ORGANOMETALLIC DERIVATIVES

OF

TITANIUM

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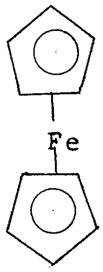

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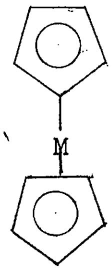


II

The 'Sandwich' Structure[5,6] for the compound, whose unique stability was atributed to possession by the iron atom of an outer valence shell of eighteen electrons has been confirmed by X-ray crystallographic analysis.[7,8,9,10] It was also found that the two rings are 'staggered' such that the molecule (I) is a pentagonal antiprism. The analogous dicyclopentadienyl compounds of ruthenium [11] and osmium[12] have been found to possess the opposed conformations (II).

Ferrocene behaves as an aromatic system,[13] and has been shown to undergo typical electrophilic substitution reactions,[14] e.g. Friedel-Crafts acylation, sulphonation, metallation, formylation, halogenation, etc.

The Preparation of Metallocenes.

Since the discovery of ferrocene, many Organometallic Compounds have been synthesised and their structures and properties have been studied. At present, practically all of the elements of the three transition series have been shown to form dicyclopentadienylmetal compounds of the general formula:

$(C_5H_5)_2M_n \; X_{n-2}$ where n is the oxidation number of the metal, M and X are univalent metal and halogen atoms respectively.

There are several methods known for the preparation of metallocenes. One of the most useful methods involves the reactions of cyclopentadienide anion, $C_5H_5^-$, with an anhydrous salt of the appropriate transition metal, according to the following equation:

$$2C_5H_5^-B^+ + MX_2 \longrightarrow (C_5H_5)_2M + 2B^+X^-.$$

The cyclopentadienide ion may be in the form of the lithium salt,[15] or the sodium salt [16] dissolved in liquid ammonia or in an ether, such as tetrahydrofuran or 1,2 - dimethoxyethane. It may also be used as the Grignard reagent; this is relatively unreactive with the insoluble dihalides of iron, nickel and cobalt, but by the use of the soluble acetylacetone [17,18] complexes of these metals, yields of these dicyclopentadienylmetal compounds have been greatly increased.

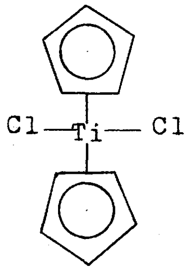
Solutions of sodium cyclopentadienide [19] in tetrahydrofuran react very smoothly with insoluble halides, while in liquid ammonia, the complex ammines of certain metals e.g. nickel, cobalt etc., gave a series of cyclopentadienides e.g. (III), which readily lose ammonia on heating to give the neutral dicyclopentadienylmetal compounds :-

$$2C_5H_5Na + M(NH_3)_6\,(SCN)_2 \rightarrow 2NaSCN + \underset{(III)}{M(NH_3)_6{}^{++}}(C_5H_5$$

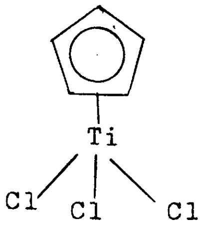
$$M(NH_3)_6{}^{++}(C_5H_5{}^-)_2 \xrightarrow{\text{heated}} (C_5H_5)_2M + 6\ NH_3$$

where M = Ni, Co etc.

Dicyclopentadienyltitanium dichloride (IV) has been prepared by Wilkinson and Birmingham [20]. Dicyclopentadienyltitanium dichloride could be readily converted to monocyclopentadienyltitan trichloride (V) by refluxing with titanium tetrachloride [21].



IV



V

Birmingham, Seyferth and Wilkinson[22] have prepared dicyclopentadienyltitanium dichloride by the reaction of cyclopentadiene with titanium tetrachloride and a proton acceptor such as triethylamine or pyridine.

$$2C_5H_6 + TiCl_4 + 2\ \text{Base} \longrightarrow (C_5H_5)_2TiCl_2 + 2\text{Base}.\ HCl$$

A number of Organometallic derivatives of titanium have been described in the Patent Literature, [23,24] chiefly as a result of work done at the National Lead Co.

Recently Shavindlerman, Topchiev and Golenko [25] have been successful in preparing dicyclopentadienyltitanium dichloride by treating the sodium salt of cyclopentadiene with titanium tetrachloride in suspension in an aromatic bydrocarbon.

Drozdov, Klebanskii and Bartashev [26] have prepared dicyclopentadienylbis(2,2,2- trifluoroethoxy)titanium of the following formula:

$$(\pi\text{-}C_5H_5)_2\ Ti\ (OCH_2\text{-}CF_3)_2$$

Birmingham, Fischer and Wilkinson [27] have found that dicyclopentadienyltitanium dichloride can be reduced to dicyclopentadienyltitanium chloride by the action of zinc dust in tetrahydrofuran, dimethylcellosolve, methanol or acetone.

Metal Alkyls and Aryls.

In spite of the failure of previous workers to isolate any alkyl or aryl titanium compounds using titanium tetrahalides or titanium metal as starting materials, Herman and Nelson [28] were able to isolate and characterize a compound containing a titanium-carbon bond. Since then, a number of simple alkyls and aryls of titanium have been isolated.

Summers and Uloth [29] studied the reaction of dicyclopentadienyltitanium halides with several lithium aryls and prepared compounds containing two titanium-carbon bonds according to the following general equation :

$$(C_5H_5)_2TiX_2 + 2\ LiR \longrightarrow (C_5H_5)_2\ TiR_2 + 2LiX.$$

Particularly, the compounds in which R is phenyl, p-tolyl and p-dimethylaminophenyl were prepared and their properties were investigated.

Attempts to prepare analogous titanium compounds containing naphthyl and o-tolyl groups were unsuccessful. It was observed that dicyclopentadienyldiphenyltitanium dissolves in an ether solution of phenyllithium, apparently with consumption of the latter substance, producing a dark orange brown solution. Hydrolysis of this solution gave dicyclopentadienyldiphenyltitanium. It was postulated that further uptake of phenyl anions occurs so that $(C_5H_5)_2\ Ti\ (C_6H_5)_3^-$ and possibly also $(C_5H_5)_2Ti\ (C_6H_5)_4^{--}$ are formed in solution.

Piper and Wilkinson[30] have obtained dicyclopentadienyldimethyltitanium as an orange yellow waxy solid by reacting dicyclopentadienyltitanium dichloride with methylmagnesium iodide in tetrahydrofuran.

Clauss and Bestian[31] have successfully synthesised dicyclopentadienyldimethyltitanium, in a good yield, from dicyclopentadienyltitanium dichloride and methyllithium as orange yellow needle shaped crystals decomposing above 95°C.

Other Cyclopentadienyl Metal Compounds.

The dicyclopentadienyl compounds of the type $(C_5H_5)_2M$ have been obtained from all the elements of the first transition series. The manganese compound is ionic. Fischer and Wilkinson[32] obtained dicyclopentadienyltitanium from the reaction of cyclopentadienylsodium and titanium(II) chloride in tetrahydrofuran as a green crystalline product. Later this compound was prepared by Clauss and Bestian[31] by hydrogenation of dicyclopentadienyldimethyltitanium in hexane without the use of a catalyst. Because of the instability of the product neither sample was fully characterised. In benzene or in ether, dicyclopentadienyltitanium forms a green solution.

Monocyclopentadienyl Titanium Compounds.

Titanium tetrachloride reacts on heating with dicyclopentadienyltitanium dichloride with or without a solvent, to form monocyclopentadienyltitanium trichloride[21]. Also dicyclopentadienyltitanium dichloride undergoes fission with chlorine with the formation of titanium tetrachloride, cyclopentadienyltitanium trichloride and 1,2,3,4,5-

pentachloro-cyclopentane.

Barber and Sloan[33] were able to prepare such cyclopentadienyltitanium trihalides by treating titanium tetrahalides with the magnesium salt of cyclopentadiene in Xylene.

Gorsich[21] as well as L. Pori et. al.[34] have studied the hydrolysis of cyclopentadienyltitanium trichloride and obtained a compound of the molecular formula, $(C_5H_5TiCl_2)_2O$ and with excess water, $(C_5H_5TiClO)_n$ where $n \leq 3$.

Nesmeyanov and his co-workers[35] have reported related compounds e.g. $(C_5H_5)Ti(OEt)_3$; $(C_5H_5)Ti(OBr)_2Cl$ etc.

The Nature of the Metal-Ring Bond.

While the 'Sandwich' structure of ferrocene is well established, the precise nature of the ring-metal bond is still in dispute[36]. Two hypotheses can be briefly mentioned.

