Hydride, Alkyl, and Allyl Complexes of Bis(π-cyclopentadienyl)titanium(III)

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Abstract: Formation of alkyl and allyl complexes of bis(π-cyclopentadienyl)titanium(III) in the presence of the appropriate organomagnesium or -lithium compounds in ethereal solutions can be observed by electron paramagnetic resonance. Whereas mono- and dimethyl complexes are stable at room temperature, olefin elimination occurs with ethyl and isopropyl complexes, leading to mono- and dihydride complexes of bis(π-cyclopentadienyl)-titanium(III). Alternative reactions leading to these hydride derivatives are likely to involve an autocatalyzed cleavage of the ethereal solvents. The observed conversion reactions between alkyl, hydride, and π-allyl derivatives are discussed in terms of possible reaction mechanisms.

Evidence from electron paramagnetic resonance for the formation of hydride complexes of bis(π-cyclopentadienyl)titanium(III) in the presence of Grignard reagents has been reported in a preliminary publication.[1] Results of more detailed studies are presented here. These results include further resolution of the epr spectra of the hydride complexes and observation of those of alkyl derivatives which occur as reaction intermediates and lead to a partial revision of structural assignments proposed earlier.[1,2] Study of these systems is of interest because of their activity in low-pressure ethylene polymerization,[3,4] their participation in a recently reported synthesis of π-allyl complexes,[5] and their peculiar reactivity toward molecular nitrogen.[6]

Experimental Section

A highly purified sample of $(\pi\text{-C}_5\text{H}_5)_2\text{TiCl}_2$ was obtained as a gift from Arapahoe Chemical Co., Boulder, Colo. Solutions of $(\pi\text{-C}_5\text{H}_5)_2\text{TiCl}$ in ether or tetrahydrofuran were prepared by reduction of a suspension of $(\pi\text{-C}_5\text{H}_5)_2\text{TiCl}_2$ in the respective solvent with zinc dust and subsequent filtration. This reaction, as well as the addition of organomagnesium or -lithium compounds, and the spectral measurements were conducted in an atmosphere of prepurified argon. Epr spectra were taken on a Varian 4501 spectrometer. To obtain the spectra recorded below, the spectrometer was routinely operated at microwave powers of 0.2–0.5 mw, where no saturation was ever observed with the titanocene systems. Field modulations were kept below 0.08 gauss, in order to secure full resolution of the spectra. For an analysis of hyperfine coupling constants in the more complicated epr spectra, an appropriate stick spectrum was calculated, subsequently convoluted with the derivative of a Gaussian or Lorentzian function, and plotted out for comparison with the observed spectra, by means of an IBM 7090 computer and a Calcomp plotting system.

Results and Discussion

1. Dihydride Complex. The epr spectrum of $(\pi\text{-C}_5\text{H}_5)_2\text{TiCl}$ (**1**) in 0.01–0.1 M solutions in ether or THF exhibits a signal at $g = 1.980$.[7] Upon addition of a solution of a metal alkyl compound, such as ethyl- or isopropylmagnesium halides, or ethyl- or isopropyllithium, in 10–50-fold excess over the titanium compound, this signal disappears and, through intermediary stages to be discussed below, a new signal arises, which is shifted to lower fields by *ca.* 20 gauss ($g = 1.992$) and exhibits a triplet hyperfine splitting with 1:2:1 intensity distribution.[7] The hyperfine splitting of 7–8 gauss is somewhat dependent on solvents and temperatures. A solvent dependence is also observed for the rate with which the new signal appears after addition of the ethylmagnesium or -lithium compound. In ether solutions at room temperatures, it is fully developed already within a few minutes; in tetrahydrofuran solutions, on the other hand, periods up to 1 hr or heating for 10–20 min at 60° are required for the complete development of the triplet signal.

If the completely deuterated Grignard reagent, d_5-ethylmagnesium bromide, is added to **1**, a signal with a partly resolved quintuplet hyperfine pattern appears in place of the triplet. The spectrum shows a remainder of the triplet signal still superimposed on this quintuplet, with an estimated 10–20% of the total intensity. The gross appearance of the spectrum leads to an estimation of *ca.* 2.4 gauss for the deuterium hyperfine coupling constant.[8]

The triplet pattern described above is most likely due to an interaction of the unpaired electron of bis(π-cyclopentadienyl)titanium(III) with two hydride ligands bound to the titanium(III) center. The possibility that the observed splitting is due to protons still attached to alkyl groups is ruled out by the fact that it is independent of the nature of the alkyl reagent used. Obviously, hydride ions are transferred onto the titanium center from the alkyl groups under elimination of olefin. Evolution of roughly equivalent, though somewhat irreproducible, amounts of ethylene or propene is observed during the reaction period.[9] Accordingly, the deuterated Grignard reagent produces a dideuteride complex of $[(\pi\text{-C}_5\text{H}_5)_2\text{Ti}^{\text{III}}]^+$, characterized by the quintuplet arising from two deuterium nuclei with spin $I = 1$. The occurrence, along with the deuteride transfer, of some hydride transfer in this reaction is

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[1] H. Brintzinger, *J. Am. Chem. Soc.*, **88**, 4305 (1966).
[2] H. Brintzinger, *ibid.*, **88**, 4307 (1966).
[3] W. P. Long and D. S. Breslow, *ibid.*, **82**, 1953 (1960).
[4] K. Clauss and H. Bestian, *Ann. Chem.*, **654**, 8 (1962).
[5] H. A. Martin and F. Jellinek, *J. Organometal. Chem.*, **6**, 293 (1966).
[6] M. E. Vol'pin and V. B. Shur, *Nature*, **209**, 1236 (1966).
[7] Weak satellite lines originating from ^{47}Ti and ^{49}Ti are observable in this as in most of the other spectra reported here.
[8] A complete analysis of the spectrum is complicated by the fact that, in addition to the dihydride triplet and the dideuteride quintuplet, the presence of an unresolved quartet component, arising from a hydride–deuteride species, is to be suspected in the signal.
[9] Since these reaction systems are known to have a catalytic activity for olefin polymerization, and since additional gas evolution might be due to ether cleavage reactions, this irreproducibility is not too surprising.

