POLYMER SUPPORTED TITANOCENE

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ABSTRACT

POLYMER SUPPORTED TITANOCENE

By

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A stable titanocene derivative has been prepared by attachment of $(\pi-C_5H_5)_2Ti(II)$ to the surface of a styrene-divinyl benzene copolymer with a covalent bond.

The copolymer, in the form of porous beads, was first chloromethylated, then reacted with sodium cyclopentadienide. With cyclopentadiene groups thus attached to the surface of the polymer, formation of cyclopentadienide anion by treatment with methyl lithium, followed by a reaction with $\pi-C_5H_5TiCl_3$, yielded polymer supported titanocene dichloride. Reduction of this dichloride produced a very reactive complex having at least one unpaired electron. The polymer supported complex, which cannot become coordinately saturated by simple dimerization, was found to be a far more active catalyst for the hydrogenation of olefins than were homogeneous analogs.

A homogeneous analog of the polymer supported complex was prepared by reaction of lithium benzyl cyclopentadienide with $\pi-C_5H_5TiCl_3$. Titanocene hydrides were prepared by reaction of the homogeneous analog and of titanocene dichloride with butyl lithium. These reactions are described.

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C.L.G.

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I. INTRODUCTION

The synthesis of "titanocene", bis(π-cyclopentadienyl)-titanium(II), has been reported many times in the literature over the past twenty years.

A patent application filed in 1953 by Brantley[1] describes its preparation by the reaction

$$TiCl_2 + NaC_5H_5 \longrightarrow (C_5H_5)_2Ti + 2NaCl$$

This same synthesis was reported in 1956 by Fischer and Wilkinson[2], but was later disputed by Watt and Baye[3] in 1964 when they were unable to repeat the work.

A synthesis by the reaction

$$(C_5H_5)_2Ti(CH_3)_2 + H_2 \longrightarrow (C_5H_5)_2Ti + 2CH_4$$

was reported by Clauss and Bestian[4] in 1962 although the product was characterized only by an analysis for titanium.

Synthesis of titanocene has also been reported by reduction of bis(cyclopentadienyl)titanium dichloride with sodium amalgam[5], with sodium napthalenide[6], and with sodium sand.[7]

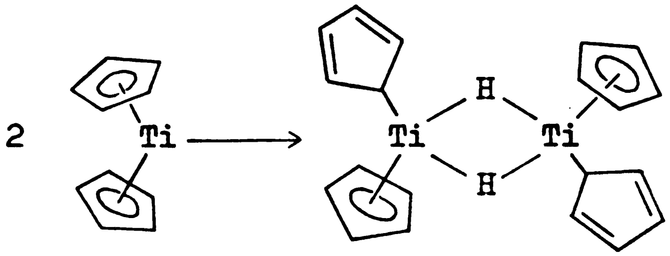
The compound isolated from these reactions was a green solid of extreme reactivity, although Watt, <u>et</u> <u>al</u>.,[6] noted that the reactivity decreased noticeably upon purification by sublimation at 100°C.

Contrary to theoretical speculation[8-11] this compound was invariably found to be diamagnetic and exhibited no esr signal.[6] It was thought to be a simple dimer of titanocene, a hypothesis supported by molecular weight determinations, although later examination of nmr and infrared spectra suggested it to be much more complex. Salzmann and Mosimann[7] concluded from this spectral evidence and from chemical evidence that the compound was not a sandwich π-type compound but rather a dimer with metal-metal bonding and both π and σ bonded cyclopentadienyl rings.

Hückle calculations by Brintzinger and Bartell[12] have predicted $(\pi\text{-}C_5H_5)_2Ti$ to be a distorted sandwich with the two rings bent away from axial symmetry to an angle of about 30° between the planes of the rings. This work suggests a relatively facile $\pi \rightarrow \sigma$ conversion and also supports earlier intuitive suggestions that titanocene would have a carbene-like reactivity.[13,14]

Citing mass spectral and chemical evidence, Brintzinger and Bercaw[15] later demonstrated that the green compound commonly referred to in the literature as "titanocene" is in fact a titanium hydride complex. The compound is dimeric and has one cyclopentadienylidene moiety (C_5H_4) per subunit. Ir data are consistent with a proposed double hydrogen bridged dimer both in solution and in the crystalline solid.

Carbenes commonly rearrange by a α-hydrogen abstraction with formation of an olefin. The formation of $((C_5H_5)(C_5H_4)TiH)_2$ from $(\pi\text{-}C_5H_5)_2Ti$ by abstraction of one of the ring hydrogens and its shift to the titanium center would be an example of the carbene-like reactivity predicted for titanocene.



Attempting to block this α-hydrogen shift pathway of deactivation, Bercaw and Brintzinger[16] undertook the synthesis of decamethyl titanocene. Bis(pentamethylcyclopentadienyl)titanium(II) was prepared and isolated although it was unstable at room temperature. The compound was found to exist in solution as a monomer-dimer equilibrium.[17]

Marvich and Brintzinger[18] recently succeeded in preparing a metastable form of titanocene by a very carefully controlled reaction of dimethyl titanocene with hydrogen gas. Under proper conditions this reaction produces a grey-green hydride complex described as a linear "polymer" rather than the previously described[4] green dimer $((C_5H_5)(C_5H_4)TiH)_2$. Dissolution of this grey-green complex in toluene results in an evolution of hydrogen with formation of a homogeneous dark solution. While titanocene could not be isolated from solution, chemical and spectral evidence supports the composition $(C_5H_5)_2Ti$. Molecular weight determination identified the metastable titanocene isomer as a dimer. Magnetic susceptibility determinations of toluene solutions revealed a noticeable paramagnetism explained by the presence of a small fraction of the complex as monomeric $(C_5H_5)_2Ti$.[17]

The preparation of a metastable titanocene dimer is very significant. It demonstrates that deactivation via an α-hydrogen shift is not inevitable. The slight paramagnetism of solutions of this dimer also suggests that titanocene itself $(\pi C_5H_5)_2Ti$ is capable of existence.

It is apparent that bis(π-cyclopentadienyl)titanium(II) has been quite an elusive species. All attempts at its preparation have led either to a deactivation by an α-hydrogen abstraction by the titanium center accompanied by dimerization or, if this is prevented, to a direct dimerization of the titanocene itself.

In spite of its elusiveness, titanocene has been credited with serving as the active species in a variety of catalytic schemes[17,19,20,21] and with being an intermediate in certain reactions of molecular nitrogen.[22-25]

It is known, however, that a major requirement for a homogeneous catalyst is an open coordination position on the transition metal which can interact with one of the reactants.[26] The titanocene dimer is a coordinately saturated species. It can be reasoned that the small equilibrium concentration of the monomer is responsible for the catalytic activity of these systems.

It has been a principle goal of this work to prepare a titanocene species which is incapable of dimerization and to investigate the catalytic activity of such a system. It was expected that constraining titanocene to a coordinately unsaturated form such as the monomer should greatly enhance its catalytic activity.

The approach toward synthesis of a monomeric titanocene species involves a heterogeneous system. In any homogeneous solution titanocene will dimerize, but if titanocene were prepared in a non-mobile heterogeneous form, dimerization would not be likely to occur.

The work of Grubbs and Kroll[27] suggests a convenient means of preparing heterogeneous catalyst systems analogous to known homogeneous types. In this work a complex analogous to Wilkinson's catalyst,[28] tris(triphenylphosphine)-chlororhodium(I), was prepared in which one of the phosphine ligands was chemically bonded to a styrene-divinyl benzene copolymer bead. This heterogeneous rhodium complex was an active catalyst for the hydrogenation of olefins and exhibited an unusual selectivity based on the molecular size of the olefin.

The synthesis of polymer supported titanocene derivatives in which one of the cyclopentadiene rings was chemically appended to the surface of a porous crosslinked polymer was thus undertaken.

II. RESULTS

Preparation of Polymer Supported Titanocene Dichloride

In his pioneering work on solid phase peptide synthesis, Merrifield[29-32] has described the use of a polymer as an insoluble support to convert a normally homogeneous synthetic sequence to a heterogeneous system. With an initial amino acid attached to a polymer by a covalent bond, peptide chains were built up with successive reactions on the surface of the polymer. The polymer used in the peptide synthesis was very carefully chosen for that purpose. Complete insolubility, chemical and physical stability, and the capability of being swollen to an open gel network were important requirements which were met with a copolymer of 98 percent styrene and 2 percent divinyl benzene in the form of small beads.

A similar copolymer was used by Grubbs and Kroll[27] in the preparation of polymer supported rhodium complexes for catalysis of olefin hydrogenation.

A polymer for the preparation of polymer supported titanocene must possess similar properties of insolubility and chemical and physical stability. Additionally, however, rather than a flexible open gel network, a high degree of rigidity was anticipated to be an important requirement.

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The primary reason for the preparation of polymer supported titanocene was the prevention of its dimerization. Flexing of the support, which would have allowed neighboring titanocene complexes to approach each other, would have defeated the whole purpose.

A copolymer of 80 percent styrene and 20 percent divinyl benzene in the form of reticulated beads with a pore size of about 600 Å was chosen. This highly crosslinked polymer is quite rigid, totally insoluble, and has a very high surface area to volume ratio due to its porous structure. Attachment of titanocene in low concentration to the surface of this polymer was expected to permit very little dimerization.

An active site for covalent bonding of the titanocene was conveniently introduced into the polymer by chloromethylation of a fraction of the aromatic rings.[33] The dried copolymer beads were slurried with an excess of chloromethyl methyl ether or with chloromethyl ethyl ether and then treated with anhydrous stannic chloride dissolved in a small amount of the ether. The extent of chloromethylation was not very reproducible due to an initial exothermic reaction, but was sufficiently slow to permit removal of aliquots and analysis for active chloride as a measure of the extent of reaction. Generally about 12 to 18 hours stirring at room temperature was required to chloromethylate 10 percent of the aromatic rings in the polymer.

Substitution of the chloride of the attached chloromethyl groups with cyclopentadienide ion was then attempted with lithium cyclopentadienide. The beads were suspended in tetrahydrofuran (THF) and treated at room temperature with a stoichiometric quantity of freshly prepared lithium cyclopentadienide.

Analysis of the washed, dried beads indicated that conversions were quite poor. After stirring for 24 hours, generally less than 50 percent of the active chloride had been displaced.

When the experiment was repeated with a THF solution of benzyl chloride in place of the chloromethylated polymer beads, the results were similar. After six hours reaction at room temperature, most of the benzyl chloride was recovered unchanged. The lack of reactivity was thus assumed to be due to the covalent nature of lithium cyclopentadienide rather than to the polymer system.

Reaction of benzyl chloride with sodium cyclopentadienide was rapid, exothermic, and quantitative, and it was thus used in subsequent work. High conversions were consistently obtained when the sodium derivative was allowed to react with the chloromethylated copolymer beads.

The cyclopentadiene thus appended to the surface of the polymer was allowed to react with methyl lithium in THF. Sufficient methyl lithium was used to convert all of the cyclopentadienyl groups to the corresponding anion as well as to convert any residual chloromethyl groups into ethyl substituents.

The slurry was then cooled to -78°C and a dry, oxygen-free THF solution of cyclopentadienyl titanium trichloride was added with a syringe. When the yellow solution was added to the slurry, the solution immediately became red. This apparent reaction in solution was unexpected and may have been due to a slight excess of methyl lithium.