Fischer and co-workers[37] regard ferrocene, and related compounds, as penetration complexes in which two negatively charged rings, each containing three pairs of electrons, are coordinated in an approximately octahedral arrangement around a positively metal atom. In ferrocene, the metal is Fe^{II}, and complete filling of hybrid d^2sp^3 metal orbitals results in an inert gas configuration.

Moffitt[38] and others regard the ring-metal bonding in ferrocene as resulting largely from a delocalised covalent bond between the metal atom and the two cyclopentadienyl radicals. Two electron bonds of this sort result from overlap of a π-orbital of suitable symmetry in each ring with $3d_{xz}$ and $3d_{yz}$ orbitals of iron. Four π-electrons thus remain in each ring which are not involved in the principal bonding, while filled 3d orbitals of the metal lie in the xy-plane between the two cyclopentadienyl rings.

Molecular orbital theory treats the molecule formation from the separated atoms as arising from the interaction of the separate atomic orbitals to form new orbitals which embrace the frame-work of the molecule. These orbitals are then filled by the electrons in order of increasing energy and subject to the Pauli principle.

Using this treatment, Jaffe[39] suggested that although the iron atom in ferrocene possesses an outer valence shell of eighteen electrons, two of these are essentially nonbonding and that each cyclopentadienyl ring is bound to the iron atom by four bonds.

Dunitz and Orgel[40] also using the Molecular orbital treatment, introduced the concept that only two bonds, i.e. four electrons are involved in the primary bonding and later[41] amplified this view to include the possible structural contribution of certain secondary bonding electrons.

Linnett[42] has shown that the above theories are not completely incompatible, and will also account for the metal-ring bonding in the arenemetal carbonyls, the compounds derived from the reaction of other unsaturated hydrocarbons with metal carbonyls and cyclopentadienylmetal carbonyls and nitrosyls[43]. The majority of stable compounds possess a complete inert gas shell of electrons about the metal atom.

Cyclopentadienylmetal Carbonyls.

Work on the new methods of preparation of dicyclopentadienylmetal complexes led to the discovery of compounds with only one cyclopentadienyl ring bonded to a transition metal. The first examples of this type were the cyclopentadienyl carbonyl compounds of molybdenum and tungsten[44] $(C_5H_5)_2Mo_2(CO)_6$ and $(C_5H_5)_2W_2(CO)_6$ respectively. Since then a number of other transition metal carbonyls have been prepared by several methods.

Dicyclopentadienyltitanium dicarbonyl has been prepared[45] by reacting dicyclopentadienyltitanium dichloride in benzene with two equivalents of cyclopentadienyl sodium, and then treating the intermediate product with carbon monoxide at 135 atm. and 100°C for eight hours. It could also be prepared by the reaction of dicyclopentadienyltitanium dichloride with two equivalents of butyllithium and then reaction with carbon monoxide.

Fischer and his co-workers[46] made the same compound by treating tricyclopentadienyltitanium with carbon monoxide at 150 atm. and 80°C.

EXPERIMENTAL

1. All reactions were carried out under nitrogen which had been deoxygenated by passing through Fieser's[47] solution and then dried by means of conc. H_2SO_4.

2. Cyclopentadiene refers to the freshly prepared material, which was shown to be not less than 90% monomeric.

3. All solvents were dried before use unless otherwise stated.

4. All melting points were determined in evacuated sealed capillaries.

5. Unless otherwise stated, all infrared spectra were recorded as 0.5-1.0% potassium chloride discs.

Dicyclopentadienyltitanium Dichloride.

Cyclopentadienylsodium prepared from freshly distilled cyclopentadiene (17.0g.) and sodium metal (5.91 g.) in tetrahydrofuran (100 ml.), was added dropwise with stirring to a solution of titanium tetrachloride (14.0 g.) in the same solvent (250 ml.). After 3 hrs. stirring under nitrogen, the solvent was removed under reduced pressure and the residue was extracted with anhydrous methylene chloride saturated with dry HCl. Filtration of the extracts and evaporation of the filtrate gave the desired product (15.0 g.) as red acicular needles, m.p.289°C. (Lit.[20], m.p. 288±2°).

Dicyclopentadienyltitanium Diphenyl.

The phenyllithium solution[52], prepared from lithium metal (0.71 g.) and bromobenzene (10.0 g.) in ether was added slowly over a period of one hour to a suspension of dicyclopentadienyltitanium dichloride (1.53 g.) in ether (50 ml.) at room temperature. An immediate reaction took place and the mixture was stirred at room temperature for about an hour and filtrated. The residue was washed with dry methylene chloride until the filtrate was colourless. The filtrate on concentration in vacuo, gave the desired product. It was recrystallised from dry methylene chloride and petroleum ether (b.p. 40-60°) as orange yellow crystals, m.p.146°C (Lit.[48] m.p. 146-148°).

Dicyclopentadienyltitanium Dimethyl.

(a). Methylmagnesium iodide prepared in ether (50 ml.)

from magnesium turnings (0.50 g.) and methyl iodide (1.42 g.) was added slowly to a suspension of dicyclopentadienyltitanium dichloride (1.0 g.) in ether (50 ml) at room temperature. Reaction took place immediately with initial darkening of colour which became orange yellow on standing. After stirring for 2 hrs. a few ml. of methanol were added. Solvent was removed rapidly in vacuo and the residue was extracted with petroleum ether (b.p. 40-60°). The product was obtained by cooling the filtrate to -80°C with drikold/acetone mixture. The product was further purified by sublimation at 40°C/10^{-4}mm. Hg. The yield was 0.01%.

(b). Methyllithium solution prepared from lithium metal (0.30 g.) in ether (50 ml.) and methyl iodide (2.10 g.) was slowly added to a suspension of dicyclopentadienyltitanium dichloride (1.01 g.) in ether (50 ml.) at room temperature with continuous stirring. The flask was covered with aluminium foil to exclude light. After the addition, stirring was continued for some time at room temperature. The solution was decomposed with ice water. The resultant orange solution was dried over solid Na_2SO_4 and the solvent was distilled off in vacuo. It was recrystallised from pentane on slowly cooling to -80°C giving orange yellow needle shaped crystals of the desired product which was very sensitive towards moisture and decomposed spontaneously above 97°C (Lit.,[31] decomposes above 95°C).

Reaction of Dicyclopentadienyltitanium Dimethyl with Cyanogen Bromide.

Freshly distilled cyanogen bromide (0.71g.) in ether (25 ml.) was added dropwise to a solution of dicyclopentadienyltitanium dimethyl (1.51 g.) in the same solvent (50 ml.). The mixture was stirred for 4 hrs. at room temperature. Evaporation of the solvent in vacuo gave an orange yellow product which was recrystallised from pentane at -80°C. It decomposes above 97°C and was identified as dicyclopentadienyltitanium dimethyl. The I.R. spectrum of the product did not show any absorption due to $C\equiv N$.

The above experiment was repeated under various conditions, e.g. stirring and refluxing overnight, but the product thus obtained did not show any absorption due to $C\equiv N$.

Reaction of Dicyclopentadienyltitanium Diphenyl with Cyanogen Bromide.

Dicyclopentadienyltitanium diphenyl (0.99 g.) in ether (25 ml.) and freshly distilled cyanogen bromide (0.34 g.) in the same solvent (25 ml.) were stirred together for 6 hrs. The solvent was evaporated in vacuo, the residue was crystallised from methylene chloride and petroleum ether (b.p. 40-60°) as orange yellow crystals, m.p. 145°C. It was identified as dicyclopentadienyltitanium diphenyl from its m.p. and I.R.

spectrum. No other product was isolated.

The above experiment was repeated under various conditions e.g. stirring and refluxing overnight but the product did not show any absorption due to C$\equiv$N.

Reaction of Dicyclopentadienyltitanium with Cyanogen Bromide.

A solution of dicyclopentadienyltitanium was obtained by hydrogenation of dicyclopentadienyltitanium dimethyl (1.80 g.) in benzene.

Freshly distilled cyanogen bromide (1.81 g.) in benzene (25 ml.) was added to this solution and the mixture stirred for 4 hrs. The mixture was filtered and the filtrate on evaporation gave an orange yellow residue. It was soluble in common organic solvents but could not be crystallised from any solvent. Its I.R. spectrum did not show any absorption due to C$\equiv$N. The above reaction was carried out under various conditions, e.g. stirring and refluxing overnight, but the product thus obtained did not show any absorption due to C$\equiv$N.

Reaction of Dicyclopentadienyltitanium Dichloride with Dicyclopentadienyltitanium Diphenyl.

Dicyclopentadienyltitanium dichloride (0.61 g.) and dicyclopentadienyltitanium diphenyl (0.76 g.) in benzene (100 ml.) were refluxed together for 4 hrs. The solvent was removed under reduced pressure and the residue was crystallised from methylene chloride giving red crystals, m.p. 286°C. It was identified as dicyclopentadienyltitanium dichloride from its m.p. and I.R. data. No other product was isolated.