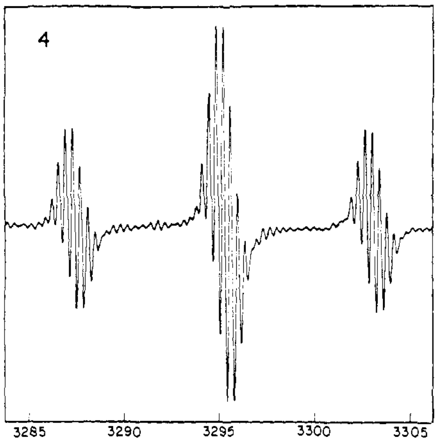

Figure 1. $[(\pi\text{-}C_5H_5)_2TiH_2]^-$. To a solution of 2.5 mg of $(\pi\text{-}C_5H_5)_2TiCl_2$ in 10 ml tetrahydrofuran is added 1.0 ml of 2 *M* ethylmagnesium chloride in ether; the solution is allowed to stand at room temperature for 2 hr: spectrum taken at −70°; $\nu = 9.188$ Gc ($g = 1.992$).

mostly likely due to an ether cleavage reaction at some intermediate stage of the reaction; very little increase of the hydride triplet is observed after the initial reaction period.

If the reaction mixtures are more dilute, so as to contain **1** in *ca.* 2×10^{-4}–2×10^{-3} *M* concentrations, additional resolution of the hyperfine splittings can be observed at temperatures between −20 and −100°. Figure 1 shows that each of the triplet components is split into a rather large number of lines. This number is not directly enumerable, because of the occurrence of weak additional lines between the main (^{48}Ti) components arising from ^{47}Ti and ^{49}Ti contributions. However, the intensity distribution of the hyperfine lines allows a detailed analysis. Simulation of the spectra from the appropriate stick spectra shows that a satisfactory reproduction of the observed pattern can be achieved only under the assumption that ten equivalent nuclei with spin $I = {}^1/_2$ cause the additional splitting. The splitting constants are 0.43 gauss in tetrahydrofuran and 0.37 gauss in ether. Line widths, 0.2 gauss under these conditions, increase sensitively with rising concentrations of **1**.

It seems fairly safe to identify the ten equivalent nuclei as the ten protons of the two π-cyclopentadienyl rings which are associated with each Ti(III) center. In titanocene derivatives, the two aromatic rings are usually not parallel, but an unrestricted rotation of the rings about the bond axis through the metal atom would make the interaction of the unpaired electron with each of the ten ring hydrogens effectively equivalent.

This additional hyperfine splitting leads to a revision of the structural assignment given for the triplet spectrum in a preliminary communication.[1] There, a dinuclear structure (**2**) was proposed to account for the interaction of each Ti(III) center with two hydrogen ligands. However, sharp epr signals of the observed kind are to be expected from such a complex only if the unpaired electrons on the two Ti(III) centers were strongly coupled to a triplet state.[10] In this case, however, an interaction with 20 hydrogen atoms should appear in the hyperfine splitting pattern. The occurrence of a splitting due to only ten hydrogen atoms indicates that a mononuclear bis(π-cyclopentadienyl)titanium(III) complex is responsible for the observed spectrum. The presence of two hydride ligands requires its formulation as the complex anion $[(\pi\text{-}C_5H_5)_2TiH_2]^-$. Whether and, if so, in which way lithium and magnesium countercations are associated with this anion cannot be inferred from the present data.[10a]

By its composition, $[(\pi\text{-}C_5H_5)_2TiH_2]^-$ has a pronounced resemblance to the well-known complexes $(\pi\text{-}C_5H_5)_2MoH_2$ and $(\pi\text{-}C_5H_5)_2WH_2$ (**3**). It seems rather likely that it is also structurally related to these complexes. If the middle hybrid orbital (ψ_x), which presumably accommodates the unshared electron pair in $(\pi\text{-}C_5H_5)_2MoH_2$,[11] is thought to contain the unpaired electron in $[(\pi\text{-}C_5H_5)_2TiH_2]^-$, structure **4** would result for the latter.

The reactivity of the novel titanocene dihydride complex, however, differs vastly from that of the molybdenum and tungsten analogs. Whereas these complexes react with acids under addition of a further proton to form the complex cations $[(\pi\text{-}C_5H_5)_2MoH_3]^+$ and $[(\pi\text{-}C_5H_5)_2WH_3]^+$, $[(\pi\text{-}C_5H_5)_2TiH_2]^+$ is immediately decomposed even by weakly acidic reagents such as water or methanol, under elimination of hydrogen, probably to the hydroxy or methoxy derivatives of **1**. Hydrogen chloride oxidizes further to the titanocene(IV) derivative $(\pi\text{-}C_5H_5)_2TiCl_2$ (identified by its absorption spectrum). This reaction distinguishes the hydride complex from the nonhydridic reductant $[(\pi\text{-}C_5H_5)_2Ti]_2$ which reacts with hydrogen chloride to form a yet unidentified purple compound different from $(\pi\text{-}C_5H_5)_2TiCl_2$.[12] If the decomposition of $[(\pi\text{-}C_5H_5)_2TiH_2]^-$ is carried out with D_2O, the evolved hydrogen gas is a mixture of H_2, HD, and D_2 in an exact 1:2:1 ratio, indicating that the water is indeed reduced by a hydride compound.[13]

This high reactivity of the titanium(III) hydride complex toward protonic agents implies that the hydrogen ligands have appreciably more hydridic character, *i.e.*, that the metal–hydrogen bond is more ionic here than in the aforenamed compounds.[14]

Other possibilities to obtain the titanocene dihydride complex include the reaction of $(\pi\text{-}C_5H_5)_2TiCl_2$ with Grignard reagents, as already mentioned.[1] The epr signal of $(\pi\text{-}C_5H_5)_2TiCl$ is observable in the reaction mixtures at intermediate stages of the reduction.