The slurry was warmed to room temperature, and the reaction was allowed to proceed for 9 days. During this time the beads became red-orange, and the solution became pale yellow-orange. The solution was then decanted, and the polymer beads were washed with THF until the washings were colorless.

The scheme for preparation of polymer supported titanocene dichloride is illustrated in Figure 1.

Polymer Supported Dimethyl Titanocene

When a THF slurry of the copolymer beads with appended titanocene dichloride was treated with methyl lithium at -78°C, the color of the beads changed from red-orange to light yellow. The color was entirely on the beads (the solution remained colorless). Excess methyl lithium was destroyed with methanol, and the beads were washed. Residual solvent was removed under vacuum. The compound appeared completely stable under argon at room temperature. This was in contrast to the thermal instabiltiy of unsubstituted $(\pi\text{-}C_5H_5)_2Ti(CH_3)_3$ which is reported[4] to decompose rapidly

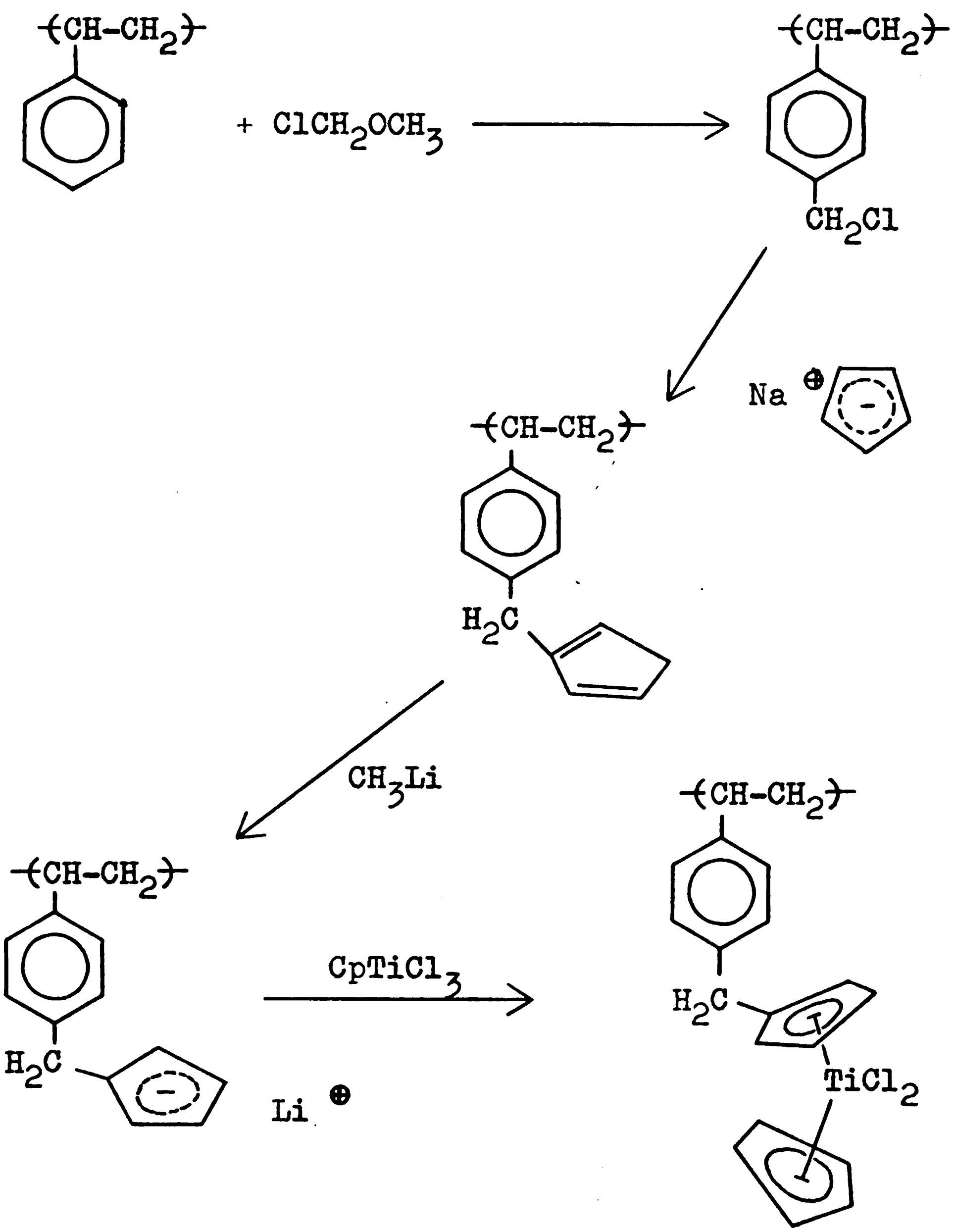


Figure 1. Scheme for Preparation of Polymer Supported Titanocene Dichloride

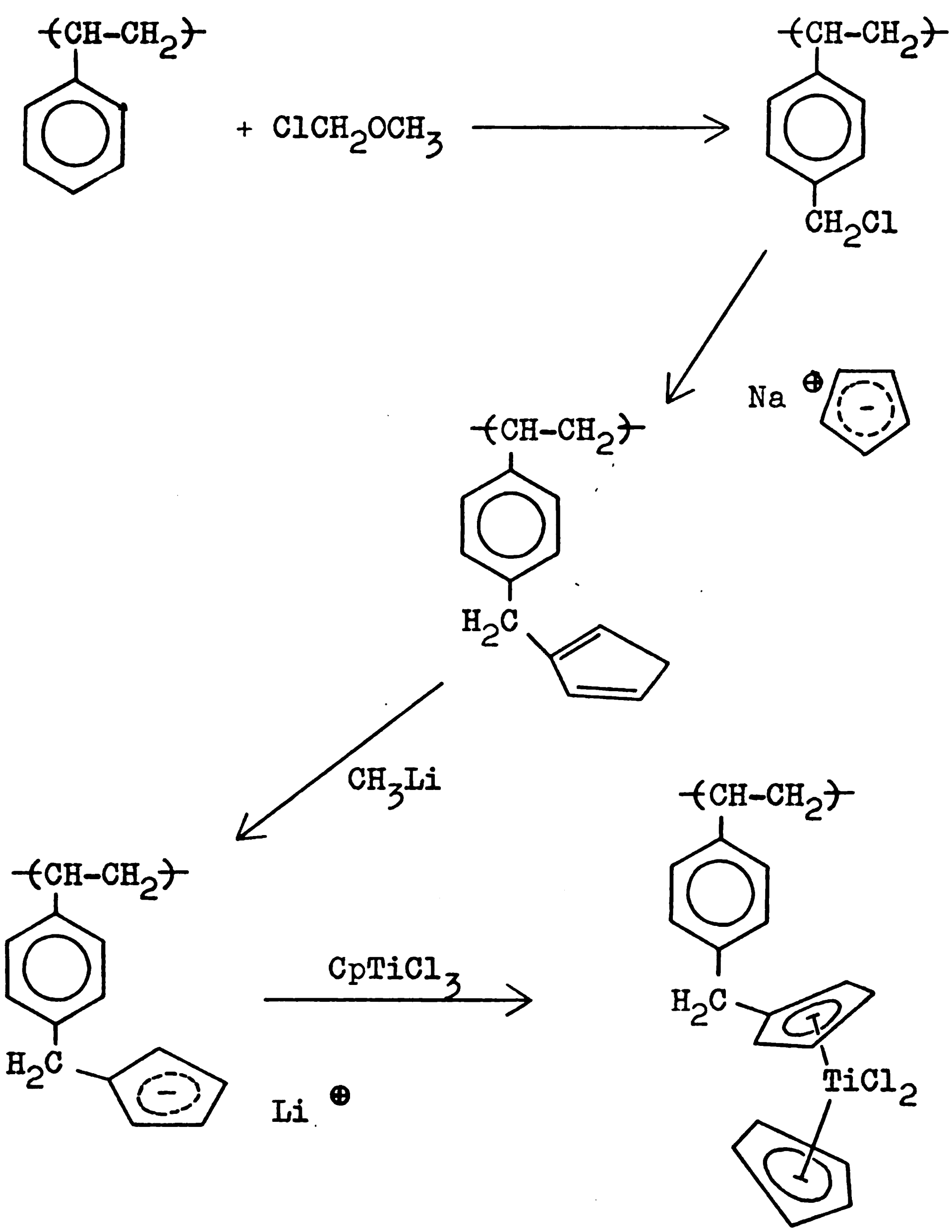


Figure 1. Scheme for Preparation of Polymer Supported Titanocene Dichloride

at room temperature.

Attempted Reduction of Polymer Supported Dimethyl Titanocene with Hydrogen

Reduction of the dimethyl derivative with hydrogen was attempted. A toluene slurry of the polymer supported dimethyl titanocene under argon was cooled to -10°C, and the argon atmosphere was displaced with hydrogen. After 30 minutes stirring at -10°C and then 60 minutes at 25°C, no methane could be detected in the gas phase. After 17 hours at 25°C, a trace of methane was detected. The slurry was warmed to 90°C, and methane was very slowly evolved. After 50 hours at elevated temperature, about 10 percent of the theoretical quantity of methane had been evolved. The color of the beads changed from light yellow to yellow-orange. This material exhibited no catalytic activity for the hydrogenation of olefins or of disubstituted acetylenes at atmospheric pressure.

The same results were obtained when this reaction was attempted with hexane as a solvent and again without solvent at 40 psig hydrogen pressure. Exposure of the toluene slurry under hydrogen to a quartz u.v. lamp yielded a small amount of methane but no apparent color changes.

Cyclopentadienylbenzylcyclopentadienyldichlorotitanium(IV)

Although the handling advantages of a heterogeneous system were obtained with the polymer-supported derivatives, characterization of reaction products was complicated by their complete insolubility and by the presence of the polymer matrix. Indirect evidence of the course of the reactions in the heterogeneous system was sought by parallel synthesis of model compounds in which one of the cyclopentadienyl rings of the titanocene derivatives was substituted by a benzyl group. The steric and electronic environment about the metal center in these derivatives would be very nearly identical to that of the polymer attached species.

Benzyltitanocene dichloride, $(C_6H_5CH_2C_5H_4)(C_5H_5)TiCl_2$, was obtained in a series of reactions exactly analogous to those used to produce the polymer supported compound. Benzylcyclopentadiene was prepared by reaction of benzyl chloride and sodium cyclopentadienide. The freshly distilled cyclopentadienyl derivative was then allowed to react with a stoichiometric quantity of methyl lithium followed by a stoichiometric amount of cyclopentadienyltitanium trichloride. Purification by crystallization from CCl_4 gave a good yield of the desired product, but mass spectrometry showed the presence of both bis(cyclopentadienyl)titanium dichloride and bis(benzylcyclopentadienyl)titanium dichloride as minor impurities. Some ligand exchange had apparently occurred in solution, a complication which should not occur in the polymeric system.

Cyclopentadienylbenzylcyclopentadienyldimethyltitanium(IV)

When a THF solution of benzyltitanocene dichloride was allowed to react at room temperature with a stoichiometric amount of methyl lithium, an immediate color change from red to yellow was observed. The solution darkened rapidly on standing at room temperature, becoming yellow-orange after 3 minutes, deep red after 15 minutes, blue-black after an hour, and finally to black after 2 hours. Exposure to air gave a greenish brown product.

