

## 1,1'-TRIMETHYLENETITANOCENE DICHLORIDE AND THE CORRESPONDING COMPOUNDS OF ZIRCONIUM AND HAFNIUM\*

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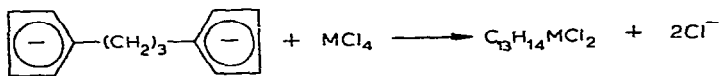
(Received March 8th, 1972)

### SUMMARY

The preparation and properties of trimethylene bridged titanocene, zirconocene, and hafnocene dichlorides are described. Additional evidence is presented of correlation between ring-ring angles and differential ring-proton shifts in the PMR spectra.

A number of derivatives of ferrocene with the rings bridged by carbon atoms have been prepared by a variety of methods<sup>1-10</sup>. Only one report<sup>11</sup> is known to us of the preparation of a carbon-bridged derivative of another metallocene, 1,1'-methylene-titanocene dichloride (MT). We have prepared three additional bridged metallocenes, 1,1'-trimethylenetitanocene dichloride (TMT) and the corresponding derivatives of zirconium (TMZ) and hafnium (TMH) and have determined some of their properties.

The method of choice for the preparation was that of Lüttringhaus<sup>10</sup> in which the dianion I is treated with a metal chloride according to the following equation:



(I)

This method is only capable of giving a monobridged derivative. For polybridged derivatives, the other methods<sup>1-8</sup> would be preferred, but the reactivity of the chlorine atoms on the metal appears to preclude using some of the reactions of these methods without preliminary extensive ancillary investigations.

The molecular structure of the titanocene derivative was established by X-ray crystallography<sup>12</sup>. The chemical constitution of the zirconocene and hafnocene derivatives was confirmed by means of UV, IR and PMR spectroscopy\*\*.

*IR spectra.* The spectra were obtained of the compounds as solids in KBr or as solutions in chloroform (Fig. 1). Two crystalline modifications of the zircono-

\* This work was performed under the auspices of the United States Atomic Energy Commission.

\*\* The determination of the crystal structures of the zirconium and hafnium derivatives is in progress and will be reported separately. Both are *Pbca* with  $a=8.21$ ,  $b=13.89$ ,  $c=22.44$  for TMZ and  $a=8.12$ ,  $b=13.91$ ,  $c=22.30$  for TMH.

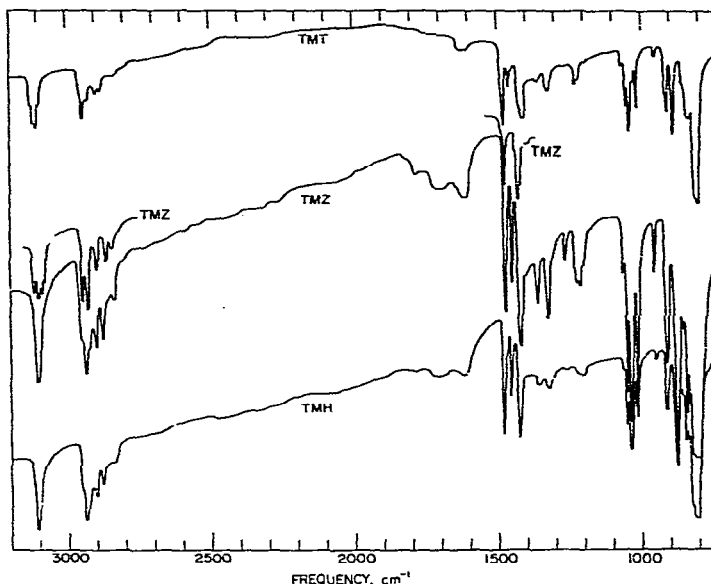


Fig. 1. Infrared spectra of TMT, TMZ, and TMH. Two crystalline modifications of TMZ were found and the spectra of both are shown.

cene derivative were obtained which differed in their solid state IR spectra in the two regions shown. Otherwise, the spectra of the two modifications were identical; in chloroform solution there were no differences.

*UV and visible spectra.* Ultraviolet and visible spectra were obtained in chloroform, which is not a satisfactory solvent in the ultraviolet. However, the compounds are very insoluble in hydrocarbons, in which spectra of ferrocene and bridged ferrocenes had been obtained and reported. The main effect of the use of chloroform as a solvent is the disappearance of a peak in ferrocene at 325 nm. A summary of the spectra obtained is given in Table 1.