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(10) Even then the anisotropic zero-field splitting would probably wipe out the hyperfine pattern in the solution spectra of such a triplet species. The author is grateful for discussions, related to this point, with Drs. R. H. Sands, A. Ehrenberg, and J. van Voorst.

(10a) Note Added in Proof. After completion of the manuscript, the author was kindly made aware by Dr. H. A. Martin of unpublished experiments which led to similar conclusions concerning the structure of this complex (Dissertation of H. A. Martin, Rijksuniversiteit te Groningen (Netherlands), 1967).

(11) G. J. Ballhausen and J. P. Dahl, *Acta Chem. Scand.*, **15**, 1333 (1961).

(12) G. W. Watt, L. J. Baye, and F. O. Drummond, Jr., *J. Am. Chem. Soc.*, **88**, 1138 (1966).

(13) Two moles of hydrogen per mole of titanocene should be evolved by decomposition with water. Figures close to 2 were indeed reported for this H_2/Ti ratio by G. N. Nechiporenko, G. M. Tabrina, A. K. Shilova, and A. E. Shilov, *Dokl. Akad. Nauk USSR*, **164**, 1062 (1965). In our hands, however, the yields of hydrogen were appreciably lower.

(14) This ionic character of the metal hydride bond might be related to the observation by B. D. James, R. K. Nanda, and M. G. H. Wallbridge, *Chem. Commun.*, 849 (1966), that $(\pi\text{-}C_5H_5)_2TiBH_4$ is not split by amines to $(\pi\text{-}C_5H_5)_2TiH$ and the base adduct of BH_3. In contrast to the derivatives of quadrivalent metals, where this reaction was found to occur, it can be expected that a high ionicity of the Ti^{III}–H bond would give $(\pi\text{-}C_5H_5)_2TiBH_4$ much of the stability of $LiBH_4$ against decomposition by amines.

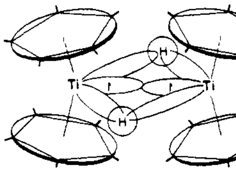
The epr spectrum of the dihydride complex **4** appears also in tetrahydrofuran or ether solutions of $[(\pi\text{-}C_5H_5)_2Ti^{II}]_2$, after addition of ethylmagnesium chloride or ethyllithium. It is not obvious which reagents in this reaction mixture could bring about an oxidation of the titanocene from the Ti(II) to the Ti(III) stage. Only by involvement of solvent is it possible to formulate a suitable stoichiometry.

$$[(\pi\text{-}C_5H_5)_2Ti]_2 + 4LiEt + 2Et_2O \longrightarrow 2[(\pi\text{-}C_5H_5)_2TiH_2]^- + 2Li^+ + 2LiOEt + 5C_2H_4 + C_2H_6$$

Yet another way to obtain the dihydride complex is the reduction of $(\pi\text{-}C_5H_5)_2TiCl_2$ in tetrahydrofuran solution by metallic magnesium. Here, involvement of the solvent as a source of the hydrogen ligands has to be invoked with necessity. In these reaction mixtures no reaction occurs for an initial period of 0.5 to 2 hr, after which, once the reactions start, the reduction to the hydride complex is complete within a few minutes, as judged by its epr spectra. Apparently, the reaction is autocatalytic with respect to one of the reduction products of $(\pi\text{-}C_5H_5)_2TiCl_2$. This is even more obvious if the reaction is carried out in ether; there, no reaction between $(\pi\text{-}C_5H_5)_2TiCl_2$ and metallic Mg occurs at all. If, however, a subequivalent amount of isopropylmagnesium chloride, *e.g.*, 0.25 mmole per mmole of titanocene, or a solution containing preformed titanocene hydride, is added to the reaction mixture, reduction to the hydride is complete within a few hours.

$$2(\pi\text{-}C_5H_5)_2TiCl_2 + 5Mg + 4Et_2O \longrightarrow 2[(\pi\text{-}C_5H_5)_2TiH_2]^- + 2MgCl^+ + MgCl_2 + 2Mg(OEt)_2 + 4C_2H_4$$

2. **Dialkyl Complexes.** Addition of methyl-, ethyl-, or isopropyllithium in a 20–50 fold excess to solutions of **1** in tetrahydrofuran at *ca.* −70° produces the spectra given in Figure 2a–c. Identical spectra are obtained on addition of the respective organomagnesium halides. The septet hyperfine splitting with methyl, the quintuplet with ethyl, and the triplet with isopropyl compounds correspond in all cases to an equivalent splitting due to the α-hydrogen atoms of two respective alkyl groups and leave no reasonable doubt that dialkyl complexes are formed under these conditions. As with the dihydride, the presence of two alkyl ligands on the Ti(III) derivative requires their formulation as complex anions (**5–7**).



