Chemistry of μ-(η^1:η^5-Cyclopentadienyl)-tris(η-cyclopentadienyl)dititanium(*Ti-Ti*). 2. Reactivity with Hydrogen and Nitrogen and Catalytic Properties

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Abstract: Solutions of $(\eta\text{-C}_5\text{H}_5)_2\overline{\text{Ti-}\mu\text{-}(\eta^1\text{:}\eta^5\text{-C}_5\text{H}_4)\text{-Ti}}(\eta\text{-C}_5\text{H}_5)$ (I) in toluene reversibly bind N_2 and H_2. With nitrogen a deep blue colored complex of composition $[(C_5H_4)(C_5H_5)_3Ti_2]_2N_2$ is formed. Treatment of the complex with potassium naphthalene, followed by acid hydrolysis results in the recovery of most of the ligand N_2 as NH_3. In the presence of hydrogen, I absorbs 1 mol of H_2 to form a titanium hydride compound which may be isolated as a green-gray solid. Solutions of I catalyze various hydrogenation and double bond migration reactions of olefins. The hydrogenation of cyclohexene (to cyclohexane) (concentration of I = 8.51×10^{-3} M in C_6H_{10}) proceeds with a first-order rate constant of $3.81 \times 10^{-4}\ s^{-1}$ at 20.8 °C; there is no apparent loss of activity after 430 catalyst turnovers. I catalyzes the isomerization of 1-heptene to 2-heptene and of cycloocta-1,5-diene to cycloocta-1,3-diene. The chemical and catalytic properties of I are compared with those of the various other "titanocenes" that have been described in the literature.

In the preceding publication[1] we discussed the synthesis structure and spectral properties of $(\eta\text{-C}_5\text{H}_5)_2\overline{\text{Ti-}\mu\text{-}(\eta^1\text{:}\eta^5\text{-C}_5\text{H}_4)\text{-Ti}}(\eta\text{-C}_5\text{H}_5)$ (I) and of its bis(tetrahydrofuran) adduct $(\eta\text{-C}_5\text{H}_5)_2\overline{\text{Ti-}\mu\text{-}(\eta^1\text{:}\eta^5\text{-C}_5\text{H}_4)\text{-Ti}}(\text{C}_5\text{H}_5)(\text{C}_4\text{H}_8\text{O})\cdot\text{C}_4\text{H}_8\text{O}$ (II). The unusual feature of these molecules is the presence of a high degree of steric and coordinative unsaturation, about the titanium–titanium linkage. As may be expected, the materials are highly reactive towards small unsaturated molecules including N_2. In this paper we will discuss the chemical reactivity of I with HCl and alkyl halides, the reversible coordination of I with H_2 and N_2, and finally the catalytic behavior of I and II in hydrogenation and isomerization reactions of olefins.

Results and Discussion

Thermal Decomposition of $(C_5H_5)_3(C_5H_4)Ti_2$ (I). Reactivity with HCl and Alkyl Halides. Solutions of I in toluene are fairly stable at room temperature.[1] However, on heating for several days at 100–110 °C under argon, the solutions deposit a light green precipitate of $\mu\text{-}(\eta^5\text{:}\eta^5\text{-C}_{10}\text{H}_8)\text{-}\mu\text{-}(\text{H})_2\text{-}((\eta\text{-C}_5\text{H}_5)\text{Ti})_2$ (III) (yield 40%). This hydride III was identified by its infrared and mass spectrum.[2,3] As a further means of characterization, III was reacted with methyl iodide under vacuum. Approximately 86% of the expected quantity of methane was evolved. Our compound $(C_5H_5)_3(C_5H_4)Ti_2$ (I) appears to be more thermally stable than the $[(C_5H_5)_2Ti]_2$ prepared by Brintzinger et al. which is said to quantitatively rearrange into III on heating for 2 h at 110 °C.[5]

We have studied the reactivity of I and II with HCl and alkyl halides in order to confirm their composition and, in particular, to decide on the possible presence of a hydride atom which might not have been seen in the x-ray structure of $(C_5H_5)_3(C_5H_4)Ti_2(C_4H_8O)\cdot C_4H_8O$ (II). Reaction of I in toluene with HCl at −80 °C to room temperature yields a mixture of $[(C_5H_5)_2TiCl]_2$, $(C_5H_5)_2TiCl_2$, and hydrogen. The extent of this reaction of I with HCl is somewhat variable, depending on the conditions employed (see Experimental Section). The stoichiometry ranges from approximately

$$(C_5H_5)_3(C_5H_4)Ti_2 + 3HCl \rightarrow 0.5[(C_5H_5)_2TiCl]_2 + (C_5H_5)_2TiCl_2 + H_2$$

to nearly complete oxidation of the metal to the dichloride

$$(C_5H_5)_3(C_5H_4)Ti_2 + 4HCl \rightarrow 2(C_5H_5)_2TiCl_2 + 1.5H_2$$

It seems unlikely that I or II should contain a hydride atom, since we would then expect to collect more H_2, and in this instance, the amount of H_2 evolved should be equivalent to the quantity of HCl consumed, i.e.

