Journal of Organometallic Chemistry
Elsevier Publishing Company Amsterdam
Printed in The Netherlands

MONO- AND DIALKYLTITANOCENE DICHLORIDES

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(Received August 18th, 1966)

INTRODUCTION

The reaction of fulvenes with reagents such as alkali metals, metal halides, and organolithium compounds to produce alkylcyclopentadienide salts has been applied to the preparation of disubstituted ferrocenes[1,2,3,4] and nickelocenes[5]. The reaction of mixtures of such substituted cyclopentadienide ions and unsubstituted sodium cyclopentadienide with ferrous chloride produced monoalkyl ferrocenes[6] in approximately statistical proportions.

The fulvene approach to the preparation of dialkyltitanocene dichloride derivatives has been explored, and the method has been found especially useful for preparing monosubstituted titanocene dihalides by reaction of substituted cyclopentadienide ions with the stable, isolable cyclopentadienyltitanium trichloride[7,8]. This obviates the necessity of handling mixed cyclopentadienide ion solutions with the resulting laborious separations of unsubstituted, monosubstituted, and disubstituted metallocene products that are obtained in the ferrocene preparations.

Of particular interest was the reductive coupling of dialkylfulvenes to form dianions and subsequently bridged ferrocenes[9,10,11] in which the cyclopentadienyl rings are no longer coplanar. Early, it was suggested from dipole moment measurements, that titanocene dichloride is approximately tetrahedral about the central titanium atom[12]; more recently, Alekseev and Ronova[13] reported, from electron diffraction studies, that titanocene dichloride has a wedge-shaped sandwich structure with an angle of 58.5° between the planes of the two five-membered rings. The titanium–carbon bond distances were found to be equivalent and of 2.38 Å. Thus, it seemed that formation of two-carbon bridges between the rings might be more easily accomplished in this series by procedures analogous to those used for ferrocene.

RESULTS AND DISCUSSION

The product from the addition of lithium aluminum hydride to dimethylfulvene, when added to titanium tetrachloride or cyclopentadienyltitanium trichloride, gave in moderate yields 1,1′-diisopropyltitanocene dichloride (I) and isopropyltitanocene dichloride (II), respectively (Fig. 1). Similarly, diarylfulvenes are converted by lithium aluminum hydride and the appropriate titanium chloride to substituted titanocene dichlorides. In this manner 1,1′-dibenzhydryltitanocene di-

