Synthesis and Crystal Structure of Some Novel Titanocene Phosphido Compounds by P−H Activation in the Presence of Hydrosilanes

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Abstract: The reaction of dimethyltitanocene (Cp$_2$TiMe$_2$) with PhSiH$_3$ in hexane in the presence of Cy$_2$PH (Cy = cyclohexyl) is photoinitiated to give paramagnetic Cp$_2$Ti(SiH$_2$Ph)(PHCy$_2$), characterized in solution by EPR spectroscopy (a(H) of phosphine = 4.8 G, a(P) = 26.9 G, g_{iso} = 1.9950). Under the same conditions, a similar reaction with Ph$_2$SiH$_2$ gives a crystalline solid, shown by an X-ray structure determination to be [(Cp$_2$Ti)$_2$(μ-H)(μ-PCy$_2$)] (**1**). Under continuous photolysis Cp$_2$TiMe$_2$ reacts with CyPH$_2$, in the presence of either PhSiH$_3$ or Ph$_2$SiH$_2$, to give crystals of [Cp$_2$Ti(μ-PHCy)]$_2$ (**2**). *rac*-[(EBTHI)Ti(μ-H)]$_2$ (EBTHI = ethylene-1,2-bis(η^5-4,5,6,7-tetrahydro-1-indenyl)) reacts with PhPH$_2$ to give crystals of the complex (EBTHI)Ti(P$_2$Ph$_2$) (**4**). In this reaction, excess PhPH$_2$ is polymerized by dehydrocoupling to a mixture of linear and cyclic oligophosphanes. The diphosphane is produced as an equal mixture of the two diastereoisomers. Due to precipitation of the highly insoluble **4**, the catalytic reaction eventually ceases. The mechanisms of these reactions are discussed in terms of the oxidative addition of phosphines to Cp$_2$Ti^{II}, conproportionation of Cp$_2$Ti^{II} and Cp$_2$Ti^{IV} to Cp$_2$Ti^{III}, and σ-bond metathesis reactions of P−H, Ti−H, and Ti−P compounds.

Introduction

Among the cyclopentadienyl compounds of the transition metals, metallocenes of group 4 exhibit a particularly wide range of activities covering various stoichiometric and catalytic reactions.[1−11] Although there are many similarities between the chemistries of the three metallocenes of this group, titanocene derivatives exhibit a distinctive and rich chemistry in that all of the common oxidation states II, III, and IV are represented by an important number of isolated and well-characterized compounds. In particular, the more or less easy access to the lower oxidation states is due to the relatively low Ti(IV)/Ti-(III) reduction potential, compared to the other members of the group, and also to the tendency of Ti(III) to disproportionate.[12] This particularity, while increasing the number of possible

reactive species, and thus contributing to the diversity of catalytic properties, makes the isolation and definitive identification of reaction intermediates difficult. Consequently, the definition of reaction pathways in titanocene chemistry is a considerable challenge.

The recent implication of these metallocenes in Si−H bond activation opened a new and important area of interest.[3−10] Parallel to the development of useful catalytic reactions, a number of Ti(III) compounds with Ti−Si bonds have been isolated and fully characterized.[4,13−16] Their active role as catalyst intermediates was supported by trapping them in a stable form with tertiary phosphines (e.g., [Cp$_2$Ti^{III}(PMe$_3$)(SiH$_2$Ph)]).[14] The isolation and characterization of Cp$_2$Ti(PMe$_3$)Ph$_2$SiH$_2$ by Buchwald and co-workers,[16] under conditions similar to those which produced the latter silylphosphine complex, illustrates the sensitive dependence of the product on reaction conditions.

The successful use of tertiary phosphines to stabilize non-bridging Ti−Si bonds raises the question as to whether a primary or secondary phosphine would behave in the same way, or whether a competitive P−H bond activation would intervene, leading to different types of products. This question has been partially addressed by Stephan and co-workers,[17a,b] who obtained a phosphido-bridged dimer with the system Cp$_2$ZrCl$_2$/Mg/PCy$_2$H

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where previously Cp$_2$Zr(PMe$_3$)$_2$ had been obtained with PMe$_3$.[18] On the other hand, extensive studies by several groups have shown that a range of interesting phosphine, phosphido, and phosphinidine complexes of group 4 metallocenes can be prepared[16,19–25] by classically known methods which consist of reacting Li or K salts of dialkylphosphides with Cp$_2$M^{IV} dihalides, or with Cp$_2$M^{II} species generated in situ.