$$(C_5H_5)_3(C_5H_4)Ti_2H + 4HCl \rightarrow 2(C_5H_5)_2TiCl_2 + 2H_2$$

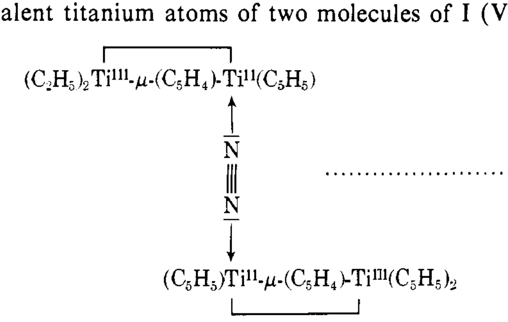
Reaction of I with DCl under similar conditions yields a mixture of D_2, HD, H_2, and some partially deuterated cyclopentadienyl titanium chlorides. Both I and II readily react with methyl chloride and with methyl iodide, liberating from 0.33 to 0.39 mol of methane per mole of starting material. If I contained a hydride function, i.e., $(C_5H_5)_3(C_5H_4)Ti_2H$, we would then expect that 1 mol of methane per hydride atom should be evolved, as it is for the hydride III.[6] We interpret the formation of the D_2, HD, H_2 mixture and the less than stoichiometric quantity of methane, as arising from a partial exchange or loss of hydrogen from the cyclopentadienyl rings during these oxidative addition reactions. This is not unreasonable in view of the presence of the η^1:η^5-bound cyclopentadienyl ligand, and the observed exchange of the cyclopentadienyl hydrogens in III with deuterium (see below). It is difficult to completely rule out the possibility that there exists a metal hydride function n our metallocenes. Nevertheless, the reactions described seem to be consistent with the description of I as $(C_5H_5)_3(C_5H_4)Ti_2$ rather than the hydride $(C_5H_5)_3(C_5H_4)Ti_2H$. However, hydride intermediates, e.g., $(C_5H_5)_2(C_5H_4)_2TiH$, may be involved in these reactions.

Reactivity with Hydrogen and Nitrogen. Solutions of $(C_5H_5)_3(C_5H_4)Ti_2$ in toluene on exposure to hydrogen (at 1–10 atm of pressure) slowly darken and after several hours yield a green-gray precipitate IV. The latter is only slightly soluble in toluene and can be readily isolated as a dry solid by filtration under an atmosphere of hydrogen. When the solid, IV, is mixed with toluene under vacuum, it slowly dissolves to give a solution of $(C_5H_5)_3(C_5H_4)Ti_2$ (I) and 1 mol of H_2. When IV is prepared by reacting $(C_5H_5)_3(C_5H_4)Ti_2$ (I) and H_2 at 1 atm of pressure all the H_2 absorbed can eventually be recovered; the reaction of I with H_2 is thus totally reversible under these conditions. The stoichiometry of compound IV is thus $[(C_5H_5)_3(C_5H_4)Ti_2]\cdot H_2$. The infrared spectrum of IV shows the typical metallocene bands of $(C_5H_5)_3(C_5H_4)Ti_2$[1] as well as a broad intense absorption at ~1140 cm^{-1}. This band is shifted to lower frequencies upon substitution by deuterium, which serves to identify it as a metal hydride vibrational mode.

The unusually low frequency of this vibration suggests that it arises from one or two bridging hydrogen atoms in the molecule, i.e., $(C_5H_5)_2Ti$-μ-(C_5H_4)-μ-$(H)_2$-$Ti(C_5H_5)$ or $(C_5H_5)_2Ti$-μ-(H)-$Ti(C_5H_5)_2$. In di-μ-hydrido-bis(dicyclopentadienyltitanium), $(C_5H_5)_2Ti$-$\mu(H)_2$-$Ti(C_5H_5)_2$, for example, the antisymmetric metal hydrogen vibration is seen at 1450 cm^{-1}.[4] Unfortunately, from the infrared spectrum alone we can draw no definite conclusions about the structure and disposition of the cyclopentadienyl ligands in IV. This compound that we have described is very similar in its appearance, infrared spectrum, and chemical behavior to the "gray-green polymeric hydride", $[(C_5H_5)_2TiH]_x$, reported by Brintzinger and co-workers.[5] The latter was not, however, adequately characterized and its relationship with our material IV thus remains unclear.