To avoid the decomposition which was apparently occurring, the reaction was repeated at -78°C. In this case an instant color change from red to yellow again occurred but the yellow solution was stable at -78°C for at least 4 hours. Anhydrous oxygen-free methanol was added to destroy any excess methyl lithium, and the solvent was evaporated with the temperature held below -10°C. The yellow waxy residue was then extracted with petroleum ether. The solvent was partially evaporated and then cooled to -95°C whereupon yellow benzyltitanocene dimethyl crystallized. The purified product was stable as a yellow liquid at room temperature in the absence of oxygen.

Reaction of Cyclopentadienylbenzylcyclopentadienyldimethyltitanium(IV) with Hydrogen

When benzyltitanocene dimethyl as a CCl_4 solution was exposed to hydrogen at room temperature for 10 hours, no reaction occurred. There were no detectable changes in the nmr spectrum and no visible color changes.

The reaction was also attempted without solvent at -78°C and at 25°C and in hexane solvent at -78°C and at 25°C. Only traces of methane were detected in all cases.

Like decamethyltitanocene dimethyl,[17] the benzyl substituted compound is apparently very unreactive toward hydrogen. The reason for this lack of reactivity is uncertain but may be related to the much greater thermal stability of the substituted species. Whereas titanocene dimethyl is reported[4] to decompose rapidly at room temperature, the monobenzyl compound is stable at 50°C when pure.

The lack of reactivity of decamethyltitanocene dimethyl with hydrogen was overcome by simply heating the compound. One mole of methane was eliminated at 110°C with formation of $C_{10}(CH_3)_9CH_2TiCH_3$ which was then readily reduced with hydrogen.[16] An analogous reaction of the monobenzyl derivative as shown in Figure 2 was attempted.

When benzyltitanocene dimethyl was heated at 100°C under argon or under hydrogen a quite sudden change from yellow to black occurred. The reaction appeared to start at certain points on the wall of the vessel, spread rapidly, and effervesced. The residue was dissolved in $CDCl_3$ to give a yellowish black solution. Only broad, ill-defined absorptions were noted in the nmr spectra, perhaps due to paramagnetism in the products. An apparent reaction with the solvent gave red solutions within 30 minutes.

When hexane solutions of benzyltitanocene dimethyl were irradiated by use of a quartz u.v. lamp, a steady evolution of methane occurred. After about 90 minutes a sudden color change from cloudy yellow-orange to greyish green occurred. Methane evolution ceased at this point. Again only

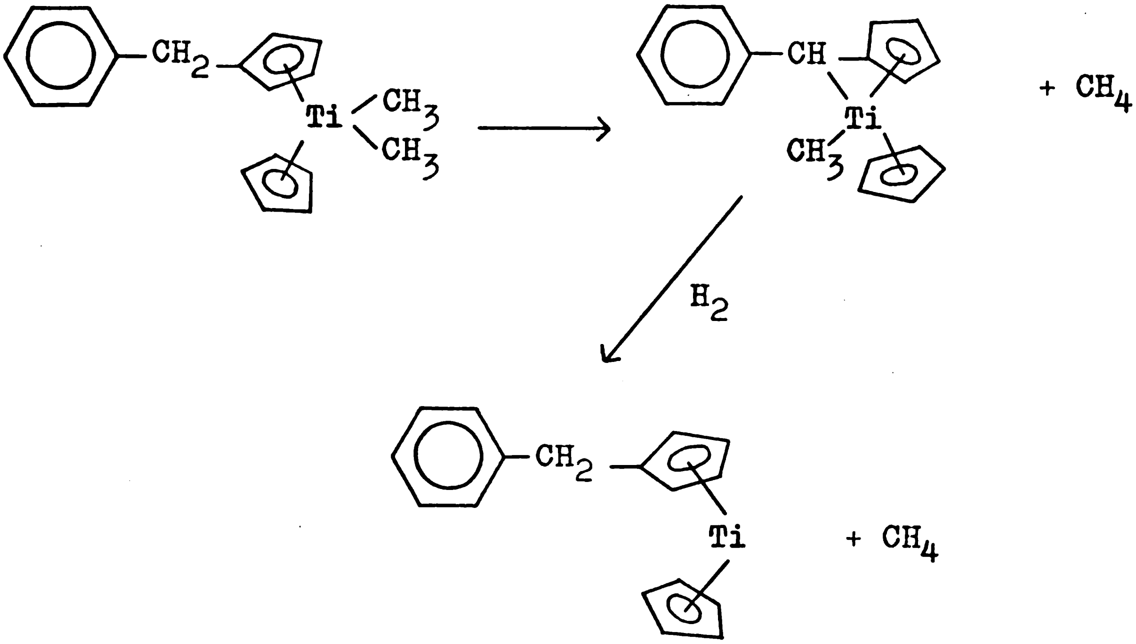


Figure 2. Attempted Reduction of Benzyltitanocene Dimethyl by Thermal Elimination of CH_4 Followed by Reaction with H_2.

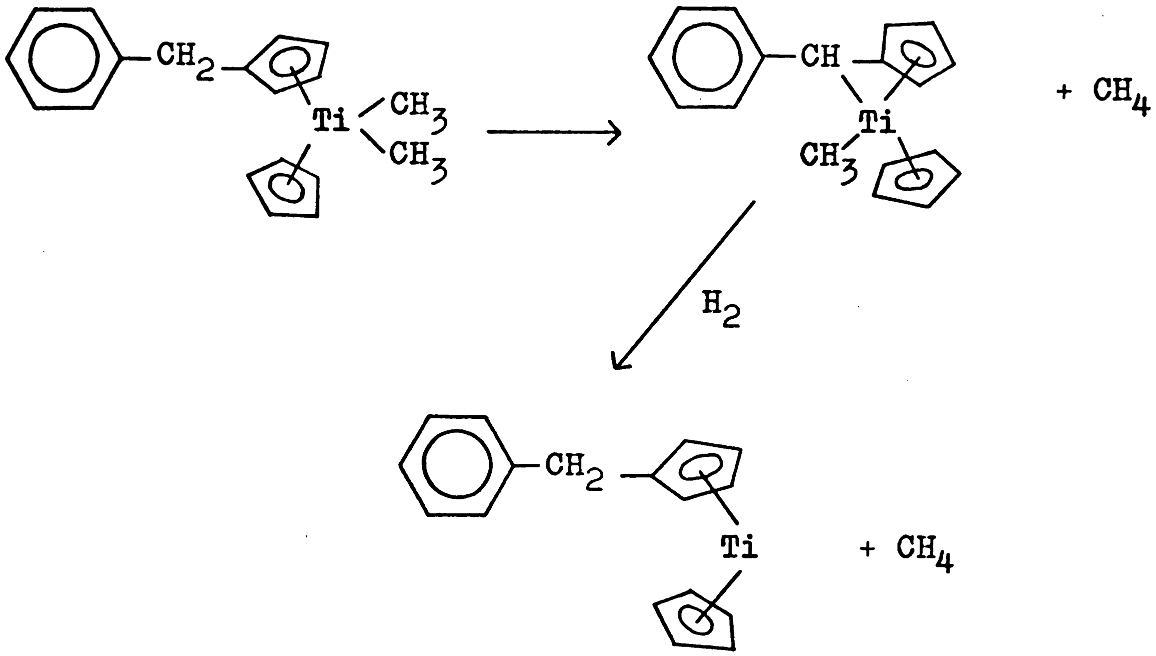


Figure 2. Attempted Reduction of Benzyltitanocene Dimethyl by Thermal Elimination of CH_4 Followed by Reaction with H_2.

very broad peaks were noted in the nmr spectrum. The product was very air sensitive, becoming bright yellow on exposure to air.

This reaction was repeated in d_6 benzene in an nmr tube with the same result.

Although ultraviolet radiation resulted in a rapid evolution of methane from benzyltitanocene dimethyl, the nature of the product is uncertain. Irradiation of the polymer supported derivative also resulted in evolution of methane, but in this case the yields were low, and no color changes were noted.

Direct Reduction of Polymer Supported Titanocene Dichloride

Reduction of the dimethyl derivative proving unsuccessful, direct reduction of the dichloride was attempted.

A THF slurry of the polymeric titanocene dichloride was treated with a slight excess of sodium napthalenide under argon. The excess reagent was removed by washing with THF. The purified beads were dark grey and extremely oxygen sensitive, becoming light brown on exposure to air. These grey beads were subsequently demonstrated to be an active catalyst for the hydrogenation of olefins.

A similar grey color was produced on reduction of the polymer supported titanocene dichloride with $NaBH_4$. The model compound, benzyltitanocene dichloride, however, exhibited no reactivity toward $NaBH_4$.

A very convenient method of reduction was the treatment of the dichloride with butyl lithium. When the orange-red beads were slurried with hexane under argon, then treated with an excess of butyl lithium, the color changed to a dark grey concomitant with evolution of gas.

When the gas was analyzed by gas liquid chromatography at least four components were observed. Retention times of the components corresponded to those of butane, which was known to have been present in the butyl lithium reagent, 1-butene, _cis_-2-butene, and _trans_-2-butene. These latter three compounds were not present in the reagents.

It seems likely that butyl lithium reacts with the titanocene dichloride in a manner analogous to the reaction of methyl lithium. Apparently a β-hydrogen abstraction occurs to produce 1-butene and form a titanocene hydride. The titanocene hydride thus produced promotes the isomerization of the primary olefin initially formed to the more stable internal butene.

The grey polymer beads prepared by reaction of the polymeric titanocene dichloride with butyl lithium showed properties similar to the product from sodium napthalenide reduction. These beads were very air sensitive and a very active catalyst for the hydrogenation of olefins and acetylenes.

Direct Reduction of Benzyltitanocene Dichloride

Since direct reduction of the polymer supported titanocene dichloride was apparently successful, similar reductions were attempted with the homogeneous analog. Neither sodium hydride nor, interestingly, sodium borohydride reacted with cyclopentadienylbenzylcyclopentadienyldichlorotitanium(IV). Sodium borohydride reacted readily with the polymer supported titanocene dichloride to give a grey complex very similar to that obtained either by reduction with sodium napthalenide or with butyl lithium. This difference in reactivity of the polymer supported derivative and the homogeneous analog toward sodium borohydride is unexplained.

When a THF solution of benzyltitanocene dichloride was allowed to react at -80°C with lithium aluminum hydride, an immediate color change from red to pale violet occurred. This color change was very similar to that which occurred when benzyltitanocene dichloride in hexane was treated with butyl lithium under a hydrogen atmosphere. This reaction is discussed in the next section.

The violet THF solution was filtered at -80°C. On warming to room temperature the color changed from violet to brown. This behavior is quite similar to that reported[34] for the violet Di-μ-hydrido-bis(dicyclopentadienyltitanium(III)) which was cleaved on warming in THF solution to form a brown ether adduct.

Di-μ-hydrido-bis(dicyclopentadienyltitanium(III))

The reaction of dimethyl titanocene, $(\pi\text{-}C_5H_5)_2Ti(CH_3)_2$, with hydrogen gas in hydrocarbon solvents has been shown[15] to yield $(C_5H_5TiH)_2C_{10}H_8$, the green compound commonly referred to as "titanocene." In the original report on this reaction,[4] Clauss and Bestian noted the occurrence of a fleeting violet intermediate. When Bercaw and Brintzinger[34] carried out this same reaction at 0°C in the absence of solvents, this violet material was isolated as the main product. They identified the compound as $((\pi\text{-}C_5H_5)_2TiH)_2$, a dimeric hydride complex having a diborane-like double hydrogen bridge between the metal centers. The compound is only marginally stable, converting to a grey-green isomer upon standing at room temperature.