The above experiment was repeated in toluene. Again dicyclopentadienyltitanium dichloride was obtained. No other product was isolated.

Reaction of Dicyclopentadienyltitanium Dimethyl with Phenylacetylene.

Dicyclopentadienyltitanium dimethyl (1.25 g.) in benzene (25 ml.) and freshly distilled phenylacetylene (2.0 ml.) in the same solvent (10 ml.) were refluxed for 4 hrs. The solvent was removed under reduced pressure and the residue was dissolved in the minimum quantity of benzene. Addition of heptane caused the formation of a precipitate. It was redissolved and precipitated about four times giving a greenish yellow compound m.p. 178-180°C (dec.) (0.57 g., 24.6%).

(Found: C, 79.3; H,5.8; $C_{21}H_{17}Ti$ requires C,79.5; H,5.4%)

Reaction of Dicyclopentadienyltitanium with Phenylacetylene.

Dicyclopentadienyltitanium, obtained from hydrogenation of dicyclopentadienyltitanium dimethyl (1.79 g.) in benzene (50 ml.), and freshly distilled phenylacetylene (2.50 ml.) in the same solvent (10 ml.) were refluxed together for 2 hrs. The solvent was removed in vacuo giving a green

crystalline residue. Addition of heptane to the solution of the residue in the minimum quantity of benzene gave a green crystalline product. Repetition of such treatment with heptane gave a crystalline compound. The I.R. spectrum of the compound shows phenyl absorption at 13.15μ and 14.25μ. The compound (0.45 g., 21.96%) decomposes above 180°C.
(Found: C, 74.8; H, 5.8; $C_{36}H_{32}Ti_2O$ requires C, 75.0; H,5.6%)

Reaction of Dicyclopentadienyltitanium Dimethyl with Cyanogen Gas.

Cyanogen gas[49] was bubbled through a solution of dicyclopentadienyltitanium dimethyl (2.55 g.) in benzene (50 ml.) for 2 hrs. with constant stirring. Free Cyanogen was removed by passing nitrogen through the reaction mixture. No change in colour of the solution was observed. Evaporation of the solvent under reduced pressure gave a yellow gum which decomposed on attempted crystallisation. The I.R. spectrum of the product did not show any absorption due to $C \equiv N$.

Reaction of Dicyclopentadienyltitanium with Cyanogen Gas.

Cyanogen gas was bubbled through a solution of dicyclopentadienyltitanium, obtained by hydrogenation of dicyclopentadienyltitanium dimethyl (2.85 g.) in benzene for 3 hrs. with constant stirring. The mixture was then refluxed for 2 hrs. Evaporation of the solvent under reduced pressure gave a brown residue. Extraction of the residue with methylene chloride and concentration of the extracts gave red crystals, m.p. 120°C (dec.), (0.10 g.; 3.5%). The I.R. spectrum of the product shows a strong peak due to the absorption of $C\equiv N$ (2200 cm.$^{-1}$).(Found: C, 62.9; H,5.6; N, 5.6; $C_{12}H_{10}TiN_2$ requires C, 62.60; H,4.4; N, 12.2%).

Reaction of Dicyclopentadienyltitanium Dimethyl with Mercuric Cyanide.

Dicyclopentadienyltitanium dimethyl (1.50 g.) in benzene (50 ml.) and mercuric cyanide (1.87 g.) in the same solvent (25 ml.) were refluxed together for 4 hrs. Evaporation of the solvent under reduced pressure gave a dark red solid. Extraction of this residue with methylene chloride and concentration of the methylene chloride extracts yielded orange crystals which decompose above 120°C (0.15 g; 8.8%). The I.R. spectrum of the product shows the absorption peak due to $C\equiv N$ at 2225 cm.$^{-1}$, (Found: C, 59.30; H,5.0; N, 6.8, $C_{11}H_{11}TiNO$ requires C,59.7; H,5.0; N,6.4).

Reaction of Dicyclopentadienyltitanium with/Cyanide. ∠ Mercuric

Dicyclopentadienyltitanium solution, prepared by hydrogenation of dicyclopentadienyltitanium dimethyl (1.78 g.), in benzene and mercuric cyanide (2.20 g.) in the same solvent (50 ml.) were refluxed together overnight. Evaporation of the solvent under reduced pressure gave a solid residue which on extraction with methylene chloride yielded a residue which did not show any absorption due to $C\equiv N$. Evaporation of methylene chloride extracts gave a dark red crystalline residue, which decomposed on attempted recrystallisation. The dark red residue shows a strong peak due to $C\equiv N$. This product is identical with the compound obtained in the above experiment.

Cyclopentadienyltitanium Trichloride.

Cyclopentadienyltitanium trichloride was prepared by the method of Gorsich[21]. Titanium tetrachloride (5.8 g.) and dicyclopentadienyltitanium dichloride (5.0 g.) in xylene (100 ml.) were refluxed together overnight. Filtration of the cooled reaction mixture and concentration of the filtrate under reduced pressure gave the desired product as large yellow plates, m.p. 210°C. (Lit., [21]208-211°C).

Reaction of the Potassium Salt of Pyrrole with Titanium Tetrachloride.

Potassium salt of pyrrole, prepared from potassium metal (0.51 g.) and pyrrole (1.5 ml.) in tetrahydrofuran (50 ml.), and titanium tetrachloride (2.0 ml.) in the same solvent (25 ml.) were stirred together for 2 hrs. at room temperature. Evaporation of the solvent under reduced pressure gave a brown solid which contained no titanium. It decomposes rapidly at room temperature.

Reaction of the Potassium Salt of Pyrrole with Cyclopentadienyltitanium Trichloride.

Potassium salt of pyrrole was prepared from potassium metal (0.22 g.) in tetrahydrofuran (25 ml.) and freshly distilled pyrrole (1.5 ml.) in the same solvent by stirring at room temperature.

Cyclopentadienyltitanium trichloride (1.20 g.) in tetrahydrofuran (25 ml.) was added slowly to the salt with constant stirring. The mixture was further stirred for 3 hrs. Evaporation of the solvent in vacuo gave a yellow residue. Extraction of the residue with methylene chloride and concentration of the extracts gave cyclopentadienyltitanium trichloride as yellow crystals, m.p. 210°C. No other product was isolated.

The above experiment was carried out under various conditions, but the product obtained in each case was only cyclopentadienyltitanium trichloride.

Reaction of Dicyclopentadienyltitanium with Tolan.

(a) To a solution of cyclopentadienylsodium, prepared from sodium metal (1.95 g.) in tetrahydrofuran (50 ml.) and freshly distilled cyclopentadiene (9.0 ml.) in the same solvent (20 ml.), were added, in a stream of nitrogen, titanium tetrachloride (18.0 ml.) and tolan[50] (5.0 g.). The mixture was boiled in a nitrogen atmosphere for 4 hrs. and then left overnight. Solvent was removed in vacuo and the residue was treated with benzene (50 ml.). Centrifugation separated the precipitate. The clear solution was then poured into 3-4 times its quantity of heptane. This caused the formation of a yellow brown precipitate. After standing for 2 days in a refrigerator, dark green crystals were formed. The solution and a yellow precipitate were decanted from these green crystals which were washed several times with petroleum ether (b.p. 60-80°) and dried in a desiccator. It was recrystallised from toluene giving dark green crystals, m.p. 149°C.

(b) Dicyclopentadienyltitanium, prepared by hydrogenation of dicyclopentadienyltitanium dimethyl (1.93 g.) in benzene, and tolan (3.50 g.) were boiled together for 4 hrs. and left overnight. Solvent was removed in vacuo and the residue was treated with benzene (50 ml.) Centrifugation separated the precipitate from the solution. The clear solution was then poured into 3-4 times its quantity of heptane. This caused the formation of a red precipitate. It was left in a refrigerator for two days. No crystals were formed.

Several unsuccessful attempts were made to prepare titanocene-ditolan by the latter method.

Dicyclopentadienylzirconium Dichloride.

Cyclopentadienylsodium, prepared from freshly distilled cyclopentadiene (25 ml.) and sodium metal (5.02 g.) in tetrahydrofuran (100 ml.) was added dropwise with constant stirring to a solution of zirconium tetrachloride (16.40 g.) in the same solvent (100 ml.). After 3 hrs. stirring, the solvent was removed in vacuo and the residue was extracted with dry methylene chloride. Filtration of the extracts and the concentration of the filtrate gave the desired product as white crystals, m.p. 242°C. (Lit.,[51] 238°C).