In this paper we report on a new approach to the synthesis of P-ligated titanocene derivatives with primary and secondary phosphines in the presence of silanes as reducing agents. This approach has also led to the discovery of a catalytic dehydro-coupling reaction of PhPH$_2$ to give Ph$_2$P$_2$H$_2$ and higher oligophosphines.

Results and Discussion

It has been shown previously that the light-assisted reaction of Cp$_2$TiMe$_2$ with primary silanes proceeds vigorously with evolution of methane and hydrogen and the formation of strongly paramagnetic solutions which, in the presence of tertiary phosphines, yield crystalline titanocene(III) silyl(phosphine) compounds.[14] Since the P–H bond dissociation energy is similar to that of Si–H, it was of interest to investigate whether a primary or secondary phosphine would influence the course of the reaction by direct or indirect involvement of the P–H fragment of the phosphine. At the outset it was established experimentally that these phosphines do not react significantly, either thermally or photochemically, with Cp$_2$TiMe$_2$ alone.

Reaction of Cy$_2$PH with Cp$_2$TiMe$_2$ in the Presence of Silanes. (a) Synthesis and Structure of [(Cp$_2$Ti)$_2$(μ-H)(μ-PCy$_2$)] (1). The reaction of DMT with PhSiH$_3$ in hexane/toluene solution in the presence of Cy$_2$PH under UV–visible light is accompanied immediately by gas evolution and the formation of a dark violet solution from which, unlike a number of tertiary phosphine reactions[14,26a] no solid compound can be isolated. This is probably because the Cy groups confer high solubility on the anticipated product, Cp$_2$Ti(SiH$_2$Ph)(PHCy$_2$). Formation of this product was supported by monitoring the appearance of its intense EPR spectrum, consisting of a doublet of pseudo-triplets. This signal can be reliably attributed to coupling of the unpaired electron on Ti with one P nucleus and two slightly inequivalent hydrogen nuclei. The hyperfine pattern is temperature dependent in the range 220–290 K, which indicates that molecular tumbling is not completely averaged within this temperature range, most probably because of the bulky Cy groups.

When the reaction is performed with PhSiD$_3$, the spectrum simplifies to a doublet of doublets and can only be due to coupling of the unpaired electron with one P nucleus (a(P) = 26.9 G; 1.0 G = 0.1 mT) and with one hydrogen atom (a(H) = 4.8 G). Assuming the usual 6-fold reduction in the hyperfine coupling to the two hydrogen atoms of the silane resulting from
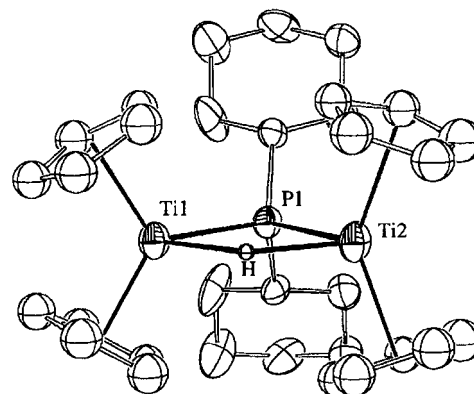
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Figure 1. ORTEP[41] diagram of [Cp$_2$Ti]$_2$(μ-H)(μ-PCy$_2$) (**1**) at 30% probability. Bond lengths (Å): Ti(1)–Ti(2) 3.456(4); Ti(1)–H 2.082; Ti(2)–H 2.018; Ti(1)–P 2.643(5); Ti(2)–P 2.643(4). Bond angles (deg): Ti(1)–P–Ti(2) 81.7; Ti(1)–P–C(1) 117.2; H–Ti(1)–P 81; H–Ti(2)–P 82; Ti(1)–H–Ti(2) 115.

deuterium substitution, the residual coupling can be confidently attributed to hyperfine interaction with the hydrogen atom of the phosphine ligand. It is interesting to note that no scrambling occurs between silyl deuterium and hydrogen on phosphorus. Formation of a compound such as Cp$_2$Ti(SiHDPh)(PDCy$_2$) would give a completely different spectral pattern so that it can be safely assumed that the spectrum is due to Cp$_2$Ti(SiD$_2$Ph)-(PHCy$_2$). It should be mentioned here that observation of hyperfine interactions with hydrogen of a phosphine ligand is very rare in paramagnetic transition metal compounds.

In order to isolate a crystalline reaction product, we sought to reduce the solubility by using Ph$_2$SiH$_2$ instead of PhSiH$_3$. Under the same conditions as above, well-shaped dark-violet crystals of [(Cp$_2$Ti)$_2$(μ-H)(μ-PCy$_2$)] (**1**) were deposited. An X-ray structure determination of **1** revealed the structure shown in Figure 1.