The grey-green isomer, having a reactivity identical to that of the violet compound, was postulated to be a linear polymer, $((\pi\text{-}C_5H_5)_2TiH)_x$, and was found to be formed directly by the reaction of dimethyl titanocene and hydrogen at 0°C in hexane.[17]

Both of these titanocene hydride complexes can be very conveniently obtained by the reaction of titanocene dichloride with butyl lithium under appropriate conditions. (See Figure 3.)

When titanocene dichloride was stirred as a suspension in hexane at -10°C under an atmosphere of hydrogen and treated with butyl lithium, a color change from red to violet was accompanied by the absorption of 1.5 moles of hydrogen per mole of titanium. On warming to 25°C, conversion to a greenish grey complex occurred.

When the reaction was carried out under an argon atmosphere at -10°C, the greenish grey complex was formed directly. This grey compound was extremely reactive with air, particularly in the absence of solvent, and no spectral data were obtained. The compound dissolved slowly in toluene, a gas evolved, and a black solution was obtained. When this black solution was cooled to -78°C and then exposed to nitrogen, a very deep blue precipitate formed. On being warmed to room temperature, the blue compound reverted back to the original black solution.

This behavior is identical to that reported[17] for $((\pi\text{-}C_5H_5)_2TiH)_x$.

Similar behavior was exhibited by cyclopentadienylbenzylcyclopentadienyldichlorotitanium(IV). When this derivative in hexane was treated with butyl lithium under an argon atmosphere, a grey insoluble complex was formed.

When the benzyltitanocene dichloride was treated with a stoichiometric amount of butyl lithium under a hydrogen atmosphere at -5°C, however, a rapid absorption of hydrogen occurred and a slightly soluble violet compound was formed. The total hydrogen absorption was 1.5 moles per mole of titanium, indicating formation of a titanium(III) monohydride. This stoichiometry and the striking similarity in color suggests a bridged complex analogous to that formed by the unsubstituted titanocene dichloride.

The thermal stability of the benzyl derivative is considerably greater than that of the di-μ-hydrido-bis(dicyclopentadienyltitanium(III)). Whereas the unsubstituted compound converted to the grey form on warming to room temperature, the benzyl derivative persisted as a bluish-violet precipitate in a greenish hexane solution for several hours.

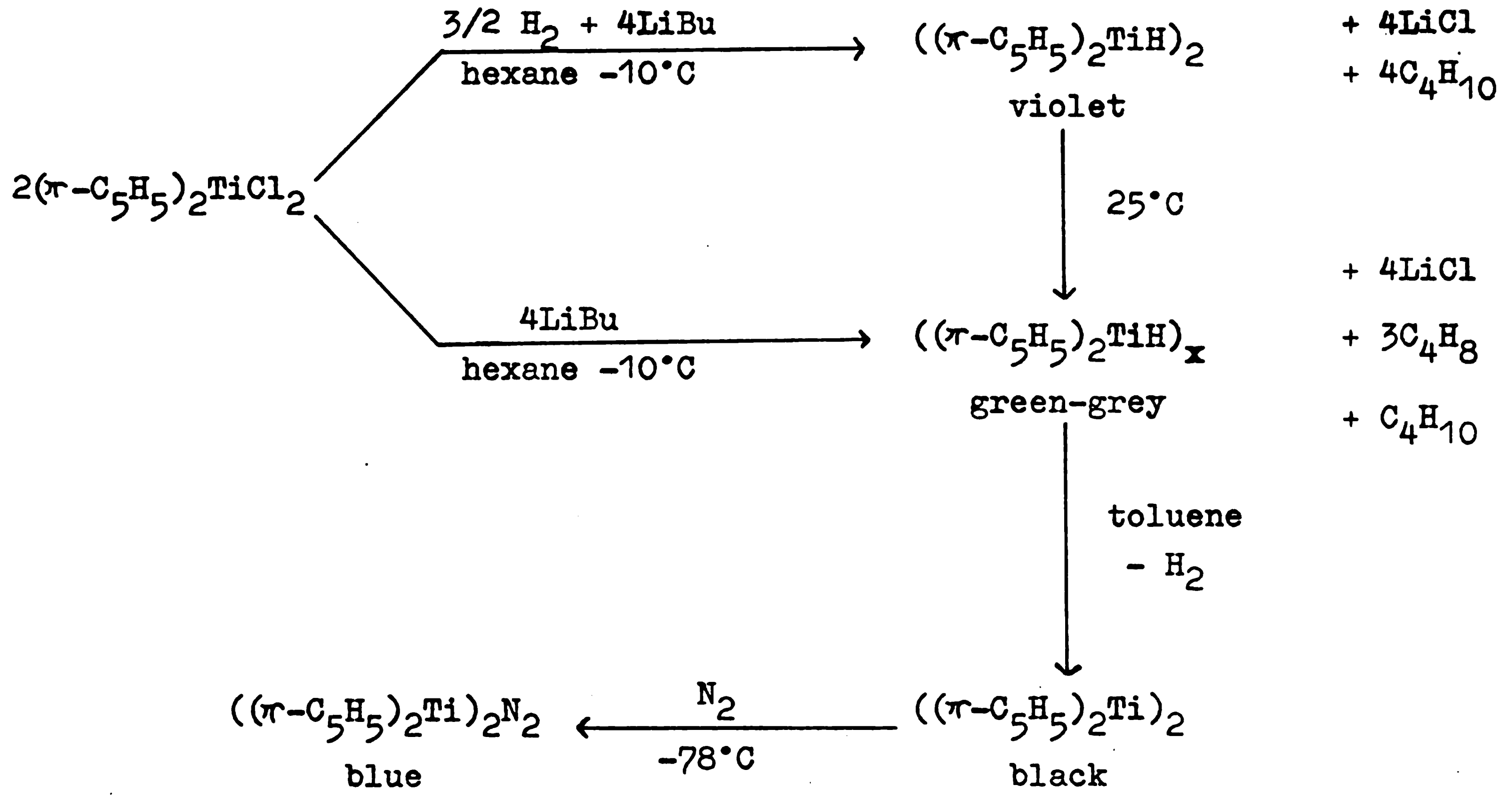


Figure 3. Preparation of Titanocene Hydrides by Reaction of Titanocene Dichloride and Butyl Lithium

Warming to 50°C was required to convert it to the greenish grey form.

The greenish grey form dissolved slowly in toluene to give a black solution in a manner analogous to the unsubstituted analog; but when placed under a nitrogen atmosphere, it exhibited no evidence of reaction with N_2 even when cooled to -78°C.

When polymer supported titanocene dichloride was treated with butyl lithium under a hydrogen atmosphere with conditions similar to those used for preparation of the violet hydrides, no violet intermediate was formed. The reaction led directly to the typical dark grey complex obtained under an argon atmosphere. This is consistent with the supposition that very little dimerization would be possible with the polymer attached complex.

Hydrogenation Catalysts

K. Shikata and coworkers[21] have shown that the reaction product of bis(cyclopentadienyl)dimethyltitanium(IV) and hydrogen, and also the reaction products of titanocene dichloride with butyl lithium are active as catalysts for the hydrogenation of olefins.

The product of the reaction of dimethyl titanocene with hydrogen is described only as a black-green precipitate which is slightly soluble in n-heptane. It is not clear whether the compound is the green dimer first prepared by Clauss and Bestian[4] and later identified as

$((C_5H_5)(C_5H_4)TiH)_2$ or whether the product is a mixture of this compound and the grey-green polymeric hydride $(\pi\text{-}C_5H_5)_2TiH_x$.

It was of interest in this work to compare the catalytic activity of the greenish grey titanocene hydride with that of the polymer supported titanocene complex. The greenish grey complex is coordinately saturated by virtue of its Ti-H-Ti bonding and should be catalytically inactive except for the extent of cleavage of this bond in solution. The polymer supported derivative however should be unable to form dimers and oligomers of this type. An esr signal exhibited by the polymer supported derivative confirms that it is indeed coordinately saturated to a significant extent. On this basis it was predicted that the polymer supported titanium complex would be a more active catalyst for the hydrogenation of olefins than would the homogeneous derivative. This prediction has been proven correct.

A typical batch of copolymer beads with appended titanocene dichloride contained 0.79 mmoles titanium per gram of beads. A 400 mg portion of these beads was suspended in hexane and treated with excess butyl lithium for several hours then washed with oxygen-free hexane to produce the dark grey catalyst. The beads were suspended in 7 ml of hexane under a hydrogen atmosphere at ambient temperature and pressure. Cyclohexene, 0.2 ml, was added and a rapid absorption of hydrogen began immediately. The hydrogen uptake rate was dependent upon the speed of agitation of the slurry indicating that the reaction rate was mass transfer limited. Hydrogen absorption ceased abruptly upon absorption of one mole of hydrogen per mole of olefin.

Cyclooctene and diphenyl acetylene were also reduced at a diffusion controlled rate. The amount of hydrogen absorbed indicated complete reduction of the acetylene. Aromatic hydrocarbons were not hydrogenated. A trisubstituted olefin, 1-methyl cyclohexene, was reduced slowly, and a tetrasubstituted olefin, 1,2-dimethyl cyclohexene, was not measureably reduced.

The rates of these reductions are illustrated in Figure 4. Except for 1-methyl cyclohexene, the reductions were obviously far too rapid for meaningful rate measurements to be made. The rates were in fact determined mainly by the efficiency of stirring of the system. A tenfold decrease in catalyst concentration was required to obtain reliable measurements of catalyst activity.

With 40 mg of catalyst beads suspended in 10 ml of hexane, 0.15 ml of cyclohexene was reduced smoothly with an initial hydrogen uptake rate of 1.8 ml/min. During the first run at this low catalyst concentration, the rate increased during the course of the hydrogenation. The expected behavior was a decrease in rate of hydrogen uptake as the concentration of the olefin decreased. The increase in activity was a result of the pulverization of a number of the rather brittle copolymer beads. A suspension of 40 mg of 20 mesh copolymer beads in 10 ml of solvent is a very sparse