Reaction of Dicyclopentadienylzirconium Dichloride with Tolan.

Cyclopentadienylsodium prepared from freshly distilled cyclopentadiene (5.0 ml.) and sodium (1.18 g.) in tetrahydrofuran (50 ml.) was added to a solution of zirconium tetrachloride (2.60 g.) in the same solvent (50 ml.).Tolan (3.10 g.) was added to the solution. The mixture was boiled for 3 hrs. The solvent was removed under reduced pressure. The residue was extracted with methylene chloride. Concentration of the methylene chloride extracts and addition of petroleum ether (b.p. 40-60°) gave white crystals, (2.8 g., 90%), m.p. 60°. The product was identified as tolan from its m.p. and I.R. spectrum. No other product was isolated.

Reaction of Dicyclopentadienyltitanium with Triphenylphosphine.

Dicyclopentadienyltitanium was prepared by hydrogenation of dicyclopentadienyltitanium dimethyl (1.77 g.) in benzene (50 ml.). A solution of triphenylphosphine (4.56 g.) in the same solvent (25 ml.) was added dropwise with constant stirring. The mixture was further stirred for 4 hrs. Solvent was removed under reduced pressure and the residue was extracted with dry methylene chloride. Filtration of the extracts, concentration of the filtrate and cooling to -80°C gave white crystals, m.p. 76°C. It was identified as triphenylphosphine from its m.p. and I.R. spectrum. No other product was isolated.

The above experiment was repeated under reflux. Again the only product thus isolated was triphenylphosphine (80%).

Reaction of Dicyclopentadienyltitanium Dimethyl with Nitric Oxide.

Nitric oxide was bubbled through a solution of dicyclopentadienyltitanium dimethyl (3.70 g.) in tetrahydrofuran (50 ml.) for 6 hrs. with continuous stirring. The clear solution was concentrated under reduced pressure leaving a highly crystalline residue. A number of unsuccessful attempts were made to recrystallise it from various solvents. It gave a positive test for nitrogen.

Reaction of Dicyclopentadienyltitanium with Nitric Oxide.

Dicyclopentadienyltitanium was prepared by hydrogenation of dicyclopentadienyltitanium dimethyl (1.75 g.) in benzene (50 ml.) Nitric oxide was bubbled through the above solution of dicyclopentadienyltitanium for 6 hrs. with continuous stirring. Free nitric oxide was flushed out by a stream of nitrogen gas. Evaporation of the solvent under reduced pressure left a residue which did not contain nitrogen.

Reaction of Dicyclopentadienyltitanium Dimethyl with 2,2' - Dipyridyl.

Dicyclopentadienyltitanium dimethyl (1.95 g.) in benzene (50 ml.) and 2,2' -dipyridyl (1.49 g.) in the same solvent were stirred together for 4 hrs. The mixture was filtered and the filtrate on concentration gave light orange coloured crystals, which were recrystallised from petroleum ether (b.p. 40-60°) as prisms, m.p. 69°C. Its I.R. spectrum and m.p. are identical with that of pure 2,2' -dipyridyl. No other product was isolated.

The above experiment was carried out under reflux. It gave a gum smelling of 2,2' -dipyridyl. It could not be crystallised from any solvent.

Reaction of Tetrabutoxytitanium with Phenyl Isocyanate.

Phenyl isocyanate (3.0 ml.) was added to tetrabutoxytitanium (10 ml.) in benzene in a drybox. The reaction was exothermic. The mixture was stirred for 2 hrs. at room temperature. Evaporation of the solvent under reduced pressure gave a liquid. Addition of petroleum ether (b.p. 60-80°) yielded crystals, m.p. 58°C. The compound was tested for the presence of titanium, but it did not give any positive test. It was identified as a butyl ester of phenyl carbamic acid from its m.p.

(Found: C, 68.1, H, 7.6, $C_{11}H_{15}NO_2$ requires C, 68.4, H, 7.7).

Reaction of Dicyclopentadienyltitanium Dimethyl with Phenyl Isocyanate.

Dicyclopentadienyltitanium dimethyl (1.92 g.) in benzene and phenyl isocyanate (2.5 ml.) in the same solvent (25 ml.) were stirred together for 4 hrs. at room temperature. Evaporation of the solvent under reduced pressure gave a residue which was crystallised from petroleum ether (b.p. 60-80°) as white crystals, m.p. 275°-276°C. The compound did not contain titanium. The compound was identified by its m.p. as the trimer of phenyl isocyanate.

Tetrakis(dimethylamino)titanium.

Butyllithium was prepared from lithium metal (5.22 g.) in ether (25 ml.) and n-butyl bromide (45 g.) at -10°C. To this solution, anhydrous dimethylamine (15 g.) was added slowly with constant stirring at -10°C. Stirring was continued for a further 30 min. and the product was allowed to attain room temperature. Titanium tetrachloride (12.0 g.) in benzene (25 ml.) was added slowly with continuous stirring. The mixture was refluxed for 2 hrs. and the ether was replaced by benzene. The solution was filtered and evaporated to dryness. Distillation of the residue gave tetrakis(dimethylamino)titanium as a yellow liquid, b.p. 50°/0.05 mm. (11.9 g.; 84%).

Reaction of Tetrakis(dimethylamino)titanium with Cyclopentadiene.

Tetrakis(dimethylamino)titanium (1.70 g.) in tetrahydrofuran (20 ml.) and freshly distilled cyclopentadiene (1.3 ml.) in the same solvent were stirred together for 3 hrs. at room temperature. The reaction was instantaneous with the change of colour from yellow to dark red. Evaporation of the solvent under reduced pressure gave a syrupy liquid which could neither be distilled nor crystallised. Dry [illegible] was bubbled through the benzene solution of the above product. Filtration of the reaction mixture and concentration of the filtrate under reduced pressure gave yellow crystals, identified as cyclopentadienyltitanium trichloride from their m.p. (210°C) and I.R. spectrum.

Reaction of Tetrakis(dimethylamino)titanium with the sodium salt of Cyclopentadiene.

Cyclopentadienylsodium, prepared from freshly distilled cyclopentadiene (2.0 ml.) and sodium metal(0.94 g.) in tetrahydrofuran (50 ml.), was added dropwise with stirring to a solution of tetrakis(dimethylamino)titanium (2.32 g.) in the same solvent (25 ml.). The mixture was stirred for 3 hrs. Evaporation of the solvent under reduced pressure gave a gum which could not be crystallised from any solvent.

Reaction of Dicyclopentadienyltitanium Dimethyl with Anhydrous Stannous Chloride.

Dicyclopentadienyltitanium dimethyl (0.96 g.) in ether (50 ml.) and anhydrous stannous chloride (2.58 g.) in the same solvent (25 ml.) were refluxed together for 3 hrs. Immediately the colour of the solution changed from orange yellow to red. Evaporation of the solvent under reduced pressure gave a red residue which on extraction with dry methylene chloride gave red crystals, m.p. 280°C. The compound was identified as dicyclopentadienyltitanium dichloride from its m.p. and I.R. spectrum.

DISCUSSION

This work was undertaken in an attempt to add to the present knowledge relating to cyclopentadienyl and related hydrocarbon derivatives of titanium. Although our investigations are mainly focussed on titanium, a number of reactions were carried out in the zirconium series as well.

In order to gain experience of the techniques involved and the properties of the products, a certain number of literature preparations were repeated.

A variety of titanium compounds have been synthesised over the last decade. They can be divided into three catagories as follows :

1. Dicyclopentadienyl derivatives of titanium(IV).
2. Monocyclopentadienyl derivatives of titanium(IV).
3. Compounds in lower valencies.

At present, a number of compounds are well known in the literature in all the above classes. Compounds in lower valencies are highly unstable and very sensitive towards air and moisture; hence their accurate and complete characterization have been difficult. For example, dicyclopentadienyltitanium[31] has been prepared. Also tricyclopentadienyltitanium has been synthesized. They have not been fully characterized in order to give satisfactory chemical evidence of their formation.

Cyanide Complexes of the Transition Metals.

In 1704, a German scientist[53] prepared the first known coordination complex, called Prussian Blue, by heating animal refuse and sodium carbonate together in an iron pot. Stahl[54] was able to isolate potassium ferrocyanide, $K_4[Fe(CN)_6]$. Since then cyanide complexes of most of the transition metals have been prepared, as well as the simple cyanides of non-transition metals. The CN group is capable of stabilising a wide variety of stereochemical configurations and metal oxidation states: In unsubstituted cyanide complexes, coordination numbers from 2 to 8 and oxidation states from 0 to 5 are known.