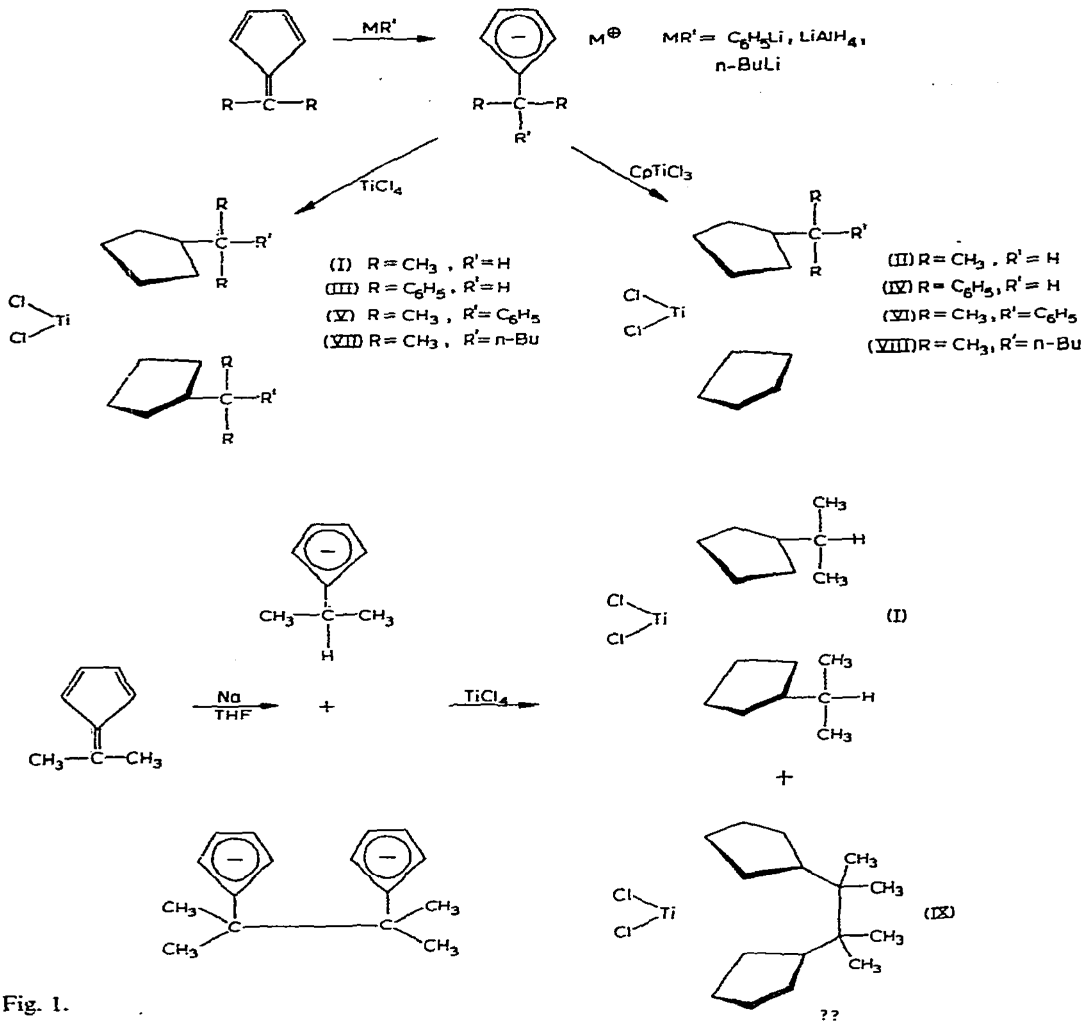


Fig. 1.

chloride (III) and benzhydryltitanocene dichloride (IV) were prepared from diphenylfulvene.

The addition of bromide-free phenyllithium to dimethylfulvene resulted in a moderate yield of 1,1'-dicumenyltitanocene dichloride (V) and good yields of cumenyltitanocene dichloride (VI). Phenyllithium prepared from bromobenzene in ether alone, however, gave a product which, although isolated in good yield, does not analyze correctly for (VI), but appears to be, from analytical and spectral data, a cumenyltitanocene dihalide mixture in which about 35% of the chloride was replaced by bromide.

Although cumenyltitanocenes and cumenylferrocenes can be prepared from the addition of phenyllithium to dimethylfulvene, the addition of phenyllithium to diphenylfulvene is not so straight forward. Subsequent treatment of the reactions mixture with ferrous chloride does not produce the expected bis(triphenylmethyl)-ferrocene, but rather a compound whose structure is as yet unassigned[2]. Monophenylfulvene seemed suitable as a means of testing the limitation of the addition of phenyllithium to the *exo* double bond of fulvenes. The product derived from the two reagents, after treatment with cyclopentadienyltitanium trichloride, produced benzhydryltitanocene dichloride identical in all respects with (IV). Phenylfulvene, then, behaves like dimethylfulvene with respect to addition of phenyllithium.

n-Butyllithium, as well, adds to dimethylfulvene in ether to give, 1,1′-bis(1,1-dimethylpentyl)titanocene dichloride (VII) and (1,1-dimethylpentyl)titanocene dichloride (VIII) when the corresponding titanium compound is treated with the addition product.

All attempts at preparing the bridged compound, 1,1′-(tetramethylethylene)-titanocene dichloride (IX) by the reductive coupling of dimethylfulvene with sodium metal in ether resulted in the isolation of only 1,1′-diisopropyltitanocene dichloride (I). When the coupling reaction was carried out in tetrahydrofuran and the products added to titanium tetrachloride, a mixture of products which could not be separated was obtained. The nuclear magnetic resonance spectrum of the mixture indicates the presence of two components in nearly equal concentration, one of which can easily be identified as the diisopropyl derivative. The second component, with a methyl singlet at 8.55 τ and two widely spaced triplets at 3.14 τ and 3.77 τ for the cyclopentadienyl rings, appears to be either the desired bridge compound or the corresponding dimer.