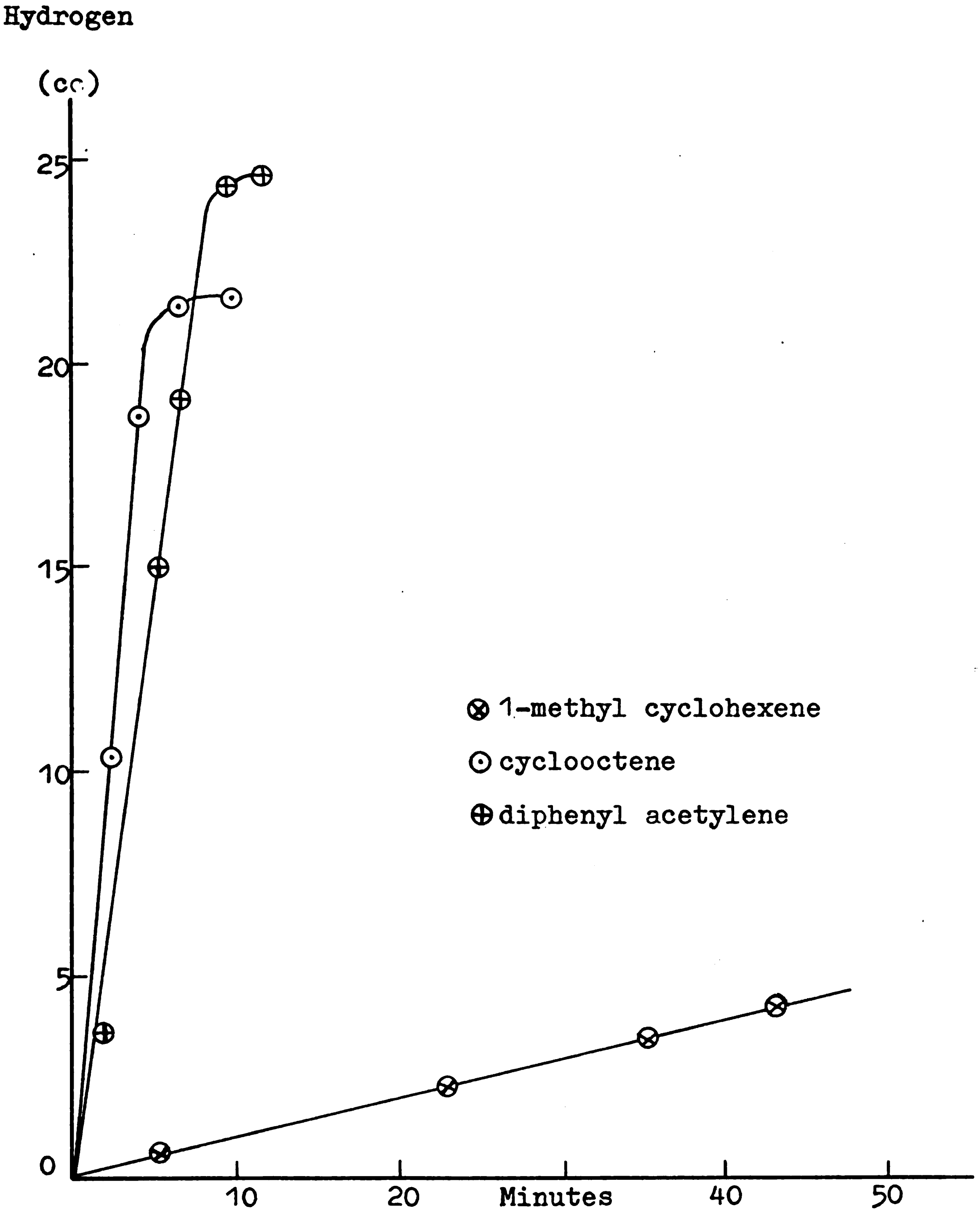


Figure 4. Hydrogenations with Polymer Supported Titanocene as a Catalyst.*

*Catalyst concentration: 400 mg of beads with 0.79 mmoles Ti/mg suspended in 7 ml hexane.

dispersion, and it is not surprising that pulverization of some of the beads to produce a more finely divided suspension increased the apparent activity of the catalyst.

Homogeneous catalysts were prepared from 50 mg (0.2 meq) of titanocene dichloride and from 70 mg (0.2 meq) of benzyl titanocene dichloride. With these catalysts in 10 ml of hexane under a hydrogen atmosphere at ambient temperature and pressure, 0.15 ml of cyclohexene was smoothly reduced with an initial hydrogen uptake rate of 2.4 ml per minute. The rate was the same, and the reduction was complete with both catalysts. (See Figure 5.)

Comparing the three catalysts on a reduction rate per milliequivalent titanium basis, the two homogeneous catalysts had an activity of 0.48 millimoles per minute per milliequivalent of titanium for a 0.265 molar solution of cyclohexene in hexane. The polymer attached derivative exhibited an activity of 2.32 millimoles per minute per milliequivalent of titanium. The apparent activity of the polymer attached derivative as a hydrogenation catalyst is thus about five times that of the homogeneous catalysts under these conditions.

It should also be noted that the trisubstituted olefin, 1-methyl cyclohexene, which was reduced at a rate of 0.0128 millimoles per minute per milliequivalent of titanium in the presence of the polymer supported catalyst, was not detectably reduced in the presence of the free catalysts.

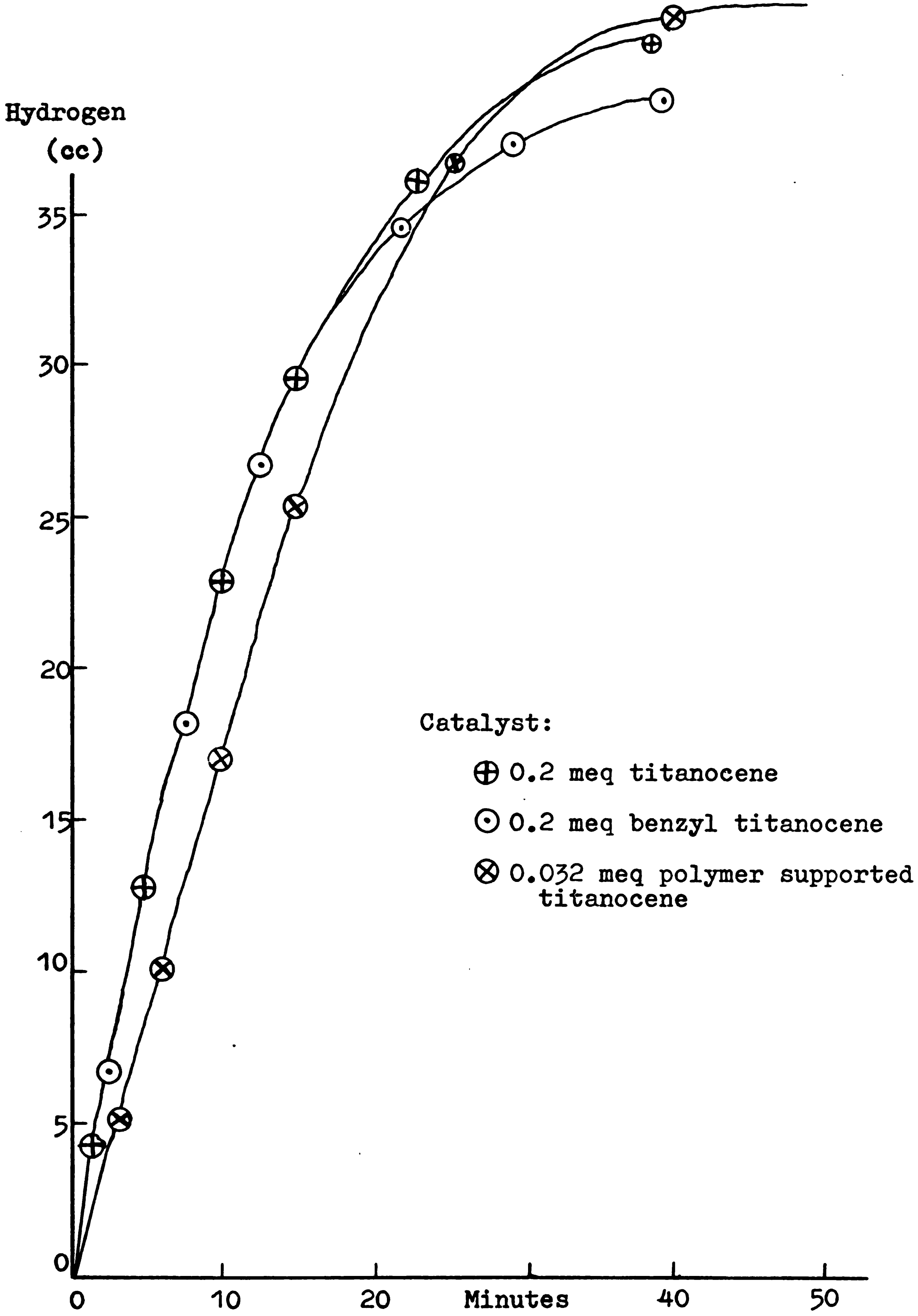


Figure 5. Reduction of 0.265 M Cyclohexene with Various Catalysts

III. CONCLUDING REMARKS

In spite of numerous references to "titanocene" which appear in the chemical literature, it has recently been demonstrated that all attempts at isolation of $(\pi\text{-}C_5H_5)_2Ti(II)$ have led either to a deactivation to $(\pi\text{-}C_5H_5TiH)_2C_{10}H_8$, or to a simple dimerization. It is clear, however, that titanocene can exist as an intermediate in certain reactions involving molecular hydrogen and nitrogen. Indeed, the catalytic activity observed for titanocene in olefin hydrogenations must be due to the disassociated form. Catalytic activity of a metal in a reaction requires a coordination of the metal with one of the reactants. The dimer, being coordinately saturated, is thus unable to interact with the olefin to promote its reaction with hydrogen. When titanocene is prepared as a totally insoluble polymer supported complex where it is incapable of dimerization, it is a far more active hydrogenation catalyst.

The success of this approach suggests the possibility of the preparation of entirely new catalyst systems. In only a few exceptional cases has it been possible to prepare unsaturated complexes which are stable in solution. Generally, reactions designed to produce such complexes yield coordinately saturated dimers or result in side reactions which ultimately yield saturated products. It should be possible to apply the principles used in the preparation of polymer supported titanocene to prepare a number of heretofor inaccessible complexes.

Besides the possibility of discovering new catalysts, the preparation of polymer supported transition metal complexes may afford the opportunity to study the behavior of metal atoms in unusual environments. With a metal complex attached to an insoluble support, ligand removal or alteration, or valence changes could be carried out.

Many reactions which normally must be run at high dilution because of competing dimerization, polymerization, disproportionation, or other undesirable molecule-molecule interaction might also be more conveniently run with a heterogeneous system.

IV. EXPERIMENTAL

General Techniques

A number of the compounds encountered in this work were extremely oxygen sensitive. Thus, standard Schlenk apparatus and techniques were used in their preparation and manipulation.

Gases were obtained from Matheson and were prepurified grade. Argon was used as received. Nitrogen and hydrogen were further purified by passage through columns of heated BASF catalyst.

Reagent grade toluene, hexane, tetrahydrofuran (THF), diethyl ether, and the olefins employed in the hydrogenation experiments were purified immediately prior to use by distillation from sodium under a purified nitrogen atmosphere.

Butyl lithium was obtained from Foote Chemical and was used as received. Methyl lithium was obtained from Alfa Inorganics and was standardized prior to use by titration with 2-butanol in xylene using o-phenanthroline as an indicator.

Nmr spectra were obtained with a Varian A-60 nmr spectrometer using tetramethyl silane (TMS) as a reference at 0 ppm.

Description of the Experiments

Chloromethylation of copolymer beads. A 500 ml round bottom flask was charged with 25 g of copolymer beads and 100 ml of freshly distilled chloromethyl methyl ether and stirred for 90 minutes to swell the beads. An additional 25 ml of the ether was cooled in an ice bath and treated with 4.2 ml of $SnCl_4$. This catalyst solution was then added to the slurry of beads. The flask was protected with a drying tube, and the slurry of beads was stirred for 12 hours at room temperature. The slurry was then treated with 50 percent aqueous dioxane containing 10 percent concentrated HCl, then with 50 percent aqueous dioxane until the washings gave a negative test for chloride. A final wash with pure dioxane was followed by drying under vacuum.

Chloride analysis showed the beads to have 0.791 meq/g chloride.

Chloride analysis of chloromethylated beads. About 400 mg of dry chloromethylated beads were weighed into a test tube and heated with 3 ml of pyridine at 100°C for 2 hours, and the mixture was stirred occasionally. The slurry was then transferred to a flask with 30 ml of 50 percent acetic acid and 5 ml of concentrated nitric acid. Chloride was then determined by the Volhard method.