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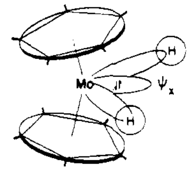

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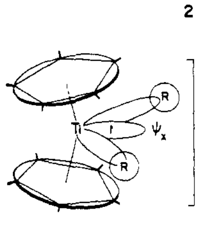
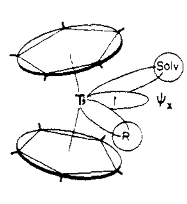
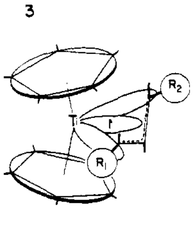


4 : R = -H
5 : R = -CH$_3$
6 : R = -CH$_2$CH$_3$
7 : R = -CH(CH$_3$)$_2$



1 : R = -Cl
8 : R = -H
9 : R = -CH$_3$
10 : R = -CH(O-CH$_2$-CH$_2$-CH$_2$) (tetrahydrofuran-2-yl)



11 : R$_1$ = R$_2$ = -H
12 : R$_1$ = R$_2$ = -CH$_3$
13 : R$_1$ = H, R$_2$ = -CH$_2$CH$_3$

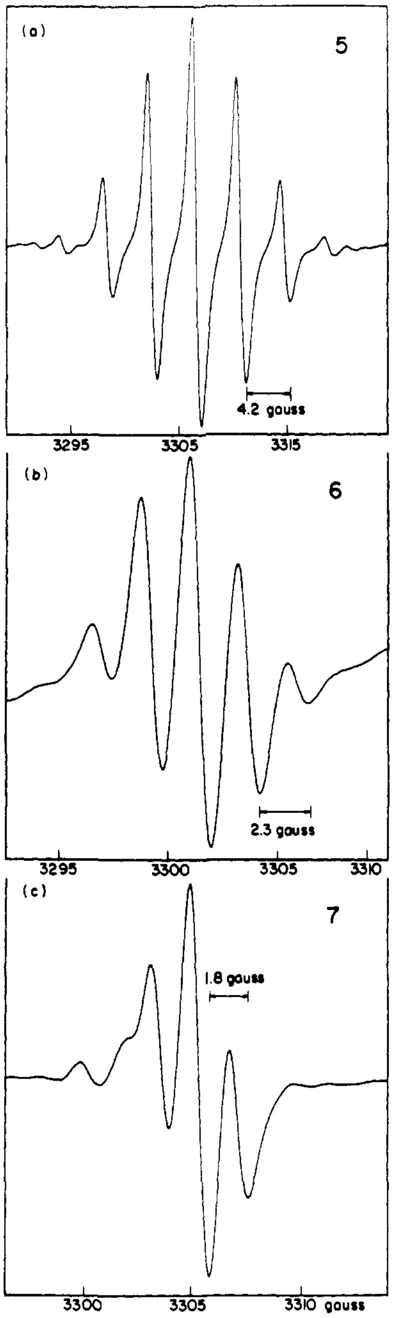


Figure 2. (a) $[(\pi\text{-}C_5H_5)_2Ti(CH_3)_2]^-$. To 5 ml of a 5×10^{-3} *M* solution of $(\pi\text{-}C_5H_5)_2TiCl$ in ether is added, at room temperature, 1 ml of 1.5 *M* methyllithium in ether: spectrum taken at −65°, ν = 9.214 Gc (g = 1.99$_0$). (b) $[(\pi\text{-}C_5H_5)_2Ti(CH_2CH_3)_2]^-$. To 8 ml of a 10^{-2} *M* solution of $(\pi\text{-}C_5H_5)_2TiCl$ in tetrahydrofuran is added 1 ml of 0.5 *M* ethyllithium in benzene; 1 min after addition at room temperature, the solution is cooled to −35° to obtain the spectrum: ν = 9.196 Gc (g = 1.99$_0$). (c) $[(\pi\text{-}C_5H_5)_2Ti(CH(CH_3)_2)_2]^-$. To 8 ml of a 5×10^{-3} *M* solution of $(\pi\text{-}C_5H_5)_2TiCl$ in tetrahydrofuran, cooled to −70°, is added 0.2 ml of 2 *M* isopropyllithium in benzene: spectrum taken at −50°, ν = 9.215 Gc (g = 1.99$_1$).

The isotropic coupling constants for the α-hydrogen atoms decrease in the following order: dimethyl (4.2 gauss), diethyl (2.3 gauss), diisopropyl complex (1.8 gauss). This tendency is contrary to what one might expect from the decreasing electronegativities of the organic ligands and the accordingly increasing metal–ligand covalency in this series. More likely, therefore, the size of the coupling constants of the metal–ligand