*PMR spectra.* The PMR spectra were obtained in deuterobenzene using a 60 MHz spectrometer. The compounds were sparingly soluble in deuterobenzene

TABLE 1

UV AND VISIBLE SPECTRA IN CHLOROFORM

	nm	log $\epsilon$	nm	log $\epsilon$
Ferrocene	440	2.05		
TMF <sup>a</sup>	440	2.31		
Titanocene dichloride	389	3.23	520	2.27
TMT	402	3.22	540	2.18
Zirconocene dichloride	292	3.51	333 <sup>b</sup>	2.95
TMZ	300	3.27	350 <sup>b</sup>	2.89
Hafnocene dichloride	266	3.47	305	3.09
TMH	274 <sup>c</sup>	3.47	315	2.98

<sup>a</sup> 1,1'-Trimethylenferrocene. <sup>b</sup> Shoulder. <sup>c</sup> Doublet.

and, especially in the case of the titanocene derivative, a very good signal to noise ratio was not achievable. The PMR spectrum of the titanocene derivative was also obtained in deuteriochloroform in which it was a little more soluble. In deuterobenzene, where the peaks are better resolved because of the interaction of ring currents of the solvent, all three compounds have two multiplets near  $\tau=4$  due to the ring protons and a peculiar assortment of peaks near  $\tau=8$  due to the methylene protons. A small peak at  $\tau=4.06$  in the bridged hafnocene and at 4.02 in the bridged zirconocene is probably due to the parent non-bridged metallocene occurring in the sample as a small impurity. Evidence can also be found for a small amount of TMZ occurring as an impurity in the TMH. A summary of all of the shifts is in Table 2.

TABLE 2

PMR PROTON SHIFTS ( $\tau$ )

	Ring protons	Methylene protons
TMT <sup>b</sup>	3.51, 3.55	7.5, 7.8
TMT <sup>a</sup>	3.61, 4.21	8.3, 8.7
TMZ <sup>a</sup>	3.73, 4.28	8.2, 8.6
TMH <sup>a</sup>	3.82, 4.34	8.1, 8.6

<sup>a</sup> In perdeuterobenzene. <sup>b</sup> In deuteriochloroform.

The splitting of the ring protons into two multiplets has been attributed to the tilting of the rings in the case of bridged ferrocene derivatives<sup>1,2,4,6-9,14</sup>. Ring tilting causes nonequivalence of the ring protons and differences of shielding between the protons on the proximal side of the rings from the protons on the distal side of the ring. The differences in shielding have been attributed to properties of the iron-ring bonding orbitals<sup>14,15</sup>. The fact that the splitting of the ring protons does not occur<sup>16</sup> for titanocene dichloride itself, where the rings are already tilted in the absence of a bridge, is attributable to the rapid spinning of the rings. In a related compound (tetracyclopentadienyltitanium)<sup>17</sup> the spinning apparently still obtains at  $-100^\circ$ .

TABLE 3

CORRELATION OF RING-ANGLE WITH RING-PROTON SPLITTING<sup>a</sup>

	Ring-ring angle ( $^\circ$ )	$\Delta\tau$
1,1'-Trimethyleneferrocene <sup>6,18</sup>	8.8	0.17
1,1',3,3'-Bis(trimethylene)ferrocene <sup>6,20</sup>	9.0	0.29
1,1',2,2'-Bis(trimethylene)ferrocene <sup>6</sup>		0.31
1,1'-Trimethylenehafnocene dichloride		0.52
1,1'-Trimethylenezirconocene dichloride		0.55
1,1'-Tetramethylethyleneferrocene <sup>6,19</sup>	23.2	0.55
1,1'-Trimethylenetitanocene dichloride <sup>12</sup>	47.4	0.60
1,1'-Methylenetitanocene dichloride <sup>b,11</sup>		0.92

<sup>a</sup> Except as otherwise indicated the solvent used was perdeuterobenzene. <sup>b</sup> Solvent not given, splitting indicates perdeuterobenzene was probably used.

Bridging of the titanocene dichloride eliminates the ring spinning and permits the observation of the proton splitting.

Some correlation has been found between the degree of ring tilting and the magnitude of the proton splitting<sup>14</sup>. A summary of the ring-proton splittings is in Table 3. The crystal structures<sup>12,18-20</sup> of four bridged compounds have been determined. One<sup>18</sup>, however, is of a carbonyl derivative of 1,1'-trimethyleneferrocene. For the purposes of the correlation the assumption was made that the ring-ring angle was the same for the reduced compound even though the additional strain of the trigonal carbonyl probably causes the ring-ring angle in the carbonyl compound to be greater than the angle in the reduced compound. The three new metallocene derivatives (TMT, TMZ, and TMH) maintain the correlation of ring-ring angle with proton splitting, although some effect on the magnitude must be attributable to the differences in the metal and the presence of the chlorine atoms. The largest splitting known was found<sup>11</sup> for the highly strained methylenetitanocene dichloride.

In 1,1'-trimethyleneferrocene, the methylene protons exhibit a single sharp peak in the PMR spectrum. This has been attributed<sup>1,2,14</sup> to rapid inversion of the chain in addition to a coincidental magnetic equivalence of the two different kinds of methylene groups. The methylene protons fall into two broad, structured peaks (ratio of areas is 2/1) in the PMR spectra of TMT, TMZ and TMH (this is best seen in the spectrum of the hafnium derivative), indicating that inversion in these compounds is not rapid. Similar results had been obtained<sup>2</sup> for 1,1'-tetramethyleneferrocene. Furthermore, if the interpretation of relatively slow inversion is correct, then this implies that there is no shielding of the ring protons by the central methylene group. Such shielding would have caused the ring protons to behave as an ABCD system rather than as an AA'BB' system\*. The PMR spectrum of 1,1'-trithiaferrocene is reported to indicate this type of effect<sup>21</sup>. That is, noninversion of the trisulfide bridge is observed in the shifts of the ring protons. In this last case the ring protons are shielded by a sulfur atom. The AA'BB' structure was reported to have been observed at elevated temperatures.