As a control experiment, the bridged ferrocene was prepared under exactly the same conditions and isolated in pure form[9].

The nuclear magnetic resonance spectra of the derivatives prepared show the expected singlet for an unsubstituted cyclopentadienyl ring and a multiplet for a substituted ring. The cyclopentadienyl multiplet for compounds containing an α-phenyl substituent appears as two triplets.

The same compounds clearly show the effect of the phenyl ring current on the chemical shift of the cyclopentadienyl ring *opposite* to that ring which bears the substituent. The effect is more pronounced in the benzhydryl derivatives than in the cumenyl cases as might be expected from the differences in steric requirements. For example, the substituted ring in (IV) appears at 3.55 τ as compared to 3.83 τ for the unsubstituted ring and 3.42 τ for the parent titanocene dichloride[14]. 1,1′-Dibenzhydryltitanocene dichloride exhibits two apparent triplets centered at 3.99 τ, a shift of 0.57 τ from the parent and 0.44 τ from the substituted ring in (IV), bearing the same substituent but not subject to a ring current effect. The NMR data is summarized in Table 1.

The infrared spectra of substituted titanocene dichlorides deserves some comment. The 9–10 rule, useful in interpretation of the infrared spectra of substituted ferrocenes[15], appears to have its counterpart in this series. That is, the infrared spectrum of a disubstituted titanocene dichloride is essentially the same as that of the monosubstituted derivative except for the absence of peaks at 818–825 cm^{-1} ($\sim$12 μ) and 1015–1020 cm^{-1} ($\sim$10 μ).

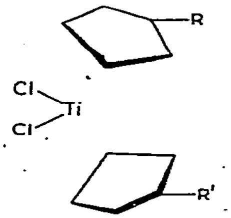
EXPERIMENTAL

General

All hydrocarbon solvents, both aliphatic and aromatic, were reagent grade and dried over Linde Molecular Sieves types 13× and 4A. Tetrahydrofuran was purified by preliminary drying over molecular sieves followed by distillation from $LiAlH_4$ prior to use and Mallinckrodt anhydrous diethyl ether was used without further purification. n-Butyllithium was purchased from Foote Mineral Co. as a 15.18% solution in n-hexane and phenyllithium was obtained from Alfa Inorganics Inc. as a solution in 70:30 benzene/ether. Purified titanium tetrachloride was obtained from Fisher Scientific Co. Cyclopentadienyltitanium trichloride was prepared by the method of Gorsich[7] and purified by sublimation at 0.01 mm Hg and 145–150°.

TABLE 1

PROTON MAGNETIC RESONANCE SPECTRA OF SUBSTITUTED TITANOCENE DICHLORIDES IN $CDCl_3$ WITH TETRAMETHYLSILANE AS INTERNAL STANDARD



Compound	Unsub. Ring	Sub. Ring	Others
R, R' = isopropyl		3.64 (m)	CH_3, 8.79 (d)
(I)			isoprop H, 6.77 (7)
R = isopropyl	3.45 (s)	~3.54 (m)	CH_3, 8.79 (d)
R' = H (II)			isoprop H, 6.77 (7)
R, R' = cumenyl		3.52 (t)	phenyl, 2.76 (m)
(V)		3.90 (t)	CH_3, 8.22 (s)
R = cumenyl	3.69 (s)	3.38 (t)	CH_3, 8.23 (s)
R' = H (VI)		3.55 (t)	phenyl, 2.75 (dist. s)
R, R' = benzhydryl		3.82 (t)	phenyl, 2.84 (m)
(III)		4.16 (t)	bzh H, 4.29 (s)
R = benzhydryl	3.83 (s)	3.45 (t)	phenyl, 2.79 (m)
R' = H (IV)		3.65 (t)	bzh H, 4.32 (s)
R, R' = 1,1-dimethylpentyl		3.53 (m)	CH_3, 8.68 (s)
(VII)			n-bu, ~8.2–9.3 (m)
R = 1,1-dimethylpentyl	3.47 (s)	3.50 (m)	CH_3, 8.69 (s)
R' = H (VIII)			n-bu, ~8.4–9.3 (m)

All operations involving formation and manipulation of cyclopentadienide salts were performed under an atmosphere of dry nitrogen as were operations involved in the formation of titanocene dichloride derivatives. A slow stream of nitrogen was also maintained as a precautionary measure during extractions requiring the use of a Soxhlet apparatus.