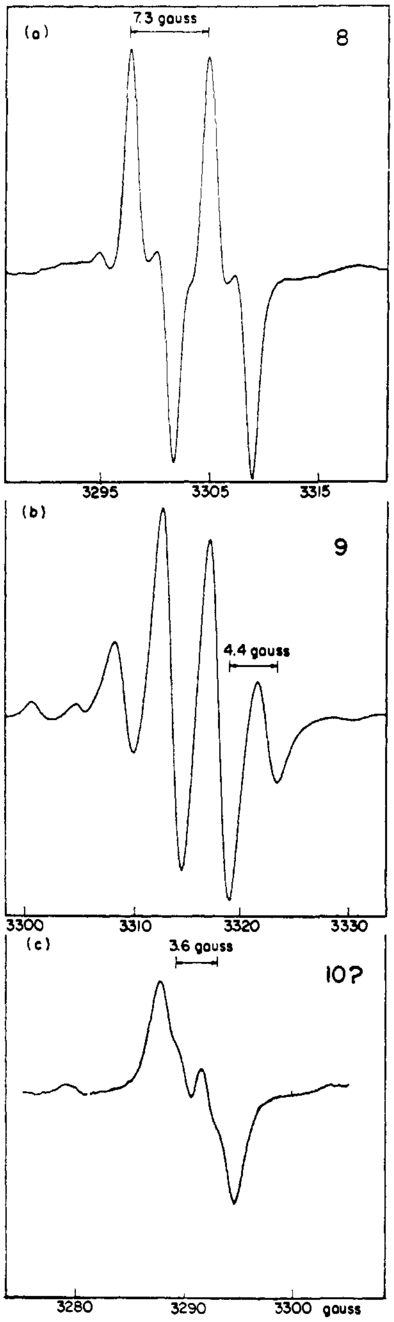


Figure 3. (a) $(\pi\text{-}C_5H_5)_2TiH \cdot solv?$. To 8 ml of a 5×10^{-3} *M* solution of $(\pi\text{-}C_5H_5)_2TiCl$ in tetrahydrofuran, cooled to −70°, is added 0.2 ml of 0.6 *M* isopropyllithium in benzene. The solution is allowed to warm to room temperature for 5 min, then cooled again to −60° to obtain the spectrum: $\nu = 9.211$ Gc ($g = 1.99_2$). (b) $(\pi\text{-}C_5H_5)_2TiCH_3 \cdot solv?$. To 8 ml of a 5×10^{-3} *M* solution of $(\pi\text{-}C_5H_5)_2TiCl$ in tetrahydrofuran is added, at room temperature, 1 ml of 2 *M* methylmagnesium iodide in ether: spectrum of the supernatant taken at −65°, $\nu = 9.215$ Gc ($g = 1.98_6$). (c) $(\pi\text{-}C_5H_5)_2Ti(C_4H_7O)? \cdot solv?$. To 8 ml of a 5×10^{-3} *M* solution of $(\pi\text{-}C_5H_5)_2TiCl$ in tetrahydrofuran is added, at room temperature, 0.2 ml of 0.5 *M* isopropyllithium in benzene: spectrum taken at −70°, $\nu = 9.195$ Gc ($g = 1.99_1$).

bonds is governed by geometric factors, like lateral displacements or rotational restrictions due to interactions between alkyl and ring ligands, which in turn would affect the overlap of α hydrogens with the ψ_x-hybrid orbital containing the unpaired electron. No hyperfine interaction due to the cyclopentadienyl protons, as in the dihydride complex, was observable with any of the dialkyl complexes. This again, if not due to experimental limitations, might be caused by steric interactions between the alkyl ligands and the aromatic rings, hindering these from free rotation (an increase in line width from 0.2 gauss to 0.4 gauss is sufficient to completely swamp the eleven-line hyperfine structure from the ring protons and would indeed produce a gaussian signal envelope with an apparent line width of *ca.* 1 gauss, as is observed in the spectra of Figures 2 and 3).

The three dialkyl complexes show striking differences in stability as their solutions are warmed to room temperature. The diisopropyl complex is only stable in tetrahydrofuran solutions at low temperatures; at room temperature it is decomposed, within 2–3 min, either to the dihydride complex discussed above or, at lower excess concentrations of the isopropyllithium or magnesium compound, to a monohydride complex (see below). Even at *ca.* −50° incipient decomposition is noticeable in the epr spectrum. The dimethyl complex, on the other hand, shows no perceptible decomposition in ether or tetrahydrofuran solutions at room temperature. The diethyl complex shows an intermediate behavior in that tetrahydrofuran solutions of this complex are completely decomposed to the dihydride only after a period of *ca.* 1–2 hr at room temperature. In ether solutions, however, this complex decomposes to the dihydride within *ca.* 5 min.

The spectrum of the diethyl complex has been observed earlier,[2] but was erroneously interpreted at that time. In solutions containing the product of the Vol'pin–Shur reaction[6] with nitrogen, a five-line signal was observed after partial acidification with gaseous HCl. This signal is now found to be identical with the one in Figure 2b, *i.e.*, to be due to formation of the diethyl complex under these conditions. Obviously, the nitrogen-containing reaction product is split by local acidification of the solution, and excess ethyl Grignard still present subsequently regenerates the diethyl species. The signal reported in ref 2 has therefore no direct relevance for the structure of the product of the nitrogen reaction except that its occurrence indicates the presence of the intact $(\pi\text{-}C_5H_5)_2Ti$ moiety in this reaction product.

3. Monohydride and Monoalkyl Complexes. A species with a hyperfine pattern assignable to one hydride ligand was obtained when a tetrahydrofuran solution of the diisopropyl complex **7** containing only a *ca.* two- to threefold excess of isopropyllithium was warmed to room temperature for *ca.* 5 min and then cooled again to −70° (spectrum in Figure 3b). The splitting constant of 7.3 gauss is practically the same as that observed with the corresponding dihydride complex, thus supporting a structure with one hydride ligand directly attached to the titanium center (structure **8**). No hyperfine interaction due to the ten-ring hydrogens is resolved in the spectra, but an additional splitting due to a single hydrogen atom, with a coupling constant of 1.7 gauss, is observed in addition to the main splitting. No safe interpretation for the origin of this splitting can be offered at the moment, but it seems possible that a solvent molecule is coordinated in such a way as to expose one of its hydrogen atoms to a dominant interaction with the unpaired electron in the ψ_x orbital.

If the solution is warmed to room temperature for another 5–10 min, the spectrum of the monohydride disappears again, giving way to a complicated superposition of several many-line spectra, the interpretation of which has not been attempted yet.[15] Occasionally the monohydride spectrum was observed also upon addition of lower concentrations of ethyllithium or ethylmagnesium bromide to tetrahydrofuran solutions of **1**. However, unlike the other spectra reported here, the occurrence of this spectrum was not safely reproducible. Obviously, the period of time at room temperature after which the conversion reactions have to be quenched at $-70°$ in order to stabilize this species is critically dependent on some yet unidentified factors.