Very few facts are known about the stabilities of cyanide complexes, and they are certainly insufficient to justify general conclusions. No cyanide complex has been reported for zirconium or hafnium. A Titanium(III) complex exists[55]. It is highly unstable and prone to hydrolysis in an aqueous solution. The reason for instability of the cyanide is presumably that there are not sufficient d_{π} -electrons for back donation to the ligand and hence for stabilisation of the complex.

Wilkinson and his co-workers[56] have been successful in preparing a cyclopentadienyl cyano-complex of iron. They have prepared cyclopentadienyl dicarbonyl-cyano-iron(II) by refluxing cyclopentadienyl dicarbonyl chloro-iron and sodium cyanide in methanol. We were unsuccessful in preparing a cyano complex of titanium by reacting sodium cyanide and dicyclopentadienyltitanium dichloride in benzene.

The possibility of replacing one or two methyl groups in dicyclopentadienyltitanium dimethyl by cyano group was studied. However, all the attempts were unsuccessful.

When dicyclopentadienyltitanium dimethyl and cyanogen bromide were reacted in ether at room temperature, dicyclopentadienyltitanium dimethyl was the only product isolated from the reaction. Under refluxing condition, a crystalline product (m.p. 310°) which had an infra red spectrum and m.p. identical with dicyclopentadienyltitanium dibromide (m.p. 312°C.) was isolated.

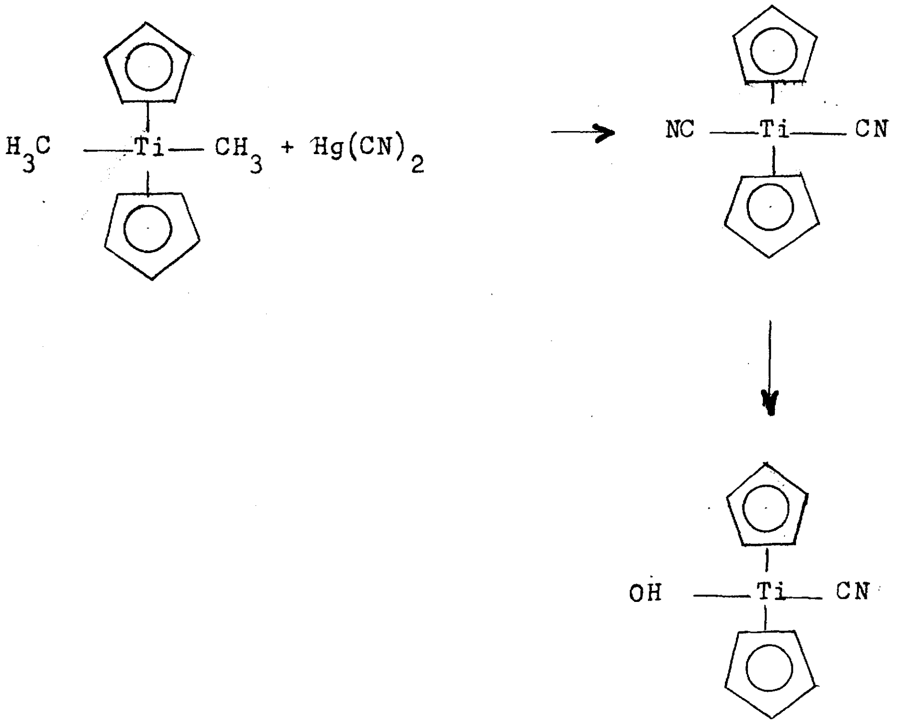
Similarly, reactions between dicyclopentadienyltitanium and cyanogen bromide were carried out under different conditions, Again, the only product isolated was identical in m.p. and infra red spectrum with dicyclopentadienyltitanium dibromide.

The failure of dicyclopentadienyltitanium dimethyl and dicyclopentadienyltitanium to form a cyanide complex may be due to the fact that the dibromide compound is more stable and more readily formed, while the cyano complex may be readily decomposed during the working up conditions.

Several attempts have been made to synthesise dicyclopentadienyltitanium dicyanide by treating dicyclopentadienyltitanium diphenyl and cyanogen bromide under various conditions. Efforts to replace one or both phenyl groups by cyano groups under various conditions were unsuccessful. Here again, a crystalline compound having m.p. and infra red spectrum identical with dicyclopentadienyltitanium dibromide was obtained.

In order to investigate whether it is possible to prepare a cyano compound by other routes, cyanogen gas was employed in the place of cyanogen bromide in the above reactions. When cyanogen gas was bubbled through a solution of dicyclopentadienyltitanium dimethyl, no change in colour took place. No cyano compound was formed.

However, when cyanogen gas was bubbled through a solution of dicyclopentadienyltitanium, dark red crystals were formed which decomposed above 120°C. The product shows a strong peak due to $C \equiv N$ absorption in the infra red spectrum. It appears from the analytical data that initially there may be a formation of the expected compound which hydrolyses slowly giving a mixture of dicyclopentadienyltitanium dicyanide and dicyclopentadienyltitanium cyano hydroxide. Dicyclopentadienyltitanium dicyanide seems to be very sensitive towards moisture and appears to decompose slowly, giving the hydroxycyanide. Further attempts were made to isolate a cyano compound by reacting dicyclopentadienyltitanium dimethyl with mercuric cyanide under various conditions. Reaction of dicyclopentadienyltitanium with mercuric cyanide gave a red crystalline solid which gave a strong absorption peak in the 2100-2200cm^{-1} region, clearly due to a $C\equiv N$ group. Attempted recrystallisation caused complete decomposition. A cyano complex of empirical formula, $C_{11}H_{11}TiON$ was isolated as orange yellow crystals, from the reaction of dicyclopentadienyltitanium dimethyl and mercuric cyanide according to the following equation:



Dicyclopentadienyltitanium hydroxy cyanide was identified by analysis as well as strong absorption at 2225 cm.$^{-1}$ in the $C\equiv N$ region of the infra red spectrum; the remainder of the spectrum showed a strong resemblance to that of dicyclopentadienyltitanium dichloride.

Hübel and his co-workers[57,58,59,60,61] have extensively investigated the reactions of iron carbonyls with a variety of acetylenes, mainly with phenyl acetylene and tolan. They have obtained many products including e.g. those with the general formulae $(C_2R_2)_2Fe_2(CO)_6$ and $(C_2R_2)_2Fe_2(CO)_7$[59,62].

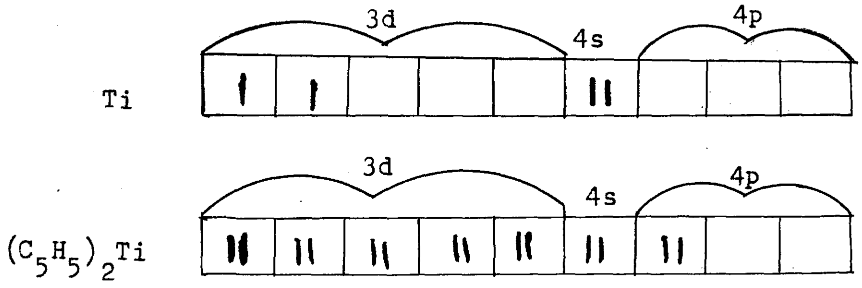
Vol'pin and his co-workers[63] have made study of the 'carbenoid properties' of some transition elements. They postulated the following conditions for compounds of the transition metals to possess such properties.

(a) 'Inner' vacant d-orbitals (with a smaller principal quantum number, than its valency s-or p-electrons) must be engaged in bond formation.

(b) The central atom will have at least one pair of s-or p-electrons free (or will have two unpaired electrons).

(c) There must be at least one free p-orbital (or two unpaired electrons in two p-orbitals).

From the above considerations, they have arrived at a conclusion that a compound like dicyclopentadienyltitanium can be said to possess such 'carbenoid properties', since the electronic configuration of titanium in this compound satisfies all the above conditions,



It is possible to expect that dicyclopentadienyltitanium may be able, like carbene, to react with unsaturated compounds with the formation of two or more new carbon-titanium bonds.

Taking into consideration the above assumption, Vol'pin and his co-workers[64] were able to isolate and characterize a compound, titanocene ditolan, by treating dicyclopentadienyltitanium with tolan. Titanocene was prepared by treating titanium tetrachloride with excess of cyclopentadienylsodium in the presence of tolan.