When solutions of $(C_5H_5)_3(C_5H_4)Ti_2$ (I) in toluene are contacted with deuterium at 350 Torr pressure, exchange of D_2 with the cyclopentadienyl hydrogen atoms takes place. Analysis of the gas over the solution shows the presence of H_2, HD, and D_2 in amounts corresponding to somewhat less than expected from a statistical exchange between all the hydrogen and deuterium atoms in the system. The measure of the extent of exchange is complicated by precipitation of small amounts of the hydride IV from the reaction mixture. We envisage the exchange as occurring either by H (and D) transfer via the (C_5H_4) ring, or possibly via a reversible dehydrogenation of one of the $-C_5H_5$ ligands as postulated earlier. We have not seen any exchange of D_2 with the hydrogen atoms of the solvent (toluene). Niobium and tantalum cyclopentadienyl hydrides, e.g., $TaH_3(C_5H_5)_2$, are known to catalyze the exchange between D_2 and the protons of benzene.[7a]

The most striking chemical property of $(C_5H_5)_3(C_5H_4)Ti_2$ (I) is its facile reactivity with molecular nitrogen. Solutions of I in benzene or other aromatic solvents instantly turn blue on contact with nitrogen gas. The absorption of nitrogen (over a short time period) is reversible; the coordination is favored by concentrated solutions of substrate, low temperatures, and high nitrogen pressures. The affinity of I for N_2 is indeed remarkable: Saturated solutions of I in toluene at −80 °C give the blue coloration on exposure to as little as 3 Torr pressure of nitrogen gas. We have carefully measured the stoichiometry of nitrogen uptake by $(C_5H_5)_3(C_5H_4)Ti_2$ (I). Even under very favorable conditions for coordination (N_2 pressure = 11.3 atm, 0 °C) *one* molecule of N_2 is bound by *two* molecules of $(C_5H_5)_3(C_5H_4)Ti_2$. The N_2 is most probably held between the divalent titanium atoms of two molecules of I (V). In this model, each N atom occupies the same coordination site on (formally) divalent titanium as does tetrahydrofuran in the crystalline THF adduct: $(C_5H_5)_3(C_5H_4)Ti_2(C_4H_8O)\cdot C_4H_8O$ (II).[7b] From its stoichiometry of formation V clearly contrasts with the apparently similar deep blue "titanocene"-nitrogen complex $[(C_5H_5)_2Ti]_2N_2$ reported by Brintzinger et al.[5]



V

The blue complex V can also be prepared in solutions of *n*-hexane and in diethyl ether. It does not form in THF, at least not at N_2 pressures less than 20 atm. It may be conveniently prepared as a dry blue solid (containing ca. 70% $[(C_5H_5)_3(C_5H_4)Ti_2]_2N_2$ (V)) by evaporating diethyl ether solutions at −35 °C under vacuum. We have by this method prepared dry samples of V using both $^{14}N_2$ and $^{15}N_2$. From the infrared spectra of these materials in Nujol and *n*-hexadecane-d_{34} oil mulls, we have found no evidence of an N–N stretching mode, however weak. This is as might be expected for the centrosymmetric model V shown above, although even for this structure an antisymmetric titanium–nitrogen vibration should be discernible.

As mentioned above, over a short period of time the absorption of N_2 by I is reversible. We have noted, however, that solutions of V under N_2 slowly lose their blue color on standing at room temperature. Within 1–3 days all the bound N_2 is evolved.

Mixtures of $(C_5H_5)_2TiCl_2$ with strong reducing agents are known to reduce N_2 to "titanium nitride" species which yield ammonia on hydrolysis.[8] The N_2 ligand in V is also readily reducible. In one experiment, treatment of 1 mol of $[(C_5H_5)_3(C_5H_4)Ti_2]_2N_2$ prepared in diethyl ether, with potassium naphthalene under nitrogen, gave, after hydrolysis, 1.4 mol of ammonia. In an attempt to see if the nitrogen ligand in V could be reduced by hydrogen gas, we treated a solution of $(C_5H_5)_3(C_5H_4)Ti_2$ in xylene with an ~2:3 mixture of H_2/N_2 at 12 atm of pressure. The familiar deep blue color of the N_2 complex was immediately evident. On standing, however, the blue color faded somewhat more rapidly than in the absence of hydrogen. The green organometallic residue, when analyzed by infrared spectroscopy and elemental analyses, was found to contain the hydrides III and IV and no nitrogen. It seems that although N_2 is initially coordinated by $(C_5H_5)_3(C_5H_4)Ti_2$ (I) even in the presence of H_2, it is eventually, at least to some extent, displaced by H_2 to yield $[(C_5H_5)_3(C_5H_4)Ti_2]\cdot H_2$ (IV). It is somewhat surprising that this hydride and the N_2 complex can coexist for a time in solution without any apparent reduction of the N_2 (to a titanium ammonia derivative) taking place.