When methylmagnesium iodide is added to **1** so as to introduce only a slight excess concentration, which can be conveniently achieved by using tetrahydrofuran as a solvent in which the organomagnesium iodides have fairly low solubilities, the spectrum in Figure 3b is observed. The quartet hyperfine splitting shows that only one methyl ligand is complexed to the titanocene cation now. The splitting constant of 4.4 gauss, practically the same as was found in the septet of the dimethyl complex, also supports this assignment. Further alkylation or dimerization of this complex is possibly prevented by a solvent molecule complexed to the otherwise vacant coordination site (structure **9**). The quartet spectrum of the monomethyl complex shows no noticeable changes on standing at room temperature.

If isopropyl- or ethyllithium is added to THF solutions of **1** at room temperature, in amounts insufficient to produce the dihydride complex (in *ca.* two- to threefold excess), two species are observed in approximately equal concentrations by their epr spectra. One of them has a *g* value very close to that of **1** and might thus be either unreacted titanocene(III) chloride (**1**) or else some alkoxy derivative of **1**.[15] The other species, the concentration of which increases with increasing excess of isopropyllithium until finally the dihydride complex begins to be formed, has its signal occurring in the *g*-value region of the alkyl and hydride complexes of **1**. The signal is split by an interaction with two nonequivalent hydrogen atoms (Figure 3c). A main doublet splitting of 3.6 gauss is in turn split by a second hydrogen atom with 1.7 gauss. Both signals are stable at room temperatures.

No unambiguous structural assignment is obvious for this latter species. The main splitting of 3.6 gauss is much lower than the splittings observed with hydride ligands and rather in the range of the alkyltitanocenes. However, the fact that the same species is obtained irrespective of the nature of the added organolithium compounds excludes the possibility that the observed spectrum is due to a monoalkyl species. The distinct possibility exists that a monohydride which is primarily formed from the monoalkyl species converts subsequently, by hydrogen abstraction from the ether solvents, to species like **10**.[16] Species of this kind might, by analogy to the alkyl complexes, give rise to a doublet splitting in the observed range. The origin of the smaller splitting (1.7 gauss) remains obscure, like that observed in the monohydride spectrum (Figure 3a). Further identification of these two species must obviously await additional analytical and synthetic information.

4. π-Allyl Complexes. According to Martin and Jellinek, π-allyl complexes of bis(π-cyclopentadienyl)-titanium(III) are obtained by reaction of **1** either with allylmagnesium bromide or with isopropylmagnesium bromide and a diolefin.[5,17] When ether solutions of **1** are treated with a slight (two- to threefold) excess of allylmagnesium bromide, the spectrum in Figure 4a is obtained. This spectrum, which is undoubtedly due to the complex $(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\pi\text{-C}_3\text{H}_5)$ present in these solutions, exhibits at least 28 lines, separated by *ca.* 0.4 gauss each. The spectrum is slightly unsymmetrical; this is possibly caused by the presence of minor amounts of some species, the spectrum of which would then be superimposed on that of the allyl complex. In view of this unsymmetry, an analysis of the intensity pattern in terms of contributions from the various hydrogen atoms has not been undertaken. However, from the number of lines it is clear that splitting due to the ten ring hydrogens must be observable. The smallest resolved splitting, 0.4 gauss, is quite similar to that observed for the ring hydrogens in the dihydride complex. It is quite likely, therefore, that here also this splitting is due to the ring hydrogens and that the splittings from the various allyl hydrogens are approximate multiples of this number.

In the spectrum of the dimethylallyl complex obtained from **1**, isopropylmagnesium bromide, and 1,3-pentadiene (1:2:20) superposition of spectra from two species is clearly discernible (Figure 4b). With each of the two components at least 16 lines are observed, separated by *ca.* 0.4 gauss again. Theoretically, three *syn–anti* isomers might be expected for the 1,3-dimethyl-π-allyl complex **12**. In addition, the diolefin might be added in such a way as to form the 1-ethyl-π-allyl complex **13**. Martin and Jellinek[5] have given evidence that this 1-ethyl-π-allyl complex is present in significant amounts in the original reaction mixtures. It seems very probable, therefore, that it is responsible for one of the superposed spectra of Figure 4b.

5. Interconversion Reactions. A first observation on the equilibria in the reaction systems studied concerns the state of the starting compound **1** in these solutions. According to a recent report,[18] this compound is dimeric in the crystalline state and in benzene solution. The dimer involves supposedly two chlorine bridges and exhibits an antiferromagnetic interaction between the two titanium centers, amounting to 192 cm^{-1}. In the ether and tethydrofuran solutions studied here, the occurrence of a sharp signal at $g \approx 2$ would suggest, however, that the compound is present, at least in part, as the monomer. Coordination of an ether molecule to the vacant coordination site in **1** is probably

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(15) It is to be assumed that the monohydride **8** induces, at room temperature, a cleavage reaction of the ether solvents leading to alkoxy and alkyl derivatives of **1**. This might, among others, explain the facts that only at initial stages of the formation of the dideuteride complex hydride is incorporated into **4** from the ether solvents, and that small amounts of hydride catalyze the conversion of Cp_2TiCl_2 to the hydride complex by metallic magnesium and ether.

(16) Chromium complexes of this type have been postulated by J. Müller, Dissertation, University of München (Germany), 1964, in order to explain the amount and composition of gases evolved in the reaction between CrCl_3 and isopropylmagnesium bromide in ether. It also has been pointed out by Müller that from these complexes the hydride might be regenerated *via* an elimination of the corresponding vinyl ethers.