All cyclopentadienide salts, derived from either $LiAlH_4$ or organolithium compounds and appropriate fulvenes, were prepared in a specially designed 500 ml flask equipped with an outlet at the bottom of the flask. The rate of addition to either $TiCl_4$ or the trichloride could easily be controlled by means of a Teflon stopcock.

Melting points were determined on a Kofler hot stage and are uncorrected. Infrared spectra were recorded as KBr disks with a Perkin–Elmer Model 237 Grating Infrared Spectrophotometer. NMR spectra were recorded on a Varian Model A-60 Spectrometer with $CDCl_3$ as solvent and tetramethylsilane as an internal standard.

Microanalyses were performed by Alfred Bernhardt, Mikroanalytisches Laboratorium im Max-Planck-Institut für Kohlenforschung, 433 Mülheim (Ruhr)

TABLE 2

MELTING POINTS, YIELDS AND ANALYTICAL DATA FOR SUBSTITUTED TITANOCENE DICHLORIDES

Substituent	*M.p.* (°C)	*Yield* (%)	*Empirical formula*	*Found* (*calcd.*) (%)	
				C	*H*
1,1'-Diisopropyl- (I)	170–172	14.4	$C_{16}H_{22}TiCl_2$	57.93 58.16 (57.68)	6.63 6.66 (6.66)
Isopropyl- (II)	145–152	50.5	$C_{13}H_{16}TiCl_2$	54.18 (53.64)	5.35 (5.54)
1,1'-Dicumenyl- (V)	217–218	46.6	$C_{23}H_{30}TiCl_2$	69.39 (69.29)	6.87 (6.23)
Cumenyl- (VI)	194–196	74.0	$C_{13}H_{20}TiCl_2$	62.38 (62.15)	5.60 (5.49)
1,1'-Dibenzhydryl- (III)	199–201.5	64.9	$C_{36}H_{30}TiCl_2$	74.96 (74.36)	5.16 (5.20)
Benzhydryl- (IV)	210–212	58.3	$C_{23}H_{20}TiCl_2$	65.80 (66.53)	4.69 (4.86)
1,1'-Bis(1,1-dimethylpentyl)- (VII)	142–145	44.2	$C_{24}H_{38}TiCl_2$	64.57 (64.72)	8.34 (8.60)
(1,1-Dimethylpentyl)- (VIII)	150–152	61.0	$C_{17}H_{24}TiCl_2$	59.09 (58.81)	6.87 (6.97)

and are listed in Table 2. Samples for carbon and hydrogen analyses were combusted with V_2O_5 and improved results were obtained presumably by inhibition of formation of titanium carbide.

Preparation of 1,1'-*dicumenyltitanocene dichloride*

The following procedure for formation of the substituted cyclopentadienide salt was used in all similar preparations and therefore will be presented for this preparation alone.

The reaction flask was equipped with a mechanical stirrer, a nitrogen inlet, and an adapter fitted with a serum cap. The flask was flamed and flushed with dry nitrogen and was charged with 100 ml of Et_2O and 10.6 g (0.10 mole) of dimethylfulvene[16]. Sufficient phenyllithium was added with stirring, by means of a syringe, to discharge the yellow fulvene color. The rate of addition was such that reflux was prevented. The copious, suspended white solid was added slowly as a slurry through the outlet at the bottom of the flask to 9.5 g (0.05 mole) of $TiCl_4$, stirred magnetically in 100 ml of benzene at 0°.

The resulting dark red mixture was stirred at room temperature for an additional hour and filtered to yield a red solid and red filtrate. The solid was extracted in a Soxhlet apparatus with CH_2Cl_2 until the extracts were colorless. Removal of solvent at aspirator pressure produced 8.5 g of the crude product. An additional 3.8 g of impure product was obtained by removal of solvent from the original filtrate and crystallization of the resulting semi-solid from hexane. Yield 11.3 g, 46.6% of theory. Several recrystallizations from toluene gave the analytical sample, m.p. 217–218°.