Reaction of sodium cyclopentadienide with chloromethylated copolymer beads. Chloromethylated copolymer beads containing 1.17 meq/g chloride were dried by distilling toluene from them. A rigorously dried Schlenk tube fitted with a Schlenk filter was charged with 10.0 g of the beads and a stirring magnet. The apparatus was thoroughly purged with argon then evacuated and heated at 100°C for 12 hours. The apparatus was then alternately flushed with argon and evacuated several times. Tetrahydrofuran (THF), 60 ml, which had been distilled from sodium under nitrogen was then added with a syringe, and the argon flush alternating with evacuation was repeated several times. Sodium cyclopentadienide, 10 ml of a 2.5 M solution in THF, was added with a syringe, and the apparatus was stirred in the dark at room temperature for 72 hours. The orange-red solution was filtered, and the beads were washed with THF, with 1:1 THF-methanol, with methanol, with 50 percent aqueous dioxane until washes were chloride free, then with pure dioxane, and finally with toluene. This procedure removed essentially all color from the polymer. The residual toluene was removed under vacuum and the beads were analyzed for chloride. The remaining chloride was 0.317 meq/g indicating about 73 percent conversion of chloride to cyclopentadiene.

<u>Preparation of polymer supported titanocene dichloride</u>. Copolymer beads with appended cyclopentadiene groups were dried by boiling with toluene in a Schlenk apparatus followed by heating in a vacuum. Ten grams of the beads were slurried with 60 ml of dry, oxygen-free THF under an argon atmosphere and treated with 14.6 ml of 0.8 M methyl lithium in

ether. This was sufficient methyl lithium to react with both the chloride and cyclopentadiene present on the beads. Gas evolution (methane) was observed, and the beads rapidly turned purple. The beads were stirred for 9 hours. The slurry was cooled to -78°C, and 2.8 g of cyclopentadienyl titanium trichloride in 25 ml of THF was injected. The solution immediately turned red-black. After being stirred for 30 minutes at -78°C, the slurry was warmed to room temperature. During a seven day reaction period, the solution slowly became lighter in color while the beads assumed a dark red-orange color. The pale yellow-orange solution was then decanted, and the beads were washed with THF until no further color was removed. Storing under THF for 3 days resulted in no loss of color. The beads were dried *in vacuo*.

Preparation of polymer supported titanocene dimethyl. Copolymer beads with appended titanocene dichloride, 1.0 g, and 15 ml of dry, oxygen-free THF were added to a Schlenk tube and filter and thoroughly purged with argon. The slurry was cooled to -78°C and treated with 2 ml of 1.9 M CH_3Li in Et_2O. The slurry was stirred at -78°C for 1 hour, then at room temperature for 4 hours. The beads changed from red-orange to yellow-orange and finally to purple. The slurry was cooled to -78°C and treated with 1 ml of oxygen-free methanol. The beads immediately became yellow. The solvent was removed by filtration after the mixture had warmed to room temperature, and the beads were washed with methanol then with dry, oxygen-free THF. The yellow beads were dried under vacuum and stored under argon. Ir spectra (Nujol mull) were dominated by absorptions characteristic of polystyrene.

Preparation of benzyl cyclopentadiene. Under an argon atmosphere, 13.2 g (0.105 moles) of benzyl chloride was added slowly to 40 ml of 2.5 M sodium cyclopentadienide in THF. The solution was cooled in an ice bath. When the addition was complete, the solution was warmed to room temperature, treated with water, and extracted with ether. The ether was evaporated, and the resulting yellow oil was vacuum distilled at aspirator pressure. After a small forecut (bp 60°C), essentially pure (by nmr) benzylcyclopentadiene was collected in a receiver maintained at -78°C. No attempts were made to maximize the yield. A center cut (bp 110°C) was used immediately for the preparation of benzyl titanocene dichloride.

Preparation of benzyl titanocene dichloride. A dry argon purged 100 ml flask with a side arm covered by a rubber septum was charged with 20 ml of freshly distilled oxygen-free THF. Benzyl cyclopentadiene, 8.3 meq, was added with a syringe, and the solution was cooled to -78°C. Methyl lithium, 4.4 ml of 1.9 M ether solution, was injected. A rapid effervescence was observed. A solution of 1.81 g of $CpTiCl_3$ in 20 ml of THF was added with a syringe, and an instant formation of a very dark turbid reddish brown color was observed. After 30 minutes the turbidity was no longer apparent, and the solution was deep red. No further color changes were observed after standing 2 days at room temperature.

The solution was treated with 20 ml of concentrated HCl, then was extracted with 60 ml of chloroform. The chloroform was dried over sodium sulfate, filtered, and evaporated. The red-brown residue was washed with hexane, then dissolved in 40 ml of warm carbon tetrachloride. On cooling to -10°C copper-red plates formed. They were removed by filtration and redissolved in chloroform. A green-black tarry material that was insoluble in chloroform was removed, and the chloroform solution was again evaporated. The residue was crystallized twice from 50 ml of carbon tetrachloride to yield 1.4 g of red crystals (mp 135-142°C). The nmr spectrum was a singlet at 7.27 δ (5), a complex multiplet at 6.5 δ (9), and a singlet at 4.1 δ (2).

The composition of this compound was also confirmed by its mass spectrum. A trace amount of bis(benzyl)titanocene dichloride was present in the sample as evidenced by a peak at m/e = 392 of relative intensity 0.007 corresponding to loss of HCl from the molecule. (See Table 1.)

<u>Preparation of benzylcyclopentadienylcyclopentadienyldimethyltitanium(IV)</u>. Benzyl titanocene dichloride, 20 mg (0.059 mmole), and 2.0 ml of dry, oxygen-free THF were charged into an argon filled 25 ml pear flask with a flow control adaptor and a side arm sealed with a rubber septum. The red solution was cooled to -78°C, then treated with 0.2

ml (0.16 meq) of 0.8 M CH_3Li in Et_2O. The solution instantly turned greenish yellow. After being stirred at -78°C for 4.5 hours, 0.05 ml of anhydrous, oxygen-free methanol was injected. The solvent was then removed under vacuum with the temperature maintained below -10°C. A yellow waxy residue remained.

The residue was extracted with 2 ml of dried, oxygen-free petroleum ether (bp: 37-56). The yellow product was completely dissolved, leaving behind an insoluble white residue. The yellow solution was transferred with a syringe to a dried, argon filled, vial sealed with a rubber septum. Two additional 0.5 ml petroleum ether rinses of the reaction vessel were added, and the solution was cooled to -78°C, then concentrated to 1 ml. The turbid solution was warmed slightly until it became homogeneous and then was cooled slowly to -95°C. The temperature was cycled slowly between -95°C and -78°C a few times to increase the crystal size. The solvent was removed with a very fine syringe needle at -95°C, and the yellow crystals were dried under vacuum. The product was a bright yellow liquid at room temperature. The product was dissolved in CCl_4, and the nmr spectrum was taken: (60 MHz) singlet 7.26 δ (5), singlet 6.05 δ (5), complex multiplet centered at 5.8 δ (4), singlet 3.78 δ (2), and a singlet -0.2 δ (5.5).

Reaction of polymer supported titanocene dichloride with butyl lithium. Copolymer beads with appended titanocene dichloride, 0.51 g, were charged into a Schlenk tube

Table 1. Mass Spectrum of Benzylcyclopentadienylcyclopentadienyldichlorotitanium(IV).

m/e	Intensity	Assignment[a]
302	49	$M^+ - HCl$
273	100	$M^+ - C_5H_5$
267	22	$M^+ - Cl_2$
248[b]	20	$M^+ - C_6H_5CH_2{}^+$
237	70	$M^+ - HCl, C_5H_5$
213	35	$(C_5H_5)_2TiCl^+$
200	16	$M^+ - 2HCl, C_5H_5$
183	90	$C_5H_5TiCl_2{}^+$
178	1	$(C_5H_5)_2Ti^+$
155	65	$C_6H_5CH_2C_5H_4$
148	95	C_5H_5TiCl
128	26	$C_5H_5TiCH_3$
118	17	$TiCl_2$

[a] M^+ represents the molecular ion which was not detected in the spectrum.

[b] This m/e also corresponds to the molecular ion of titanocene dichloride.

and filter apparatus. After being purged thoroughly with argon, 10 ml of oxygen-free hexane was added followed by 0.5 ml of 2.25 M butyl lithium in hexane. There was a rapid color change on the beads from red-orange to dark grey. The solution became pale yellow.

Analysis of the gas phase by gas-liquid chromatography revealed the presence of at least four hydrocarbons which were identified from their retention times as butane, 1-butene, cis-2-butene, and trans-2-butene. Isobutene, however had a retention time nearly identical to trans-2-butene under the conditions employed. Butane was present in the butyl lithium solution. The other three compounds were not.

The dark grey beads were extremely air sensitive, particularly when free of solvent. An instant change from grey to brown occurred on exposure to traces of oxygen. The dry grey beads exhibited a strong esr signal, a singlet at 3300 gauss at 9.21 GHz.

Reaction of benzyl titanocene dichloride with butyl lithium. Benzyl titanocene dichloride, 70 mg, was charged into a dry 50 ml pear flask equipped with a magnetic stirring bar, a side arm sealed with a rubber septum, and a flow control adaptor. After the apparatus was purged with argon, 13 ml of dry, oxygen-free hexane was injected. The apparatus was further purged by alternate evacuation and argon flushing. The dichloride was only partially dissolved.

The mixture was cooled to -10°C, and a 0.18 ml of a

2.25 M hexane solution of butyl lithium was added with a syringe. The mixture was stirred at -10°C for 30 minutes and then at room temperature for 12 hours. A rapid color change from red to dark greenish brown and finally to grey-black was observed. The product remained only partially dissolved.

When the solvent was removed, the product was a grey powder and was extremely air sensitive giving yellow insoluble products on exposure to air.

Reaction of benzylcyclopentadienylcyclopentadienyldichlorotitanium(IV) with butyl lithium under a hydrogen atmosphere. Benzyl titanocene dichloride, 34 mg (0.1 meq), and 7.5 ml of hexane were cooled to -5°C and thoroughly purged with hydrogen. Butyl lithium, 0.2 meq, was added, and the mixture was stirred. Hydrogen was absorbed over a period of 7 minutes as the red slurry darkened to red-brown and then to violet. A total of 3.4 ml of hydrogen was absorbed (0.155 mmoles).

The violet slurry was warmed to room temperature and persisted as a light blue-violet precipitate under a green solid. Dry, oxygen-free toluene was injected, and after being stirred for 1 hour the grey solid had dissolved to give a black solution. Stirring of this solution under nitrogen at room temperature and then at -78°C produced no evidence of reaction with nitrogen.

Reaction of titanocene dichloride with butyl lithium under a hydrogen atmosphere. Titanocene dichloride, 150 mg (0.6 meq), was slurried with 10 ml of dry, oxygen-free hexane in a 50 ml pear flask fitted with a stirring magnet, a side arm sealed with a rubber septum, and a flow control adaptor. The apparatus was thoroughly purged with hydrogen by alternate evacuation and pressurization.

The slurry was cooled to -10°C, and 0.54 ml of 2.25 M butyl lithium (1.2 meq) in hexane was added.

The mixture absorbed hydrogen at 2 ml/min as the slurry changed from red to muddy brown, then finally to violet. A total of 19.4 ml of hydrogen was absorbed. (Theoretical hydrogen consumption for formation of violet di-μ-hydrido-bis-(dicyclopentadienyltitanium(III)) is 0.9 meq or 19.4 ml at -10°C.)