Catalytic Properties. It has been known for some time that mixtures containing low-valent titanium compounds can function as olefin hydrogenation and isomerization catalysts. Thus, preparations made by mixing $TiCl_4$ with sodium cyclopentadienide,[9] or $(C_5H_5)_2TiCl_2$ with sodium naphthalene,[10] have been shown to catalytically hydrogenate alkenes. Reduced forms of $(C_5H_5)_2TiCl_2$ supported on polystyrene are reported to function as heterogeneous hydrogenation catalysts.[11] Solutions formed by treating 1-methyl-η-allyldicyclopentadienyltitanium with H_2 are particularly effective catalysts for both hydrogenation and double-bond migration reactions of alkenes.[12] We have found that $(C_5H_5)_3(C_5H_4)Ti_2$ (I) and $(C_5H_5)_3(C_5H_4)Ti_2(C_4H_8O)\cdot C_4H_8O$ (II) are effective catalysts in some olefin hydrogenation and double-bond migration reactions. These materials are the first discrete and well-characterized titanium compounds that have been shown to possess such catalytic properties.

The results of our olefin hydrogenation studies are presented in Table I. It is seen that $(C_5H_5)_3(C_5H_4)Ti_2$ (I) is a very effective homogeneous olefin hydrogenation catalyst. Ethylene, internal olefins, and diolefins are rapidly reduced to the corresponding alkanes. We have no data on the behavior of terminal olefins, since these isomerize rapidly into internal olefins on contact with I. The hydride material III can also act as a hydrogenation catalyst, but only for dienes. Thus, III selectively, catalyzes the hydrogenation of cyclohexa-1,4-diene to cyclohexene. However, under the same conditions cycloocta-1,5-diene is reduced to cyclooctane.

The hydrogenation reaction of cyclohexene in the presence of our titanium catalysts appears to be of the first order with respect to hydrogen pressure. First-order rate constants (k) and reaction half-times are presented in Table I. With $(C_5H_5)_3(C_5H_4)Ti_2$ (I) (8.51×10^{-3} M in cyclohexene), the hydrogenation proceeds without any apparent loss of activity over 430 catalyst turnovers. With $(C_5H_5)_3(C_5H_4)Ti_2$ (I) in

Table I

Catalyst	10^3[Catalyst] (M)	*T* (°C)	Substrate	[Olefin] (M)	Po(H_2) (Torr)	10^4 *k* (s^{-1})	Initial rate (cm^3 of H_2 min^{-1} $mequiv^{-1}$ of Ti)	$t_{1/2}$ (min)	Product
$(C_5H_5)_3(C_5H_4)Ti_2$[a]	8.51	20.8	Cyclohexene	9.87	550	3.81	34.2	30.3	Cyclohexane
	2.71	20.4			810	4.39	134.0	26.3	
	1.15	20.6			770	1.05	51.8	110	
$(C_5H_5)_3(C_5H_4)Ti_2$[b]	2.68	21.4			775	2.04	73.5	56.6	
$(C_5H_5)_3(C_5H_4)Ti_2$[a]	2.94	20.1	Cyclohexene in tetrahydrofuran	5.62	670	0.487		237	
Polymer-attached "$(C_5H_5)_2Ti$" ref 11		R.T.[c]	Cyclohexene in cyclohexane	1.16	(760)[d]		88.7		
$(C_5H_5)_2Ti{\cdot}C_4H_4$-$(CH_3)$ + H_2, ref 12	8.6	R.T.[c]	Cyclohexene in cyclohexane	1.76	(760)[d]			6	
$(C_5H_5)_3(C_5H_4)Ti_2$[b]	9.52	23.5	Cycloocta-1,5-diene	8.15	700	6.75		17.1	Cyclooctane
$(C_5H_5)_2(C_{10}H_8)Ti_2H_2$ (111)[e]	24.6	25.0	Cyclohexa-1,4-diene	10.57	800	0.082		1410	Cyclohexe
	11.2	22.0	Cycloocta-1,5-diene	8.15	781	0.067		1729	Cyclooctane

[a] Prepared from crystalline $(C_5H_5)_3(C_5H_4)Ti_2(C_4H_8O){\cdot}(C_4H_8O)$. [b] Product of $(C_5H_5)_2TiCl_2 + 2KC_{10}H_8$ reaction. [c] At room temperature. Exact temperature not specified. [d] Assumed to be 760 Torr. [e] Prepared from $(C_5H_5)_3(C_5H_4)Ti_2$; see Experimental Section, part a.

more dilute solution (2.71×10^{-3} M), we observed an increase in rate from $k = 4.39 \times 10^{-4}\ s^{-1}$ to $k = 6.58 \times 10^{-4}\ s^{-1}$ on re-pressuring the system with H_2, after 360 catalyst turnovers. When the hydrogenation of cyclohexene was performed with tetrahydrofuran as the solvent, the rate of H_2 uptake was markedly less and there was also a considerable deactivation of the catalyst with time. This is consistent with the previously discussed instability of I in tetrahydrofuran.[1] The material I, as obtained directly from the reduction of $(C_5H_5)_2TiCl_2$, is less pure than that prepared from crystals of II, which accounts for its somewhat lower catalytic activity. The hydrogenation rates shown in Table I are only representative; we have made no attempt to optimize the conditions for these reactions.