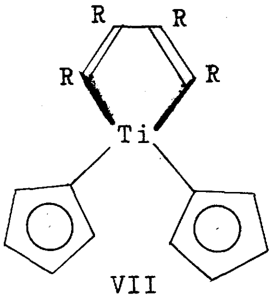
It was shown that under such conditions, two molecules of tolan combine with one molecule of titanocene as follows :

$$TiCl_4 + 4C_5H_5Na \rightarrow (C_5H_5)_2Ti + 4NaCl + (C_5H_5)_2$$

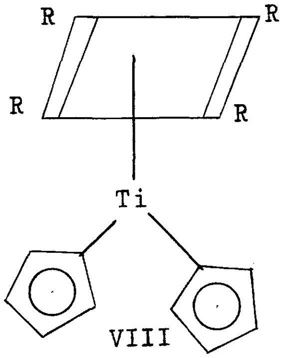
$$(C_5H_5)_2Ti + 2PhC \equiv CPh \rightarrow (C_5H_5)_2Ti(PhC \equiv CPh)_2$$

The following possible structures have been proposed from consideration of the chemical properties, molecular weight and composition :

$R = C_6H_5$



VII



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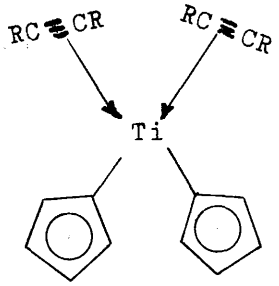


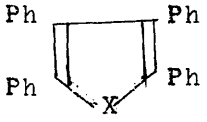
IX

The properties of titanocene ditolan, and particularly the formation of tetraphenylbutadiene by decomposition with alkalies or acids are in the best agreement with structure (VII). Thus the reaction of dicyclopentadienyltitanium with tolan proceeds with the union of two molecules of tolan with the formation of an adduct, probably possessing structure (VII). However, further investigations are required in order to confirm this structure.

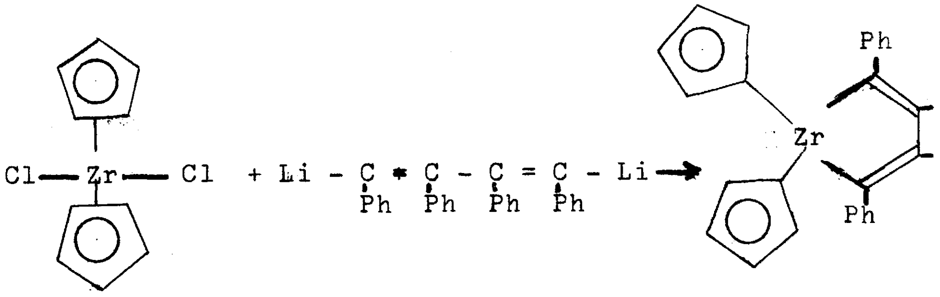
An attempt to prepare titanocene ditolan by treating titanocene, prepared by hydrogenation of dicyclopentadienyltitanium dimethyl in benzene, with tolan under the above conditions was unsuccessful. Unreacted tolan (80%) was recovered. Failure may be due to the fact that reaction takes place only at the moment of formation of titanocene while in our experiment, titanocene was already formed before addition of tolan.

Fischer and his co-workers have shown that tricyclopentadienyltitanium can also be formed under the same reaction conditions employed by Vol'pin and his co-workers. No evidence has been offered by Vol'pin for the formation of titanocene. So it is very difficult to say at this stage whether titanocene or some other compound is the intermediate involved in the method of Vol'pin and his co-workers.

Hübel and his co-workers[65] have prepared a number of heterocyclopentadienes (X) where X is zirconium, tin etc. by reacting 1,4-dilithiotetraphenyl butadiene with metal or metalloid halides. They have shown that 1,1-bis (π-cyclopentadienyl)- 2,3,4,5-tetraphenyl zirconacyclopentadiene is readily formed on treatment of dicyclopentadienyl zirconium dichloride with 1,4-dilithio-1,2,3,4,-tetraphenyl butadiene in ethereal solution as follows:



X



XI

We have repeated the above reaction under the same conditions but employing tolan in place of 1,4-dilithiotetraphenyl butadiene. However, reaction was unsuccessful and the only product isolated was tolan (90%).

Chatt et.al[66] have prepared platinum complexes of acetylene as follows :

$$2(Ph_3P)_2PtCl_2 + N_2H_4 + 2RC \equiv CR \longrightarrow 2(Ph_3P)_2Pt(C_2R_2) + 4HCl + N_2.$$

We have modified this method to form the corresponding acetylene compounds, by reacting titanocene with phenyl acetylene and dicyclopentadienyltitanium dimethyl with phenyl acetylene.

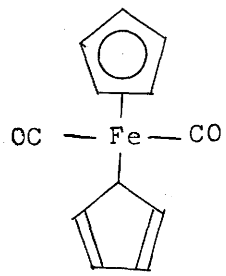
With titanocene, a greenish yellow compound which decomposed on attempted recrystallisation was obtained. Similar reaction between dicyclopentadienyltitanium dimethyl and phenyl acetylene gave a greenish yellow compound with empirical formula $C_{21}H_{17}Ti$.

Reactions of pyrrole, C_4H_5N with metal carbonyls have given rise to a number of new organometallic compounds. Joshi and Pauson[67] have prepared a yellow crystalline compound from the reaction of pyrrole and manganese carbonyl in refluxing ethylene glycol diethyl ether. It was analyzed correctly for a compound of empirical formula $C_7H_4MnNO_3$ having the structure (XII) which was confirmed by infra red, ultra violet and nuclear magnetic resonance techniques.

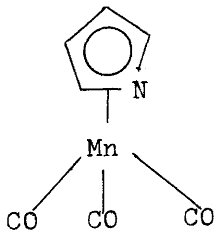
The synthesis of π-cyclopentadienyl metal complexes have been made easier by ready formation of alkali metal salts of cyclopentadiene. Pyrrole also reacts with potassium to give pyrrolylpotassium $C_4H_4N^-K^+$. Fischer and Ofele[68] have reported the reaction of pyrrolylpotassium with a transition metal halide with a view of preparing π-bonded complexes analogous to π-cyclopentadienyl metal derivatives. They did not observe any reaction between pyrrolylpotassium and hexamminonickel(II) thiocyanate.

Equally unsuccessful attempts have been made to extend this method of titanium tetrachloride. It was found that no desired compound formed from pyrrolylpotassium and titanium tetrachloride.

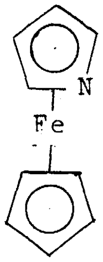
Hallam and Pauson[69] have reported that bromodicarbonylcyclopentadienyliron undergoes reaction with cyclopentadienylsodium to give a complex $(C_5H_5)_2Fe(CO)_2$ having the structure(XIII)which readily loses carbon monoxide to give ferrocene.



XIII



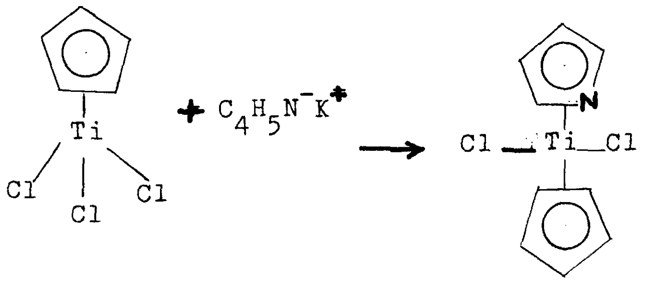
XII



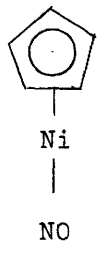
XIV

Similarly, Joshi, Pauson, Qazi and Stubbs[70] have synthesised a compound of empirical formula, $(C_5H_5)(C_4H_4N)Fe$, by reacting iodo-dicarbonyl cyclopentadienyliron with pyrrolylpotassium. Structure (XIV) has been assigned to this complex on the basis of strong '9,10' bonds in the infra red spectrum and the similarity to ferrocene of its ultraviolet spectrum. The nuclear magnetic resonance spectrum of this compound is also in agreement with the above structure.

A logical extension of the preparation of compound (XIV) appeared to be the reaction of cyclopentadienyltitanium trichloride, $(C_5H_5)TiCl_3$, with pyrrolylpotassium to give the pyrrolyl analogue of titanocene dichloride. However, addition of the pyrrolylpotassium to a tetrahydrofuran suspension of cyclopentadienyltitanium trichloride gave no desired product; cyclopentadienyltitanium trichloride (90%) was recovered. No other product was isolated. The reaction may proceed as follows :



XV



XVI

The formation of cyclopentadienylnickel nitrosyl (XVI) by the action of nitric oxide on dicyclopentadienylnickel has been reported by Wilkinson and his co-workers[71] and by Fischer et.al[72]. An attempt to prepare a cyclopentadienyltitanium nitrosyl by the action of nitric oxide with dicyclopentadienyltitanium was unsuccessful. However, reaction between dicyclopentadienyltitanium dimethyl and nitric oxides gave a crude crystalline product which showed the presence of nitrogen. It was decomposed on attempted recrystallisation.