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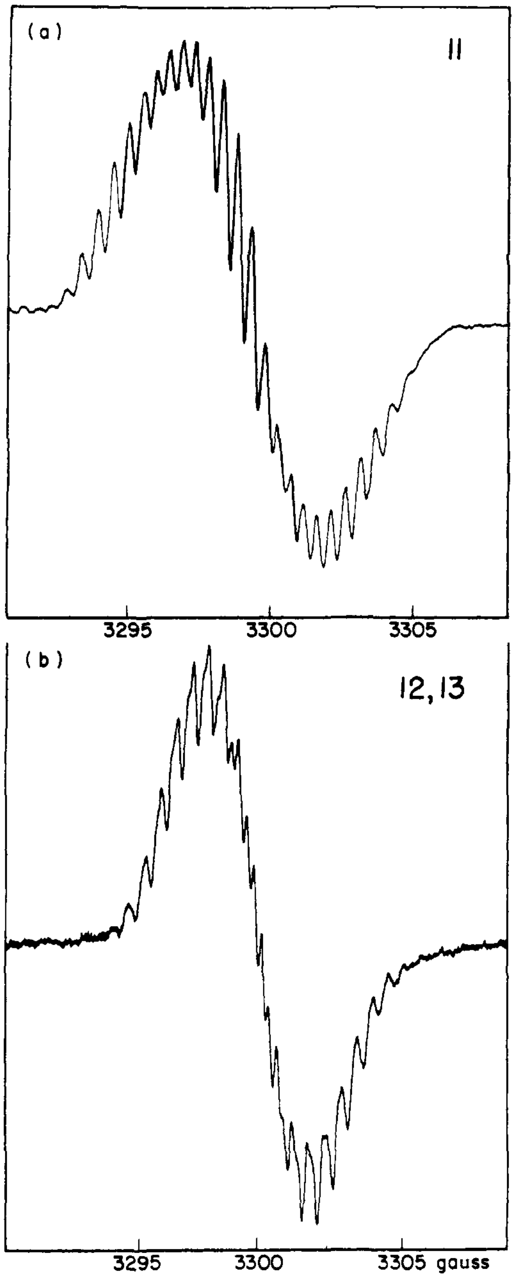

Figure 4. (a) $(\pi\text{-}C_5H_5)_2Ti(\pi\text{-}C_3H_5)$. To 2 ml of a 10^{-2} *M* solution of $(\pi\text{-}C_5H_5)_2TiCl$ in ether is added 0.5 ml of 1 *M* allylmagnesium bromide in ether. Subsequently the solution is diluted with 8 ml of tetrahydrofuran and cooled to −95° to obtain the spectrum: ν = 9.196 Gc (g = 1.99_1). (b) $(\pi\text{-}C_5H_5)_2Ti(\pi\text{-}C_3H_3(CH_3)_2)$ and $(\pi\text{-}C_5H_5)_2Ti(\pi\text{-}C_3H_4(CH_2CH_3))$?. To 2 ml of a 2 × 10^{-2} *M* solution of $(\pi\text{-}C_5H_5)_2TiCl$ in ether is added at room temperature 0.1 ml of piperylene (mixture of *cis*- and *trans*-1,3-pentadiene) and 0.2 ml of 0.5 *M* isopropylmagnesium bromide in ether. Subsequently the solution is diluted with 8 ml of tetrahydrofuran and cooled to −95° to obtain the spectrum: ν = 9.200 Gc (g = 1.99_2)

strong enough to compete with the formation of the dimer.

Transfer of one alkyl group to this complex appears to be complete, at least in the case of the methyl complex, with a low excess of Grignard or lithium compound. Accordingly, this alkyl group seems to be bound to the sandwiched titanium atom more strongly than to a magnesium or lithium atom. Transfer of a second alkyl ligand, however, requires a rather large excess of Grignard or organolithium compounds, so that this order of stability is probably reversed here. The question arises then whether for the dihydride complex **4** an analogous equilibrium exists, which in this case would have to involve the monohydride **8** and lithium hydride or a magnesium hydride species. Quite likely **8** occurs as an intermediate during the formation of **4**. However, its concentration in equilibrium with the dihydride complex **4** must be quite small, since the monohydride **8** was found to be an unstable species at room temperature whereas **4** does not show any apparent decomposition.

The olefin elimination from monoalkyltitanocenes appears to be quite fast; even at low temperatures epr spectra of these species were not observed, except for the monomethyl derivative where olefin elimination is obviously impossible. Concerning the mechanisms of this elimination, one might sensibly assume that the reaction involves essentially the reverse of an insertion step, *i.e.*, that the transfer of the hydride ion from the alkyl β position to the metal atom involves the same kind of three-center transition state as has been postulated for the metal-to-olefin hydride transfer in certain olefin hydrogenation reactions[19] and for the metal-to-olefin alkyl transfer in olefin polymerization by titanium catalysts.[20] This mechanism requires that the olefin is coordinated, in the moment of its formation, to one of the equatorial coordination sites at the titanium center. The fact that binding of the olefin in this position necessitates prior or simultaneous elimination of a solvent molecule would then explain why, in the presence of the more strongly coordinating tetrahydrofuran, olefin elimination is generally slower than with ether as a solvent. This argumentation implies, however, that the conversion of the dialkyl to the dihydride derivatives goes *via* the monoalkyl species present in equilibrium with the respective dialkyl complexes. Though quite likely in view of the much slower rate of decomposition of these complexes as compared to monoalkyl compounds, this hypothesis is to be tested further by kinetic investigations.

