diphenyl-3,4-di(pentafluorophenyl)-titanole and HCl

1,1-Bis-(η^5-cyclopentadienyl)-2,5-diphenyl-3,4-di(pentafluorophenyl)titanole (250 mg, 0.35 mmol) was dissolved in 30 ml of chloroform and an excess of aqueous HCl was added dropwise with stirring. The solution changed from green to red in a matter of minutes, and was allowed to stir for an additional 5 min after the initial color change. The layers were separated and the acid layer was washed with 10 ml of chloroform. The organic layer was washed with two 20-ml portions of water, then dried over anhydrous sodium sulfate. Evaporation of the solvent after filtration of the drying agent left a dry orange residue which was extracted with three 20-ml portions of hot heptane. The remaining insoluble red solid was dried, leaving 55 mg (63%) of titanocene dichloride, which was identified by spectral comparisons with an authentic sample. The heptane extracts were evaporated to dryness, leaving 160 mg (85%) of 1,4-diphenyl-2,3-di-(pentafluorophenyl)-1,3-butadiene. The product was further purified by column chromatography (5% deactivated alumina, 1 X 30 cm), eluting with ca. 50 ml of chloroform. Evaporation of the solvent left a cream-colored solid which was sublimed at 120°C/10^{-3} Torr to give a white solid, m.p. 149—150°C. (Found: C, 62.43; H, 2.15. $C_{28}H_{12}F_{10}$ calcd.: C, 62.47; H, 2.25%). Mass spectrum *m/e* 538 (M^+).

Acknowledgement

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