Preparation of cumenyltitanocene dichloride

Lithium cumenylcyclopentadienide, prepared as described from 3.38 g (0.032

mole) of dimethylfulvene and phenyllithium, was added slowly and with stirring to 7.0 g (0.032 mole) of cyclopentadienyltitanium trichloride in 200 ml of Et_2O and 50 ml of benzene. The red reaction mixture was stirred for an additional hour, cooled to −10°, and filtered while cold. Extraction of the resulting solid with CH_2Cl_2 in a Soxhlet apparatus and removal of the solvent at aspirator pressure produced 7.0 g of the crude product. Removal of solvent from the original filtrate followed by dissolution of the resulting oil in CH_2Cl_2 (min.) and pouring into 400 ml of n-heptane enabled isolation of 1.7 g additional material. Yield 8.7 g, 74.0%. Three recrystallizations from toluene gave the analytical sample, m.p. 194–196°.

If phenyllithium is prepared from bromobenzene in ether alone, the solubility of lithium bromide in this solvent is sufficient to allow exchange of chloride and bromide. The product thus produced contained about 35% of the halogen as bromide.

Preparation of 1,1'-*diisopropyltitanocene dichloride*

Lithium isopropylcyclopentadienide was prepared by the dropwise addition of 11.2 g (0.1054 mole) of dimethylfulvene in 100 ml of Et_2O to 4.1 g (0.1054 mole) of $LiAlH_4$ in 100 ml of Et_2O. Titanium tetrachloride etherate was prepared by the slow addition of 10.0 g (0.0527 mole) of $TiCl_4$ to 200 ml of Et_2O with rapid stirring under nitrogen at 0°. Addition of the cyclopentadienide salt to the yellow complex was performed in the usual manner at 0°. The reaction mixture was stirred for an additional hour at room temperature and 23 ml of H_2O was added dropwise to destroy excess hydride. Stirring was continued for an hour and the mixture was filtered. The filtrate was washed with brine solution, dried over Na_2SO_4, and the solvent removed at aspirator pressure. The solid material obtained from filtration of the reaction mixture was taken up in 300 ml of CH_2Cl_2, filtered, and the solvent removed. Both fractions were crystallized from 100 ml of methylcyclohexane. Yield 2.5 g 14.4%. Two recrystallizations from toluene or methylcyclohexane gave the analytical sample, m.p. 170–172°.

Preparation of isopropyltitanocene dichloride

Lithium isopropylcyclopentadienide, prepared from 3.4 g (0.032 mole) of dimethylfulvene in 100 ml of Et_2O and 1.2 g (0.032 mole) of $LiAlH_4$ in 100 ml of Et_2O, was added as a slurry to 7.0 g (0.032 mole) of the trichloride stirred magnetically in 150 ml of Et_2O. Stirring was maintained for one hour after completion of the addition. Water (7.0 ml) was added dropwise to the mixture at 0°. The reaction mixture was filtered after a short interval of continued stirring to yield a red filtrate and a green solid which became red after exposure to the atmosphere for a short time. The solid was washed with CH_2Cl_2 until the washings were colorless. The combined ethereal and methylene chloride fractions were washed once with brine solution and were dried over $CaCl_2$. Removal of solvent at aspirator pressure yielded a red oil which was crystallized with difficulty from methylcyclohexane to produce 4.7 g (50.5%) of crude product, as indicated. Several recrystallizations from methylcyclohexane gave the analytical sample, m.p. 145–152°.

Preparation of 1,1'-*dibenzhydryltitanocene dichloride*

Lithium benzhydrylcyclopentadienide was prepared from 10.5 g (0.0456 mole) of diphenylfulvene[17] in 230 ml of Et_2O and 1.73 g (0.0456 mole) of $LiAlH_4$ in 150 ml of the same solvent and added at 0° to $TiCl_4/Et_2O$ prepared from 4.35 g (0.0228 mole) of $TiCl_4$ and 150 ml of Et_2O as previously described. The black reaction mixture was stirred for one hour and was treated with 10 ml of H_2O at 0°. Methylene chloride (100 ml) was added and the mixture was filtered. The solid residue was washed with CH_2Cl_2 and the washings were combined with the filtrate. The combined solutions were washed once with brine solution and dried over $CaCl_2$. Solvent was removed at aspirator pressure from the dark red solution to yield a red viscous oil. A red-orange solid (3.4 g) was obtained by crystallization from 100 ml of CCl_4/hexane. An additional 5.2 g was obtained by concentration of the mother liquor to 50 ml followed by addition of hexane to the cloud point. Yield 8.6 g, 64.9%.