The insertion reaction proper, *i.e.*, the reverse of the observed olefin elimination, does not seem to occur appreciably with simple olefins. It is probably exemplified, however, in the reaction with isopropylmagnesium bromide and a diolefin to form the substituted π-allyl complexes. It has been suggested by Martin and Jellinek[5] that a titanocene monohydride is an intermediate in this reaction. The results presented above indicate clearly that the monohydride complex **8** occurs indeed as an unstable intermediate during the decomposition of alkyl derivatives of **1**. There can be little doubt that this monohydride will then react, instead of decomposing (*e.g.*, by an ether cleavage[15]) to add the diolefin present in the reaction mixture. Here, the forward insertion is then probably favored by the fact that the σ-allyl species primarily formed by the insertion is subsequently converted to the stable π-allyl compound **12**.

Implications of the present findings on the reaction of some of these systems with molecular nitrogen, as described by Vol'pin and Shur,[6] will be reported upon in a separate publication.

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The Preparation and Crystal Structure of 1,10-Phenanthrolinemercury(I) Nitrate, $Hg_2(phen)(NO_3)_2$[1]

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Abstract: The preparation of a new compound of mercury(I), 1,10-phenanthrolinemercury(I) nitrate, is reported, and the determination of its structure by three-dimensional, single-crystal X-ray analysis is described. The crystal is triclinic, space group $P\bar{1}$, with four mercury atoms per unit cell of parameters: $a = 6.83$ A, $b = 10.55$ A, $c = 10.58$ A, $\alpha = 98.6°$, $\beta = 93.6°$, and $\gamma = 97.6°$. The compound contains discrete $Hg_2(phen)^{2+}$ complex ions in which the phenanthroline, functioning as a bidentate ligand, is coordinated, through both of its nitrogen atoms, to one of the mercury atoms.

With few exceptions (notably the aniline complex $C_6H_5NH_2Hg_2{}^{2+}$ which has been quantitatively characterized in aqueous solution[2]), complexes of mercury(I) with nitrogen ligands generally appear to be unstable. This apparent instability has been attributed[2-4] to the tendency of such ligands to induce dismutation of the mercurous ion, due to the relatively greater stability of the corresponding mercury(II) complexes.

The possible existence of a 1,10-phenanthroline (subsequently abbreviated as phen) complex of mercury(I) is suggested by the preparation by Anderegg[5] of a salt having the composition $Hg_2(phen)_2(NO_3)_2$. This salt was reported[5] to be sparingly soluble in water, the solubility being governed by the solubility product relation $[Hg_2{}^{2+}][phen]^2[NO_3{}^-]^2 = K = 10^{-24.70}$ at 20°. While no evidence was reported concerning the existence of mercury(I)–phenanthroline complexes in solution, it should be noted that the solubility behavior described above is not inconsistent with the presence of mercury(I) in solution in the form of complex ions, *i.e.*, $Hg_2(phen)_2{}^{2+}$ and/or $Hg_2(phen)^{2+}$, under the conditions of the measurements (phenanthroline in appreciable excess over mercury(I)).

We have confirmed the preparation of $Hg_2(phen)_2(NO_3)_2$, and of the corresponding perchlorate salt, as well as of the corresponding salts of bis(2,2′-dipyridyl)mercury(I). In qualitative experiments we have also observed that the solubility of $Hg_2(phen)_2(NO_3)_2$ in water is markedly increased by the addition of $Hg_2(NO_3)_2$, presumably due to the shifting of the equilibrium

$$Hg_2(phen)_2{}^{2+} + Hg_2{}^{2+} \rightleftharpoons 2Hg_2(phen)^{2+} \qquad (1)$$

in the direction of the more soluble $Hg_2(phen)^{2+}$ complex. Furthermore, from such solutions containing $Hg_2{}^{2+}$ in large excess, we were able to obtain crystals of a new compound, $Hg_2(phen)(NO_3)_2$, whose structure determination by X-ray crystallographic analysis is described in this paper.

Attempts to obtain crystals of $Hg_2(phen)_2(NO_3)_2$, suitable for X-ray analysis, have thus far proved unsuccessful.

Experimental Section

Preparation of $Hg_2(phen)(NO_3)_2$. To a saturated aqueous solution of $Hg_2(NO_3)_2$ containing 0.1 *M* HNO_3, maintained at 70°, was slowly added, with stirring, a solution of 0.1 *M* 1,10-phenanthrolinium nitrate until the first formation of a permanent precipitate was detected. Sufficient $Hg_2(NO_3)_2$ was added to just redissolve the precipitate, and the resulting solution was cooled slowly to room temperature. On standing for several days at room temperature, small colorless, nearly prismatic, crystals of $Hg_2(phen)(NO_3)_2$, averaging about 0.2 × 0.2 × 5 mm in size, separated out.

Structure Determination. Examination of the crystals with a precession camera revealed that they were triclinic. A least-squares analysis of the data obtained using a single crystal on a General Electric XRD-5 diffractometer yielded the following cell constants and estimated errors: $a = 6.83 \pm 0.02$ A, $b = 10.55 \pm 0.03$ A, $c = 10.58 \pm 0.03$ A, $\alpha = 98.6 \pm 0.1°$, $\beta = 93.6 \pm 0.1°$, $\gamma = 97.6 \pm 0.1°$. The calculated volume per unit cell is 744 ± 4 A^3. The measured value of the density was 3.04 ± 0.06 g cm^{-3}. Assuming two molecules of $Hg_2(phen)(NO_3)_2$ per unit cell, the calculated density is 3.15 ± 0.02 g cm^{-3}.

Intensity data were collected with a General Electric XRD-5 diffractometer using molybdenum radiation, a zirconium filter, and pulse height analysis. The reflections in the sphere $\sin\theta < 0.34$ were examined with the stationary crystal–stationary counter technique (SCSC)[6] using 10-sec counts of peaks and backgrounds,

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