Although the amino derivatives of titanium and zirconium are well-known, there were no authentic example of metalloorganic compounds containing these metals bonded to alkylamino groups. Such compounds occupy positions between the well known metal alkoxide and the novel organometallic compounds, containing these metals bonded to aliphatic carbon atoms.

Bradley and Thomas[73] were able to synthesise such compounds which are quite stable in the absence of water or other hydroxylic compounds. They are prepared by heating the metal chloride with the appropriate lithium dialkylamide by the following general equation:

$$MCl_4 + 4LiNR_2 \longrightarrow M(NR_2)_4 + 4\ LiCl.$$

We have made unsuccessful attempts to prepare cyclopentadienyl derivatives of titanium by reacting either cyclopentadiene or the sodium salt of cyclopentadiene with tetrakis(dimethylamino)titanium. The reaction with cyclopentadiene gave a deep red colour instantly. A thick red liquid which could not be either distilled or crystallised was obtained. Also it was observed that the solution hydrolyses slowly. However, we have been successful in showing that a monocyclopentadienyl derivatives has been formed by passing dry HCl through a benzene solution of the product. Cyclopentadienyltitanium trichloride was obtained.

Miscellaneous Reactions of Dicyclopentadienyltitanium and Dicyclopentadienyltitanium Dimethyl.

The possibility of preparing a dicyclopentadienyltitanium phenyl chloride derivative of titanium by heating dicyclopentadienyltitanium dichloride with dicyclopentadienyltitanium diphenyl was studied. The attempted reaction caused complete decomposition of dicyclopentadienyltitanium diphenyl. The only product which could be isolated and identified from the above reaction was dicyclopentadienyltitanium dichloride.

An attempt to prepare a triphenylphosphine derivatives of titanium also proved futile as triphenylphosphine was the only product (85%) recovered from the reaction of triphenylphosphine and dicyclopentadienyltitanium.

2,2' -Dipyridyl complexes of titanium[74] of type, MCl_4L, (Where M=Ti and L=2,2'-dipyridyl) have been prepared and their properties have been studied. Titanium appears to give products of indefinite composition.

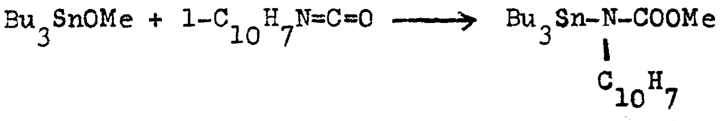
Attempts to extend this reaction by employing dicyclopentadienyltitanium have not been successful. 2,2' -dipyridyl was the only product isolated and identified from the reactions.

Jones and Lappert[75] have extensively investigated the reactions of amino derivatives of Sn(IV) with various ligands and have found that the reactivity of amino derivatives of the more electropositive elements is comparable to that of **Grignard** reagents. They have isolated a new type of compound from the reaction of dimethylamino-tri-organostannane with protic reagents such as HA where A is OH, Cl, NH_2, cyclopentadienyl or indenyl :

$$R_3Sn: NMe_2 + HA \longrightarrow R_3SnA + Me_2NH.$$

All these reactions proceed in quantitative yield and require mild conditions. They have also noted that the metal-nitrogen bond in amino derivatives of Sn(IV) and other elements is responsive to attack by multiple bonded compound such as PhNCO, CS_2, CO_2 etc., specially those normally susceptible to nucleophilic reagents.[76].

Bloodworth and Davies[77] have found that organic isocyanate reacts readily with tin(IV) alkoxides to give a new family of very reactive organotin compounds, the N-stannylcarbamates as follows:



$$Bu_3SnOMe + 1\text{-}C_{10}H_7N{=}C{=}O \longrightarrow Bu_3Sn\text{-}\underset{\displaystyle C_{10}H_7}{\underset{|}{N}}\text{-}COOMe$$

In view of the formal similarity to the above reaction, it was considered of interest to examine the reaction of phenyl isocyanate with tetrabutoxy-titanium. Addition of tetrabutoxy-titanium to phenyl isocyanate was carried out in the dry-box. The reaction was exothermic. No isocyanate derivative of titanium was formed, but a white crystalline compound containing no titanium was obtained. It was identified from physical and chemical data as butyl N-phenylcarbamate($C_6H_5NHCOOC_4H_9$). This may be due to the partial hydrolysis of phenyl isocyanate. Traces of moisture may have played an important role before the titanium compound could react with phenylisocyanate.

When dicyclopentadienyltitanium dimethyl and phenyl isocyanate were allowed to react together under the same conditions, no heat was liberated and 1,3,5- triphenyl-S-triazine-2,4,6(1H,3H,5H)-trione was isolated as the only product of the reaction. Considering the apparent ability of tin(II) chloride as either $SnCl_2$ (Solvent) or $SnCl_3^-$ to behave as a donor at least towards the platinum metals, Wilkinson and Bonati[78] were successful in synthesising a number of compounds by the interaction of tin (II) chloride with carbonyl π-cyclopentadienyl complexes ofiron, molybdenum and tungsten in polar solvents like methanol.Such reactions could be considered as being due to 'carbenoid' activity of tin (II) chloride.

An attempt to prepare the titanium analogue by refluxing dicyclopentadienyltitanium dimethyl with anhydrous tin(IV) chloride under similar conditions as employed by Wilkinson was unsuccessful. A red crystalline product was isolated. It was identified by I.R. and m.p. data as dicyclopentadienyltitanium dichloride. The formation of this compound can be explained, if we postulate that the tin(II)chloride was not completely anhydrous. Under this condition, it will liberate free HCl which will then attack dicyclopentadienyltitanium dimethyl to form dicyclopentadienyltitanium dichloride.