The published hydrogenation rates of two, related "titanocene" species have been included for purposes of comparison, in Table I. The polystyrene attached "$(C_5H_5)_2Ti$" material (prepared by reducing polymer-attached $(C_5H_5)_2TiCl_2$ with butyllithium)[11] is comparable to $(C_5H_5)_3(C_5H_4)Ti_2$ (I) as a catalyst for the hydrogenation of cyclohexene. The catalyst solution prepared by treatment of 1-methyl-η-allylbiscyclopentadienyltitanium with hydrogen,[12] appears to be more active than $(C_5H_5)_3(C_5H_4)Ti_2$ (I). Unfortunately, it is not possible here to make a more definitive comparison between these systems because of the widely differing experimental conditions employed and the lack of detailed kinetic data.

The $(C_5H_5)_3(C_5H_4)Ti_2$ compound is also active as a catalyst in double-bond migration reactions of olefins. Terminal olefins are converted into the more thermodynamically stable internal olefins. For example, 1-heptene in the presence of dissolved I isomerizes to yield a mixture of trans (~95%) and cis (~5%) 2-heptenes. The isomerization is very rapid; for a 0.028 M solution of catalyst in 1-heptene the half-life of the reaction (to yield *trans*-2-heptene) is 6.6 min at 30 °C. 1-Butene rearranges under similar conditions to yield a mixture of ~75% trans and ~25% cis 2-butenes.

A particularly interesting isomerization reaction is the conversion of cycloocta-1,5-diene to cycloocta-1,3-diene (see Figure 1). The reaction seems to proceed via the intermediate formation of the 1,4-isomer. A similar isomerization of cycloocta-1,5-diene has been observed by Martin and De Jongh with their hydrogenated 1-methyl-η-allyldicyclopentadienyltitanium catalyst.[12] Crystalline $(C_5H_5)_3(C_5H_4)Ti_2(C_4H_8O){\cdot}C_4H_8O$ (II) does not catalyze the isomerization of 1-heptene. However, the isomerization can be initiated by heating the solution to ~100 °C.

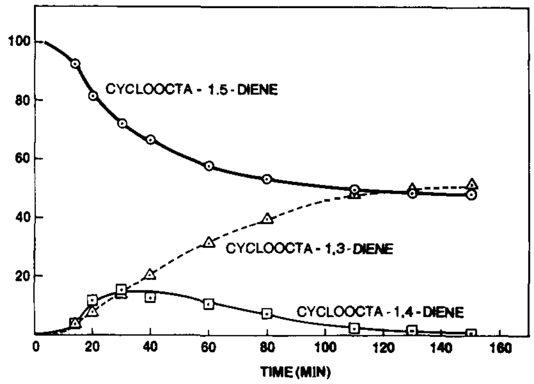


Figure 1. Isomerization of cycloocta-1,5-diene catalyzed by $(C_5H_5)_3(C_5H_4)Ti_2$ (I). Concentration of I = 2.8×10^{-2} M in C_8H_{12}, *T* = 30 °C. (Compound 1 as obtained directly from the reduction of $(C_5H_5)_2TiCl$.[1])

Conclusions

We have described the synthesis, characterization, and chemical and catalytic properties of $(C_5H_5)_3(C_5H_4)Ti_2$ (I) and $(C_5H_5)_3(C_5H_4)Ti_2(C_4H_8O){\cdot}C_4H_8O$ (II). Some of the properties of these compounds are related to those of various reactive "titanocenes" that have recently been described in the literature.[5,10,13] We know of no instance of a total correspondence in chemical and physical properties of our compounds with any of these various "titanocenes". The (η^1:η^5-C_5H_4)(η-C_5H_5)Ti unit in I and II is, as far as we are aware, the only well-established example of a dicyclopentadienyltitanium(II) moiety that has been obtained thus far.[14]

Compound I is a useful laboratory catalyst for hydrogenation and double-bond migration reactions of olefins. It is one of the very few polymetallic organometal compounds that have been shown to possess catalytic properties.[15] The most interesting property of $(C_5H_5)_3(C_5H_4)Ti_2$ (I) is its extraordinarily facile reactivity with nitrogen to yield the deep blue $[(C_5H_5)_3(C_5H_4)Ti_2]_2N_2$ complex (V). Here the N_2 is most likely attached between the divalent titanium atoms of two molecules of $(C_5H_5)_3(C_5H_4)Ti_2$(I). Compound V differs in its composition from that of other deep-blue colored dicyclopentadienyltitanium nitrogen complexes, e.g., $[(C_5H_5)_2Ti]_2N_2$[5,10] and $[(C_5H_5)_2TiR]N_2$.[16,17] In common with these other substances, the bound N_2 in V is readily reducible to ammonia by alkali metal naphthalene solutions. The blue N_2 complex V is also formed on reaction of I with mixtures of hydrogen and nitrogen. There is, however, no observed reduction of nitrogen by hydrogen over solutions of $(C_5H_5)_3(C_5H_4)Ti_2$ (I).