## EXPERIMENTAL

Generally the method of preparation of the compounds is based on that of Lüttringhaus<sup>10</sup>. Modifications were necessary due to the particular chemical properties of these metallocenes. All reactions were carried out in an inert atmosphere.

Freshly prepared cyclopentadiene monomer (0.5 moles) was added slowly to a stirred mixture of sodium hydride (0.5 moles) in 225 ml of tetrahydrofuran at 0°. 1,3-Dibromopropane (0.25 moles) was added slowly and the mixture was stirred for one hour until the reaction had ceased. The pink solution was filtered to remove the sodium bromide and unreacted sodium hydride, and the filtrate was slowly added to a stirred mixture of sodium hydride (0.5 moles) in 50 ml of tetrahydrofuran at 45-50°. This reaction takes several hours for completion. The solution was then added slowly to a suspension of the metal tetrachloride (0.25 moles in 200 ml of tetrahydro-

\* Despite the simplicity of the spectrum, an AA'BB' designation is preferred to A<sub>2</sub>B<sub>2</sub> designation<sup>8,9,14</sup>. The latter would depend on the accidental coincidence of the vicinal and cross-ring coupling constants, which is unlikely. Furan, which has a similarly simple spectrum has been recognized as an AA'BB' system<sup>22</sup>.

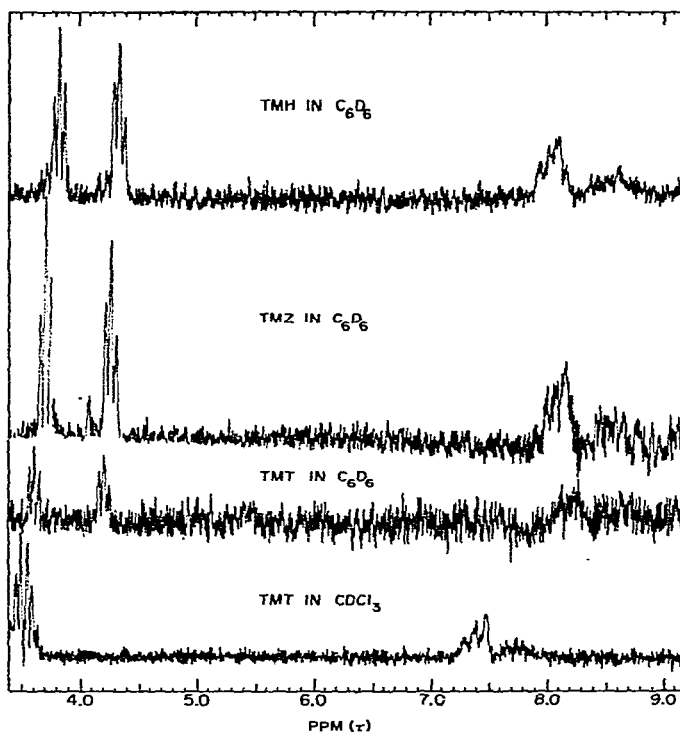


Fig. 2. PMR spectra of TMT, TMZ, and TMH.

furan, prepared by slowly adding the metal tetrachloride to tetrahydrofuran at 0° with vigorous stirring), and the mixture was stirred overnight. The solid by-products and unreacted reagents were removed by centrifugation, and the tetrahydrofuran was removed by evaporation at reduced pressure. The resulting black oil was extracted with chloroform. A black precipitate remained as residue. Additional black precipitate was obtained by addition of hexane to the chloroform solution. After separation of the solid, the solution was evaporated to yield an oil. The black solids were extracted in a Soxhlet extractor with benzene, which, upon evaporation, gave additional oil. Fractional sublimation from the combined oil at 50–150° at 10<sup>-2</sup>–10<sup>-3</sup> mm gave a colorless oil (mineral oil?), and finally sublimation of the residue at 200° at 10<sup>-3</sup>–10<sup>-4</sup> mm gave the product. Alternatively, in some experiments, after evaporation of the tetrahydrofuran, the resulting black oil was dissolved in a small amount of chloroform and dropped slowly with stirring into a large volume of hexane. A solid remained in suspension and an oil separated from the solution. The three phases were separated, and the solvent was evaporated in vacuum to give additional solid. The entire process was repeated with the separated oil. After sublimation of the solid at 50° to remove some impurities, the product was sublimed from the residue at 170° at approximately 10<sup>-4</sup> mm. The average yield for the titanium derivative was 2.8 g and the average yield for the zirconium and hafnium derivatives was 1 g.

#### ACKNOWLEDGEMENT

We are indebted to Dr. Ivan Bernal for the preliminary crystallographic data,

to Dr. Stanley Seltzer for help in obtaining the PMR spectra, and to both for valuable discussions.

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*J. Organometal. Chem.*, 42 (1972)