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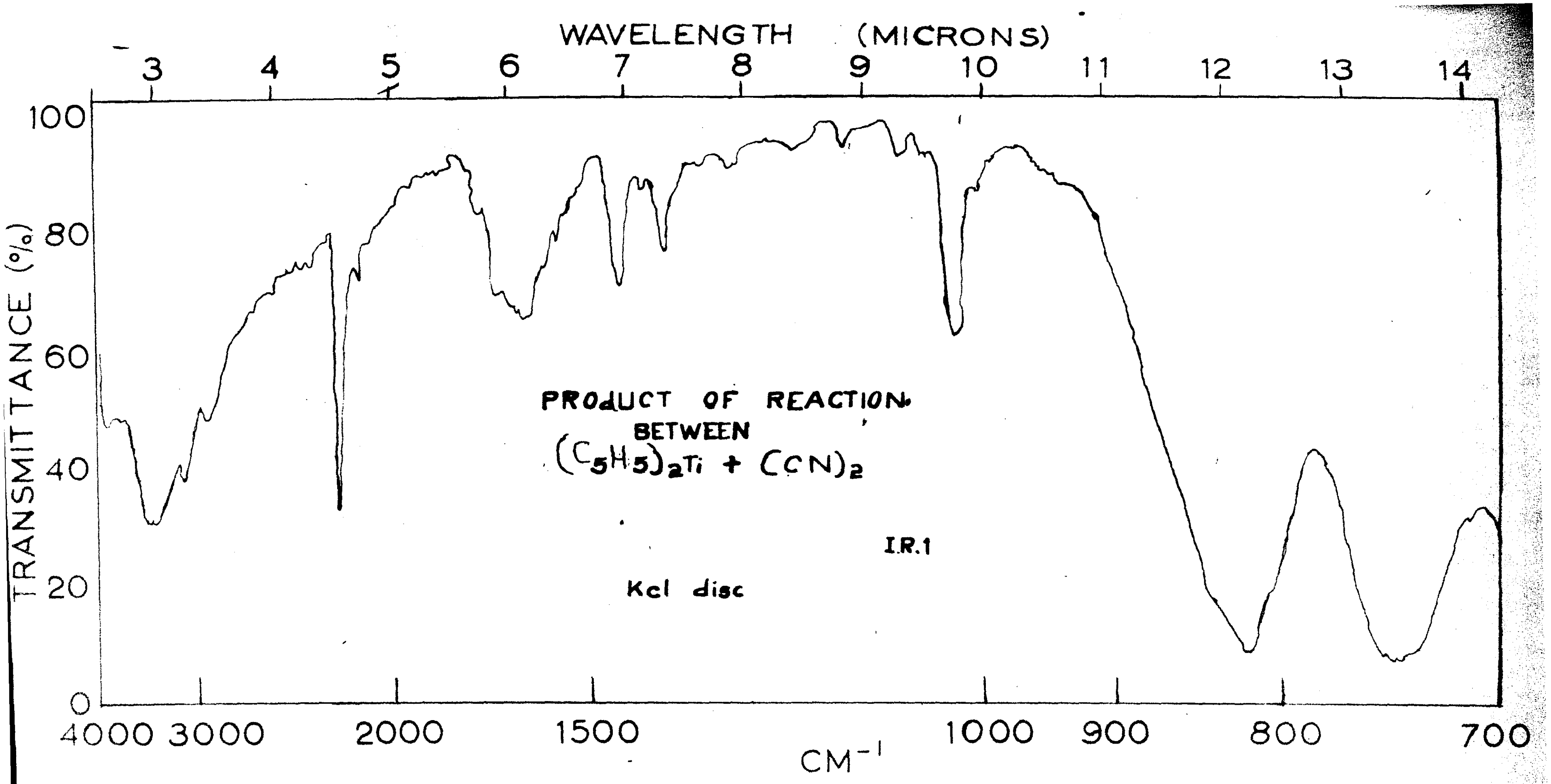
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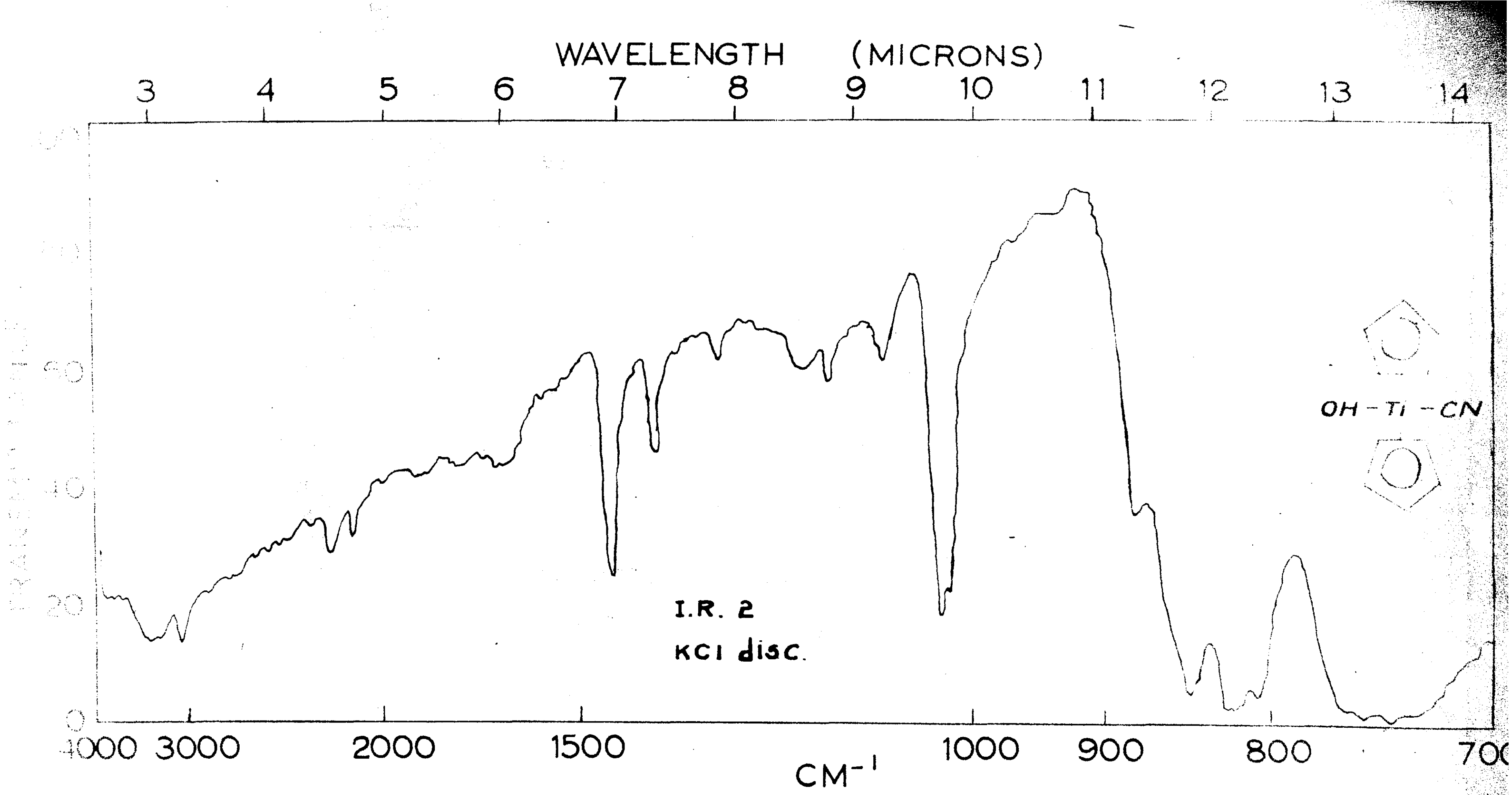
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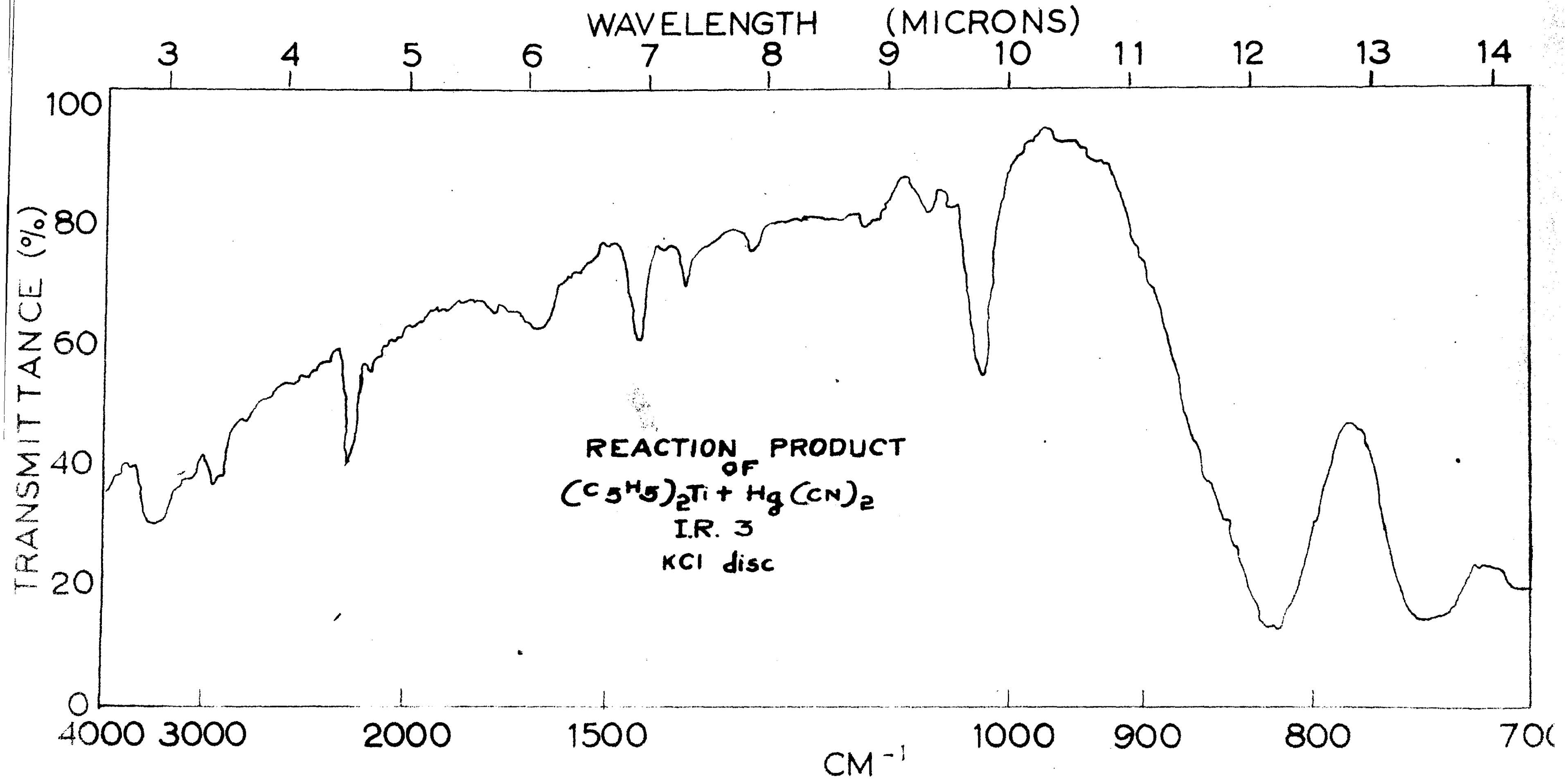
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