Experimental Section

All operations with I and II were done with rigid exclusion of air and moisture, using techniques and materials as described in the previous paper.[1]

(a) Thermal Decomposition of $(C_5H_5)_3(C_5H_4)Ti_2$ (I). An H-shaped tube containing a filter disk in the horizontal arm was loaded with 250 mg of I. The solid was dissolved in 5 ml of toluene and then covered with 1 atm of argon. The solution was heated to 100–110 °C for 10 days during which time a light green precipitate appeared. This was collected and washed with small portions of toluene and subsequently treated with 1-pentene (5 ml, 16 h). (Pentene was found to be effective in removing traces of I.) The product (100 mg) gave an infrared spectrum in Nujol identical with that reported for the hydride III.[2] Its mass spectrum gave the parent ion $C_{20}H_{20}Ti_2^+$ *m/e* 356, as the major component at an ionizing voltage of 11 eV. Observed ratio of peak intensities at 11 eV: *m/e* 356, 354, 352 = 1.00:0.50:0.28; at 80 eV greater loss of H was evident: *m/e* 356, 354, 352 = 0.29:0.69:1.00. This is in good agreement with the previously reported mass-spectral data for III.[2]

The product III (36.15 mg, 0.1015 mmol) was treated with 5 ml of CH_3I. After stirring at 23 °C for 16 h, there was no evidence of a color change; however, methane (0.150 mmol) was evolved. The solution was left stirring for a total of 7 days at room temperature. A total of 0.174 mmol of CH_4 was collected. Ratio $Ti_2:CH_4$ = 1:1.71.

(b) Reactivity of $(C_5H_5)_3(C_5H_4)Ti_2$ (I) with HCl and with DCl. Crystalline II (109.1 mg, 0.219 mmol) was treated with two 20-ml lots of toluene to remove the THF. The gray-black residue was dissolved in toluene (10 ml); HCl gas (1.210 mmol) was then added to the frozen solution at −196 °C. The mixture was then warmed with stirring to −80 °C (0.5 h), −23 °C (0.5 h), and finally to +23 °C (1.5 h). The resulting red solution was evaporated to dryness, and the solid analyzed by ir and mass spectroscopy. It was found to consist of a mixture of very approximately 4:1 (w/w) $(C_5H_5)_2TiCl_2$:$[(C_5H_5)_2TiCl]_2$. No other products, and in particular no $(C_5H_5)_2(C_{10}H_8)Ti_2Cl_2$, the reaction product of III with HCl,[2] were evident in the mass spectra. The hydrogen evolved from the reaction (0.34 mmol) was collected and measured with a Toepler pump. Hydrogen chloride gas remaining in the evaporated solvent was measured by titration against standard base. Ratio Ti_2:HCl (reacted):H_2 = 1:3.71:1.56.

In another experiment I (0.116 mmol) prepared from crystalline II was treated with DCl (1.061 mmol), in toluene (10 ml) at −196 °C. The mixture was warmed to −80 °C (0.5 h), −23 °C (0.5 h), and 23 °C (0.5 h), resulting in a yellow-brown solution. Evaporation of this solution gave a mixture of very approximately 1:1 (w/w) $[(C_5H_{5-x}D_x)_2TiCl]_2$ and $(C_5H_{5-y}D_y)_2TiCl_2$. The noncondensible gas from the reaction (0.126 mmol) was found to consist of a mixture of D_2 27.2%, HD 70%, and H_2 2.8%. Ratio Ti_2:DCl (reacted):(H_2 + HD + D_2) = 1:3.28:1.08.

(c) Reactivity of I and II with CH_3I and CH_3Cl. To 69.39 mg (0.139 mmol) of crystalline II was added 5 ml of CH_3I at −196 °C. The mixture was warmed and stirred at −23 °C for 2.5 h. A gradual color change from yellow-green to red-brown was observed. Methane (~0.04 mmol) was collected at this point. The mixture was then warmed to 23 °C and allowed to stir for 16 h. Total CH_4 collected was 0.054 mmol. Ratio $Ti_2:CH_4$ = 1:0.39.

In another experiment, crystalline II (101.5 mg, 0.203 mmol) was dissolved in 10 ml of toluene, and CH_3Cl (5.5 mmol) added at −196 °C. The solution slowly turned red-brown on warming from 0 to 23 °C. The mixture was left stirring at 23 °C for 16 h, and then pumped to dryness. Methane evolved was 0.0675 mmol. Ratio $Ti_2:CH_4$ = 1: 0.33. A red-brown solid was left in the reaction flask. Mass spectra of this product gave peaks at *m/e* 424 ($C_{20}H_{18}Ti_2Cl_2^+$), *m/e* 213–215 ($C_{10}H_{10}TiCl^+$), and *m/e* 241. The latter was assigned the composition $C_{11}H_{13}Ti_2^+$, on the basis of the observed distribution in the Ti isotopes and the precise *m/e* value under high resolution: calcd for $C_{11}H_{13}Ti_2^+$, 240.9976; found, 240.9965. The ion might be $(C_5H_4CH_3)(C_5H_5)TiH^+$ or $(C_5H_5)_2TiCH_3^+$ (presumably derived from $(C_5H_5)_2Ti(CH_3)$(I)).