Two recrystallizations from toluene gave the analytical sample, m.p. 199–201.5°.

Preparation of benzhydryltitanocene dichloride

Lithium benzhydrylcyclopentadienide was prepared from 0.87 g (0.0228 mole) $LiAlH_4$ in 100 ml of Et_2O and 5.25 g (0.0228 mole) of diphenylfulvene in 125 ml of Et_2O and subsequently added slowly to 5.0 g (0.0228 mole) of cyclopentadienyltitanium trichloride, stirred magnetically in 200 ml of the same solvent. Stirring was maintained for one hour after completion of the addition, followed by the dropwise addition of 5 ml of H_2O at 0°. The reaction mixture was stirred for two more hours, filtered, the resultant solid washed with CH_2Cl_2 until the washings were colorless and the combined filtrate and washings treated once with brine solution. Solvent was removed at aspirator pressure from the scarlet solution, after drying over $CaCl_2$, yielding a red oil which was crystallized from CCl_4/hexane to give 5.3 g of the crude product. Yield 58.3%. Several recrystallizations from toluene gave the analytical sample, m.p. 210–212°. Recrystallization from CCl_4 gives a less pure product.

Preparation of benzhydryltitanocene dichloride from phenylfulvene

Phenylfulvene was prepared by the method of Thiele[17] and purified by chromatography on alumina with hexane as eluent. Lithium benzhydrylcyclopentadienide was prepared in the usual manner from 6.0 g (0.039 mole) of phenylfulvene in 150 ml Et_2O and phenyllithium. The orange solid was added slowly as a slurry to 8.5 g (0.039 mole) of the trichloride, stirred magnetically in 300 ml of Et_2O. After an additional hour of stirring, the red reaction mixture was cooled to −78° and filtered, yielding a red solid and red filtrate. The solid was extracted with CH_2Cl_2 in a Soxhlet apparatus. Removal of solvent from the extract at aspirator pressure gave 3.5 g of the crude product. The red semi-solid, resulting from removal of solvent from the filtrate, gave 2.2 g of additional product upon crystallization from 150 ml of CCl_4. Evaporation of the CCl_4, followed by crystallization from 300 ml of methylcyclohexane yielded an additional 3.3 g. Yield 9.0 g, 54.8%. Three recrystallizations from toluene gave the analytical sample, m.p. 210–212°, identical in all respects with the sample prepared as above.

Preparation of 1,1′-*bis*(1,1-*dimethylpentyl*)*titanocene dichloride*

Lithium (1,1-dimethylpentyl)cyclopentadienide was prepared from 10.6 g (0.10 mole) of dimethylfulvene in 100 ml of Et_2O and 62 ml of 15.18% n-butyllithium in hexane (0.10 mole). The resulting yellow-orange viscous solution was added slowly to 9.5 g (0.05 mole) of the tetrachloride suspended in 100 ml of hexane and stirred magnetically at 0°. Continued stirring for one hour, followed by cooling to −78° and filtration of the solid material, subsequent extraction with 700 ml of hexane in a Soxhlet apparatus, and storage of the red extract in a cold chest overnight resulted in 8.4 g of crude material. An additional 1.4 g of material was obtained by removal of the solvent from the reaction mixture filtrate, followed by crystallization from 200 ml of hexane. Yield 9.8 g, 44.2%. Several recrystallizations from either hexane or heptane gave the analytical sample, m.p. 142–145° with prior softening. (The melting point is not well defined.)