The violet compound changed to a dark, slightly greenish, grey slurry on warming to room temperature.

Preparation of $((C_5H_5)_2Ti)_2N_2$. The grey hydride prepared as described above was carefully stripped of hexane under mild vacuum, and then stirred with 10 ml of dry, oxygen-free toluene under argon. The grey material slowly dissolved with evolution of gas to give a black solution.

The black solution was cooled to -78°C, and the argon atmosphere was partially displaced with nitrogen. Over the space of a few minutes the black solution became very deep blue. The blue color was stable in toluene at -78°C under vacuum for at least 3 hours.

On warming to room temperature the blue solid disappeared with formation of the original black solution.

<u>Hydrogenations with polymer supported titanocene</u>. In a typical experiment, 0.040 mg of polymer supported titanocene dichloride (0.79 meq titanium per gram of copolymer beads) was treated with excess butyl lithium in hexane under hydrogen.

After stirring for 4 hours at room temperature, the hexane was drawn off with a syringe, and the dark grey beads were washed several times with dry, oxygen-free hexane.

The beads were then stirred rapidly with 10 ml of hexane under a hydrogen atmosphere for a few minutes. After equilibration, 0.15 ml of dry, oxygen-free cyclohexene was added.

Hydrogen absorption began immediately and was measured with a gas buret. Ambient pressure was maintained. The initial hydrogen uptake rate was 1.8 ml/min, and the cyclohexene was completely reduced in about 30 minutes.

<u>Hydrogenations with benzyl titanocene hydride</u>. Typically, 70 mg (0.2 meq) of benzyl titanocene dichloride in 10 ml hexane was reacted with 0.4 meq of butyl lithium at room temperature under argon. The argon was then displaced with hydrogen, and the grey-black slurry was stirred vigorously for a few minutes.

Dry, oxygen-free cyclohexene, 0.15 ml, was then injected, and hydrogen uptake was measured with a gas buret.

Ambient pressure and 25°C was maintained.

The initial hydrogen uptake rate was 2.5 ml/min, and the cyclohexene was completely reduced in about 25 minutes.

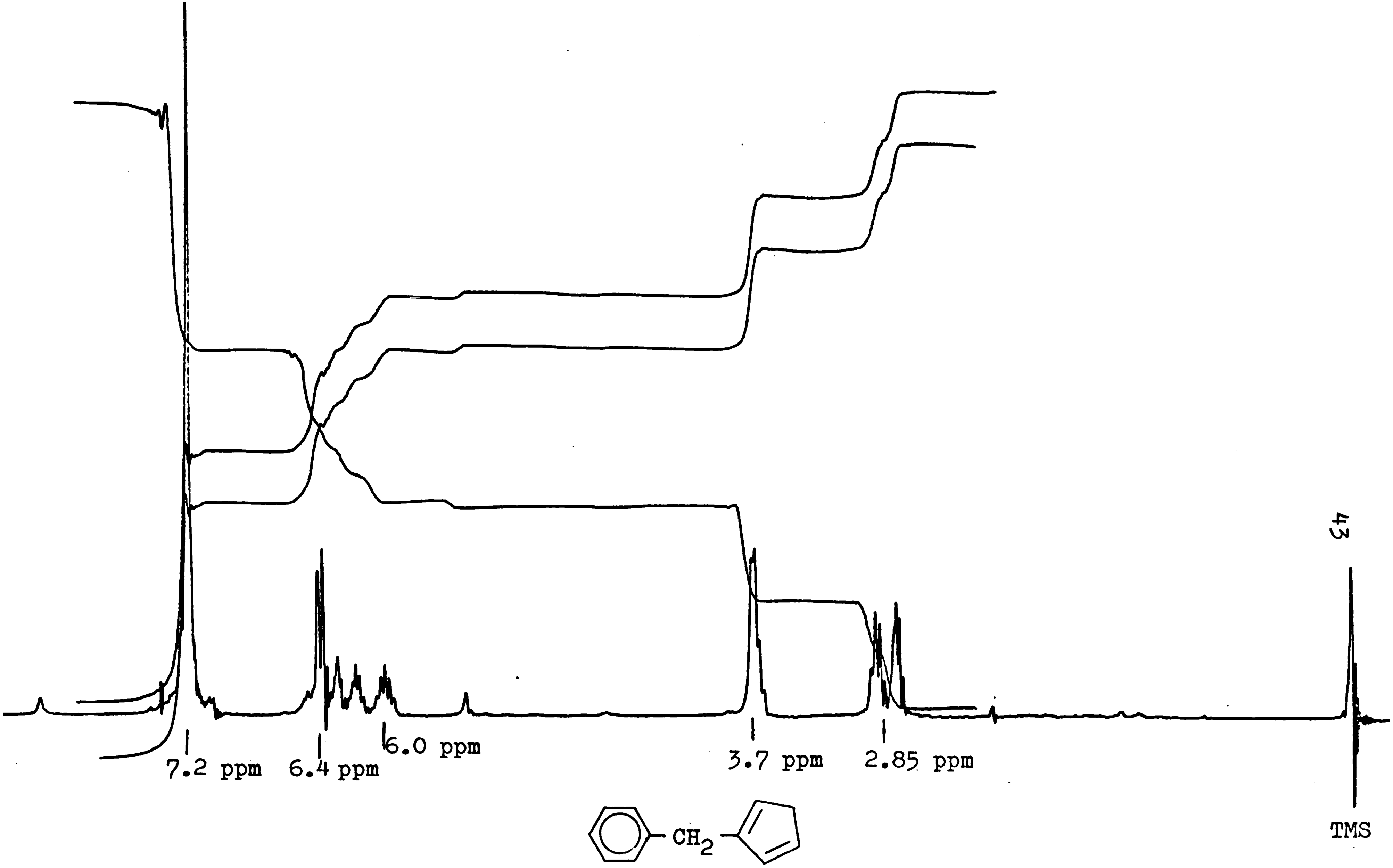
A subsequent injection of 0.15 ml of cyclohexene resulted in reduction at the same rate.

Hydrogenation with titanocene hydride. Titanocene dichloride, 50 mg, (0.2 meq) in 10 ml of hexane was treated with 0.4 meq of butyl lithium under argon at room temperature giving a grey precipitate in a black solution. The argon atmosphere was displaced with hydrogen, and the solution was stirred vigorously for a few minutes.

Cyclohexene, 0.15 ml, was then injected, and hydrogen uptake began immediately. The absorption of hydrogen was followed with a gas buret, and ambient pressure was maintained.

The initial absorption rate was 2.5 ml/min. Reduction was essentially complete within about 35 minutes.

SPECTRA



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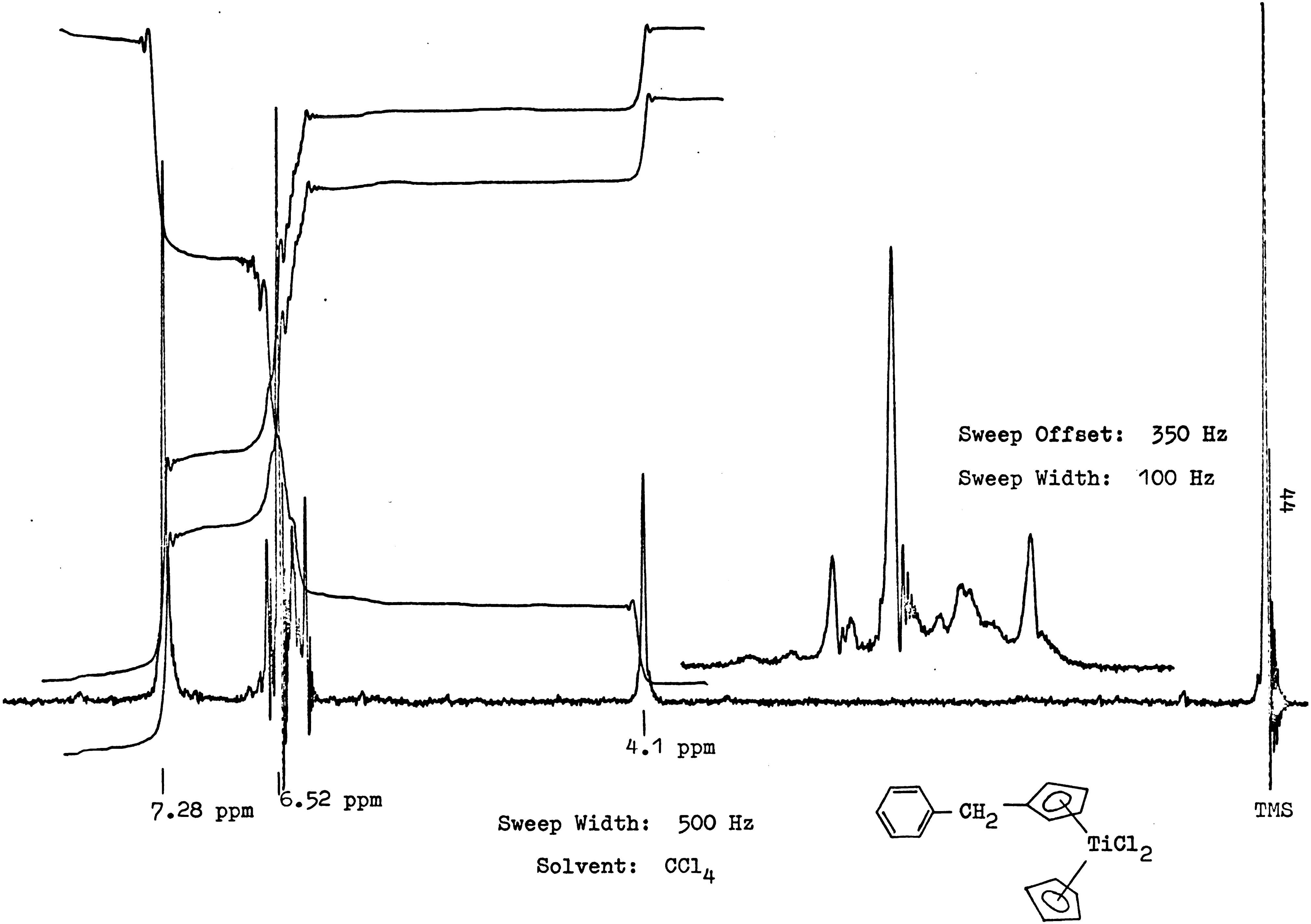
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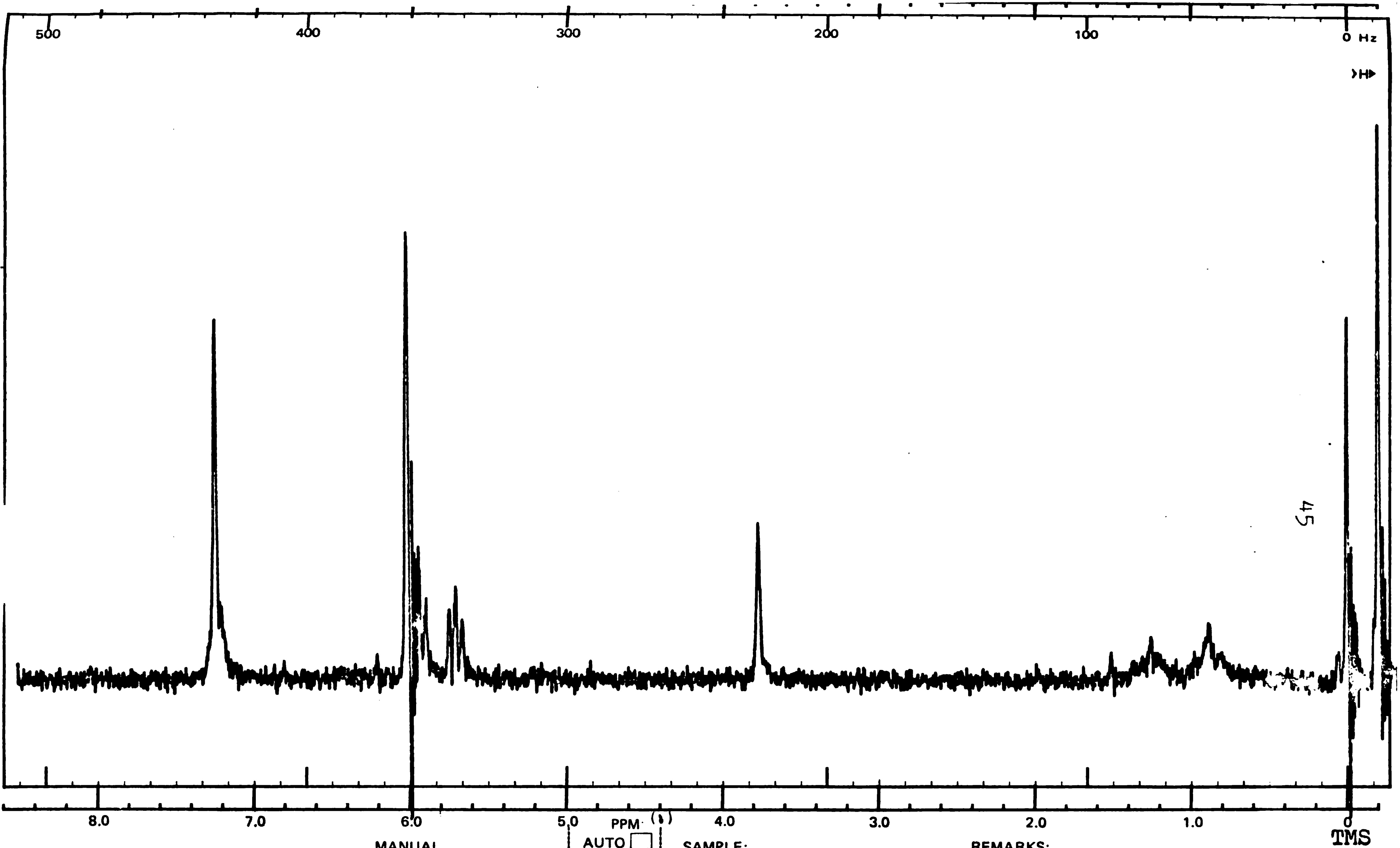