(d) Reactivity of I with Hydrogen. Crystalline II (102.54 mg, 0.2054 mmol) (weighed under argon) contained in a heavy-wall glass tube was treated with two 5-ml lots of toluene to remove the THF. The residue was then dissolved in fresh toluene (3.72 g) and the resulting solution stirred under 1.3 atm of H_2 for 1 h at 23 °C. Further H_2 was then added and the mixture stirred under 7.8 atm of H_2 for 16 h. The product, a blue-black slurry was cooled to −196 °C and evacuated first at −196 °C and then at −111 °C. Hydrogen was slowly liberated upon stirring the slurry at room temperature under vacuum. The H_2 was collected and measured by means of a Toepler pump. Additional toluene was added to the slurry (at −196 °C) and the mixture stirred at 23 °C until no more H_2 was evolved. The resulting deep green solution was evaporated and washed with octane (5 ml) to yield a dark solid. This gave an infrared spectrum identical with that of $(C_5H_5)_3(C_5H_4)Ti_2$.[1] A total of 0.232 mmol of H_2 was collected from the reaction. Ratio $Ti_2:H_2$ = 1:1.13. In a similar experiment using I as obtained directly from reduction of $(C_5H_5)_2TiCl_2$, ratio $Ti_2:H_2$ = 1:0.85. (I as obtained from the reduction of $(C_5H_5)_2TiCl_2$ is less pure than that obtained from crystalline II.[1])

In an experiment designed to confirm the stoichiometry of reaction of I with H_2; 249.2 mg of I (0.702 mmol) was dissolved in 3 ml of xylene and H_2 gas at 818 Torr added. The reactor tube was kept in a constant temperature bath at 19.5 °C and the drop in H_2 pressure monitored. A black precipitate was first noticed after 1.5 h. After 23 h, there was no further absorption of H_2. Total H_2 uptake was 0.45 mmol. Hydrogen recovered from the complex was 0.38 mmol.

(e) H/D Exchange over $(C_5H_5)_3(C_5H_4)Ti_2$ (I). Crystalline II (110.7 mg, 0.222 mmol) was treated with two 5-ml lots of toluene to convert it to I. The latter was dissolved in toluene (3 ml) and treated with 350 Torr of D_2 in a closed system. The mixture was stirred for 21 h at 23 °C. The formation of a slight black precipitate was noted. Noncondensible volatiles were collected and analyzed by mass spectroscopy: found, 0.429 mmol of a mixture of 71% H_2, 26% HD, and 3% D_2. For a statistical distribution of D atoms (from the gas phase) and H atoms (in the complex) we would expect the gas mixture to consist of 80.3% H_2, 16.36% HD, and 3.33% D_2. When a solution of I in 99.8% D toluene-d_8 was stirred over H_2, there was no detectable increase in the NMR signals of the residual protons of the toluene.

(f) Reactivity of I with Nitrogen. (1) Preparation of Dry Solid Blue N_2 Complex. Crystalline II (56.02 mg, 0.112 mmol) was treated with two 10-ml portions of *n*-octane to remove the THF. Diethyl ether was then added to make a near-saturated solution. The dark green solution was cooled to −35 °C and exposed to 1 atm of pressure of N_2. There was an immediate deep blue coloration. The solution was stirred for 30 min at −95 °C and the ether evaporated by pumping at −35 °C. A dry blue solid remained. To this was added 5 ml of toluene at −196 °C and the solution warmed to room temperature. The N_2 gas evolved was collected by means of a Toepler pump. Additional toluene was added and the system pumped at room temperature until no further N_2 was evolved, found 0.0389 mmol of N_2. Ratio $Ti_2:N_2$ = 1: 0.347.

(2) Stoichiometry of Reaction of I with N_2. The green residue from the above experiment (compound I, 0.112 mmol) was dissolved in 1.42 g of toluene. Nitrogen gas (1 atm) was added at −23 °C. The blue N_2 complex which formed was decomposed by pumping at room temperature as described above, found 0.0580 mmol of N_2. Ratio $Ti_2:N_2$ = 1:0.518. In another experiment crystalline II (162.04 mg, 0.325 mmol) was treated with *n*-octane to remove the THF and the dry solid dissolved in 2.0 ml of toluene. To this solution at 0 °C was added N_2 at 11.3 atm of pressure. The solution was stirred for 5 min at 0 °C, then cooled to −95 °C to pump off the excess N_2. The bound N_2 was liberated at room temperature as detailed above, found 0.175 mmol of N_2. Ratio $Ti_2:N_2$ = 1:0.538. The dark green organometallic residue was found, by elemental analysis, to contain no nitrogen. When this experiment was repeated with I taken directly from the reduction of $(C_5H_5)_2TiCl_2$, the observed $Ti_2:N_2$ ratio was 1:0.410.