Preparation of (1,1-*dimethylpentyl*)*titanocene dichloride*

Lithium (1,1-dimethylpentyl)cyclopentadienide was prepared from 5.3 g (0.05 mole) of dimethylfulvene in 100 ml of Et_2O and 31 ml of 15.18% n-butyllithium in hexane (0.05 mole) and added to 10.95 g (0.05 mole) of the trichloride, stirred magnetically in 300 ml of Et_2O. The reaction mixture, containing a copious amount of solid material, was stirred for an additional hour and filtered. The solid obtained by filtration was extracted in a Soxhlet apparatus with CH_2Cl_2, yielding 7.6 g of crude product upon removal of solvent at aspirator pressure. An additional 3.0 g of impure product was obtained by removal of solvent from the original filtrate, followed by crystallization from 500 ml of hexane. Yield 10.6 g, 61.0%. Several recrystallizations from toluene gave the pure product as very fluffy needles, m.p. 150–152°.

Attempted preparation of 1,1′-(*tetramethylethylene*)*titanocene dichloride*

The reaction flask was charged with 100 ml of Et_2O and 3.0 g of sodium metal freshly cut into small pieces. Dimethylfulvene (11.2 g, 0.105 mole) in 75 ml of Et_2O was added in small portions from a pressure-equalized dropping funnel over a one hour period. The resulting dark red mixture was stirred for an additional 1½ hours and added over a ten minute period to 10.0 g (0.0526 mole) of the tetrachloride in 100 ml of Et_2O. The mixture was stirred for an hour, cooled to −78° and filtered while cold. Solvent was removed from the filtrate, producing red solid material which could not be taken to dryness. Crystallization was effected from heptane and this material was combined with that resulting from filtration of the reaction mixture. Extraction with 700 ml of hexane in a Soxhlet apparatus, followed by cooling to Dry Ice temperature and filtration, produced 4.6 g of red crystals.

Recrystallization twice from CCl_4/hexane followed by sublimation at 0.01 mm Hg and 140–145° gave the analytical sample, m.p. 170–172°, which was shown to be identical in all respects with 1,1′-diisopropyltitanocene dichloride prepared directly. (Sublimation is effective as a means of purification only if the sample is essentially pure prior to sublimation.)

Attempted preparation of 1,1′-(*tetramethylethylene*) *titanocene dichloride in tetrahydrofuran*

A sodium dispersion in toluene was prepared in the usual manner from 2.2 g (0.094 mole) of sodium metal in a 300 ml, 3-necked flask. The bulk of the toluene was siphoned off when cool and 75 ml of THF was introduced. Dimethylfulvene (10.0 g, 0.094 mole) in 50 ml of THF was added dropwise at 0° with stirring. The dark red reaction mixture was stirred for an additional 3 h and added to 8.95 g (0.047 mole) of $TiCl_4$, stirred magnetically in 150 ml benzene, by means of a syringe. The mixture was allowed to stir overnight and filtered through asbestos. The solvent was removed at aspirator pressure and the dark red residue extracted with methylcyclohexane to produce 2.92 g of red solid material, m.p. 140–163°. A very dark insoluble material remained which appeared to be polymeric in nature. (If THF is used in place of benzene, a larger quantity of polymeric residue results.) Recrystallization from a variety of solvents failed to improve the melting point range substantially. Sublimation of the mixture at 130–135° and 0.01 mm Hg yielded again the mixture. Chromatography on silica gel, both thin-layer and column, resulted in decomposition. When alumina was used as the adsorbant, decomposition again appeared to be the result whether performed in the dark or light. No separation was effected by chromatography on charcoal as continued elution with hexane failed to remove the components from the adsorbant.

ACKNOWLEDGEMENTS

The authors would like to acknowledge financial assistance from the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Tennessee Eastman Co., and the American Viscose Corp. We are grateful to Mr. D. T. Roberts of this department for determination of the NMR spectra.

SUMMARY

A series of substituted titanocene dichlorides has been synthesized by the fulvene approach. The infrared and nuclear magnetic resonance spectral properties have been investigated. Derivatives with an α-phenyl substituent clearly show the influence of the phenyl ring current on the chemical shift of the cyclopentadienyl protons of the ring opposite to that bearing the substituent. An empirical generalization, similar to the 9–10 rule in ferrocene chemistry, can be drawn from the infrared spectra of these compounds. The bridged compound, 1,1′-(tetramethylethylene)-titanocene dichloride could not be isolated in pure form, although some evidence for its existence has been found.

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