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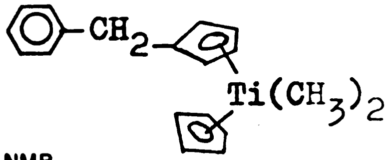

60 MHz NMR

DATE: 5/19/72

OPERATOR CLG

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THOMPSON PACKARD
(201) 777-3315
48 NOTCH ROAD, LITTLE FALLS NEW JERSEY 07424
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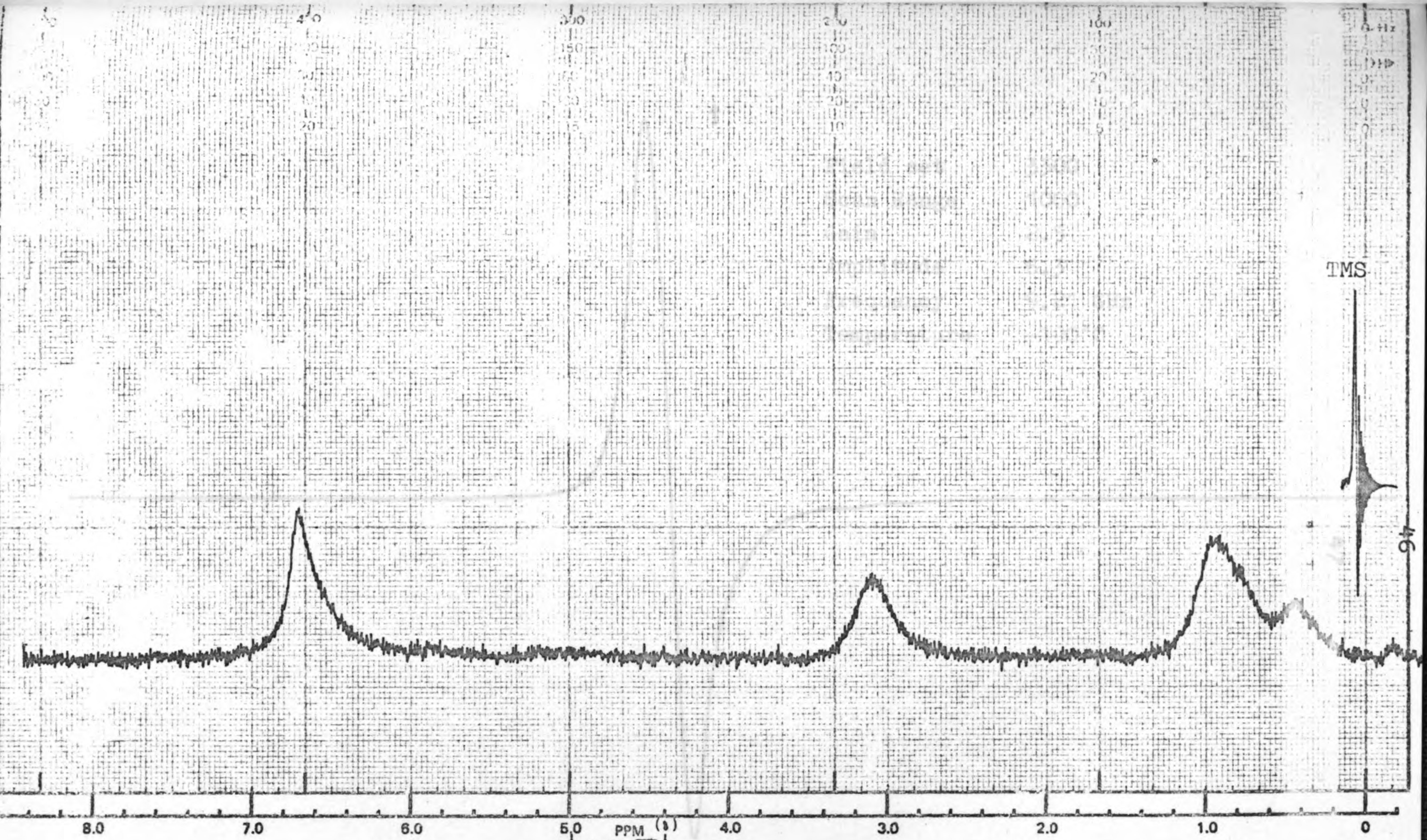

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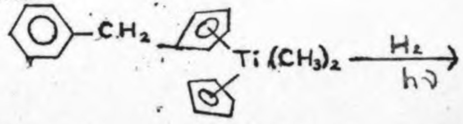

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OPERATOR

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NOTCH ROAD, LITTLE FALLS NEW JERSEY 07424
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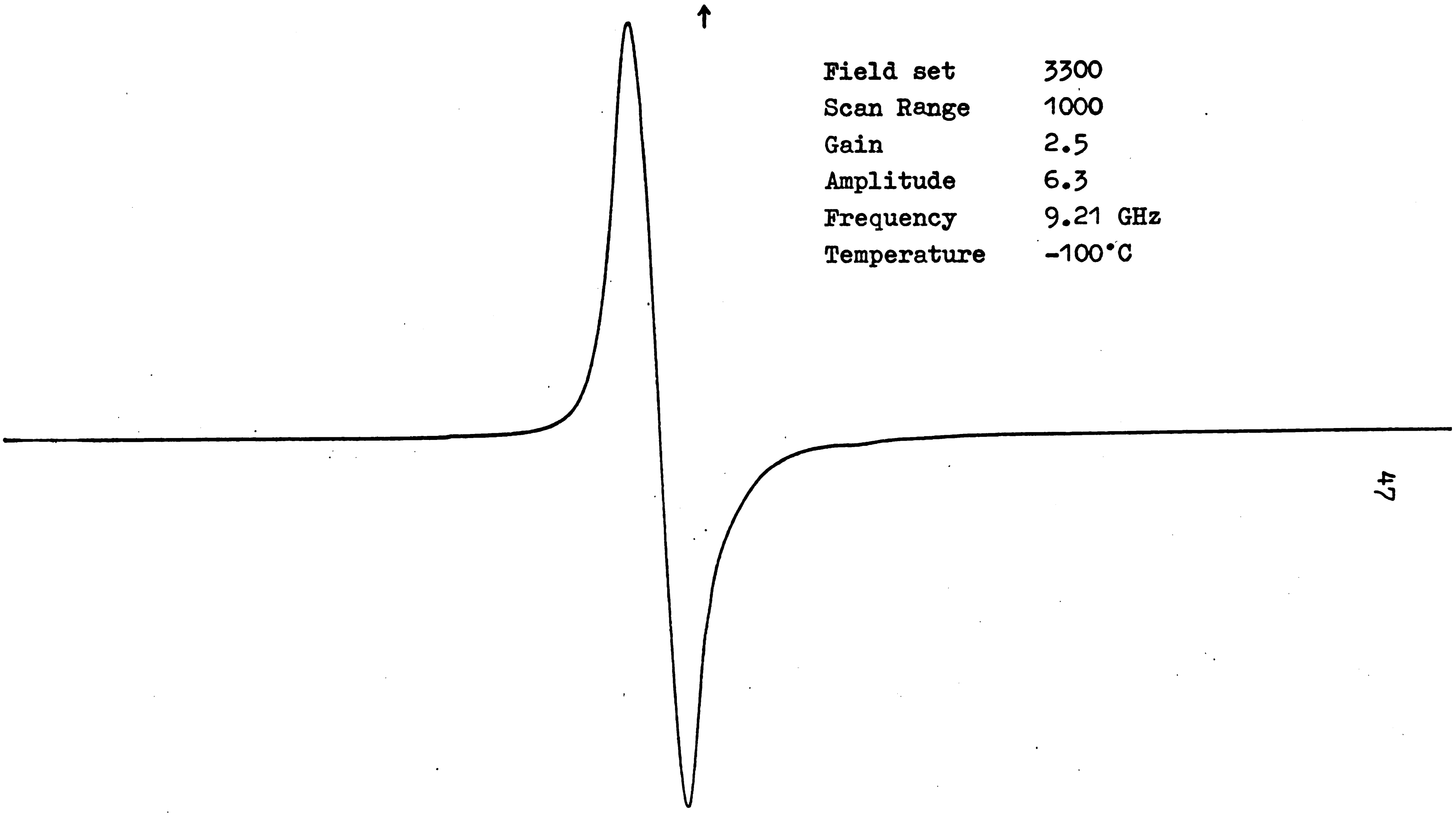

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Amplitude	6.3
Frequency	9.21 GHz
Temperature	-100°C

Polymer Supported Titanocene
(dry beads)

LIST OF REFERENCES

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