(g) Decomposition of N_2 Complex of I. A tube was loaded with 200 mg of I dissolved in 2 ml of xylene. The mixture was placed in a constant temperature bath at 19 °C. Nitrogen at an initial pressure of 695 Torr was admitted. The instantaneous deep blue coloration remained unchanged for 3 h; after 19 h a brown coloration developed which eventually turned to a light green, after 2 days. All the bound N_2 was evolved, as shown by the increase in gas pressure and by elemental analysis of the light green residue.

(h) Reactivity of I with N_2/H_2. A heavy-wall glass tube was charged with 200 mg of I and 4 ml of xylene. The tube was pressured with 12 atm of a mixture of 38% H_2 and 62% N_2. The initial deep blue color was discharged on standing for 4 h at 23 °C, to yield a light green solution. This was evaporated to dryness. An infrared spectrum of the residue gave bands characteristic of III and of the hydride $[(C_5H_5)_3(C_5H_4)Ti_2]\cdot H_2$ (IV). The residue contained no nitrogen (by elemental analysis—Dumas technique).

(i) **Catalytic Hydrogenation of Olefins.** The $(C_5H_5)_3(C_5H_4)Ti_2$ catalyzed hydrogenation of olefins was studied by following the drop in H_2 pressure in a closed reaction system. In a typical experiment, crystalline II (24.38 mg) was weighed under argon and transferred into a 300-ml flask. The catalyst was dissolved in *n*-octane and the solution evaporated to dryness. This procedure was then repeated so as to ensure complete removal of THF. After addition of cyclohexene (14.45 g) the flask was attached to a vacuum manifold and mercury manometer system of 466 cm^3 total volume. The reaction flask was held at 20.4 ± 0.2 °C. An initial H_2 pressure of 770 Torr was used. When the pressure had dropped to ~100 Torr fresh H_2 was introduced; the reaction kinetics were followed in this manner over four cycles of added H_2.

(j) Catalytic Isomerization of Olefins. The isomerization studies were carried out by dissolving the catalyst in the terminal olefin, contained in an NMR tube, and following the rise in the specific NMR resonances of the products. For example, in the isomerization of 1-heptene, 5 mg of $(C_5H_5)_3(C_5H_4)Ti_2$ (as obtained directly from reduction of $(C_5H_5)_2TiCl_2$) was dissolved in 0.5 ml of 1-heptene in a 5-mm o.d. NMR tube. The appearance of both the δ_{Me_4Si} 5.35 and 1.65 lines were monitored, to determine the rate of formation of 2-heptene. A Varian A-60 NMR spectrometer was used. The temperature of the probe was 30 °C.

Note Added in Proof. The olefin isomerization experiments described were done using $(C_5H_5)_3(C_5H_4)Ti_2$ (I) as obtained directly from the reduction of $(C_5H_5)_2TiCl_2$.[1] A 0.006 M solution of I (prepared from crystalline II[1]) in 1-hexene, after 1 h at 23 °C, gave a mixture containing ~52% *trans*-2-hexene and ~4% *cis*-2-hexene. No *trans*-3-hexene was detected under these conditions.

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The Synthesis and Structure of a Dispirotetrasilazane

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Abstract: The cyclization reaction of the tetralithio salt of 1,3-bis(trimethylsilyl)-2,2,4,4-tetrakis(anilino)cyclodisilazane, obtained from the corresponding 2,2,4,4-tetrachloro derivative, with dimethyldichlorosilane forms the novel spirocyclic derivative, 2,2,8,8-tetramethyl-1,3,7,9-tetraphenyl-5,10-bis(trimethylsilyl)dispiro[3.1.3.1]tetrasilazane. The overall synthesis is noteworthy since it proceeds through use of previously unreported tetrafunctional cyclodisilazanes. The composition and geometry of the dispirotetrasilazane have been verified by single-crystal x-ray diffraction using data collected on an automatic diffractometer. The molecular symmetry is $\bar{1}$. The four collinear silicon atoms give the molecule an extended conformation. The crystal system is monoclinic $C2/c$) with four molecules in a cell of dimensions a = 17.384 (7) Å, b = 12.289 (4) Å, c = 19.255 (9) Å, and β = 94.68 (2)°. The observed and calculated densities are 1.13 and 1.15 g/cm^3, respectively.

While numerous cyclodisilazanes have been reported,[2] little attention has been paid until recently to the preparation of spiro derivatives of cyclosilazanes in which silicon serves as the spiro atom. In 1964 Lienhard and Rochow[3] described the preparation of an octamethylspiro[3.3]trisilazane. The compound was characterized by elemental analysis and molecular weight but no evidence was presented for the claimed spirocyclic structure. More recently, as part of a study of polyspirocyclosilazanes, Andrianov and co-workers[4,5] reported the isolation in relatively low yields of several spirotrisilazanes and

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