Compound **1** can be formally considered to be the association product of either titanococene(III) hydride with a titanocene-(III) phosphide or a titanocene(IV) (hydrido)phosphide with titanocene(II). This type of ambivalence was previously discussed in relation to the structure of isoelectronic Si–H bridged titanocene dimers.[4a]

1 is almost insoluble in hexanes and is very poorly soluble in toluene. However, measurement at 253 K in the latter solvent showed that the compound is EPR silent, which confirms its diamagnetism at this temperature. The same sample, after being held at room temperature for ca. 30 min, exhibits a strong signal consisting of a singlet (g_{av} = 1.9808; a(Ti) = 9.43 G). In frozen toluene at 140 K, the **g** tensor anisotropy is cleanly resolved (g_1 = 2.0020; g_2 = 1.9853; g_3 = 1.9539). These results show that **1** dissolves at low temperature as a diamagnetic dimer, but decomposes at room temperature to give a paramagnetic Ti-(III) monomer. The singlet observed by EPR at 253 K cannot be attributed to either of the two possible Ti(III) components of the dimer, namely Cp$_2$TiH or Cp$_2$TiPCy$_2$. The exact formulation of this species is not possible because of the absence of any ligand hyperfine interaction. However, the non-axial symmetry of the frozen solution **g** tensor and the parameters show that it is a monomeric titanocene(III) entity of relatively simple structure, in agreement with previous data on this class of compounds.[26b]

The structure of the mixed hydride-phosphide-bridged compound **1** is unique among early transition metal phosphides. It is, on the other hand, isostructural with isoelectronic mixed hydride-silyl-bridged titanocene complexes reported earlier.[4] The bond distances within the Ti$_2$(μ-X)(μ-H) unit are indistinguish-

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able for X = (μ-SiHPh)(μ-H) and Cy_2P. The angles appear superficially to be different, but when the large standard deviations for angles involving H atoms are taken into account, they are also indistinguishable.

(b) Synthesis and Structure of [$Cp_2Ti(\mu$-PHCy)]$_2$ (2). The reactions of DMT with $CyPH_2$ in the presence of either $PhSiH_3$ or Ph_2SiH_2 proceed in the same manner, but differently from either of the reactions of Cy_2PH described above. They take place under sustained photolysis, as opposed to the photoinitiation required in the case of tertiary phosphines. The color of the solution is light brown in contrast to the very dark violet color observed in the latter case, and gas evolution is rather sluggish. After a while, dark-brown microcrystals of [(Cp_2Ti)-(μ-PHCy)]$_2$ (2) begin to deposit on the walls of the Schlenk tube facing the light source.

Compound **2**, formally a Ti(III) dimer, gave no EPR spectrum in toluene solution, probably due to strong antiferromagnetic coupling between the two unpaired electrons on the two Ti atoms. However, the dimeric structure seems to be labile in the presence of strong donors, as is often the case with Ti(III) dimers.[17a,25b] Thus PMe_3 reacts with **2** in either THF or toluene to give a solution that exhibits an intense EPR signal at room temperature consisting of a doublet (a(P) = 20.0 G, a(Ti) = 10.5 G, g = 1.9867) identical with that previously assigned to $Cp_2Ti(CH_2PMe_2)$.[14] If the solution is left standing at room temperature for a while, another signal develops of slightly lower intensity, composed of a doublet of doublets (a(P) = 16 G; a(P) = 3.6 G; g = 1.9828). This signal is tentatively assigned to the phosphide phosphine complex $Cp_2Ti(PHCy)(PMe_3)$. The splitting of titanocene(III) phosphide dimers by tertiary alkylphosphines has been reported by Dick and Stephan, and the structure of one such product, $Cp_2Ti(PPh_2)(PMe_3)$, was confirmed by X-ray crystallography.[25b] The low value of the hyperfine coupling to the phosphide P was attributed to the nonplanarity of the phosphorus coordination in this type of compound. In the monomeric complex $Cp_2Ti(PCy_2)$, the phosphide group is planar and the hyperfine coupling constant is larger.[27]

The extremely thin plates of **2** were marginally adequate for single-crystal X-ray structure determination, even collecting the X-ray data with a rotating anode source. The structure, shown in Figure 2, was solved with the use of the best data set, and this confirmed that **2** is a titanocene dimer containing Ti_2P_2 bridging units. This formulation is also in agreement with the elemental analysis. Despite extensive disorder in the P–Cy fragment and in the Cp rings, the resolved structure clearly supports the conclusion that **2** is the titanocene(III) phosphide dimer. This conclusion is based mainly on the fact that the phosphorus coordination is clearly pyramidal with respect to its Ti_2Cy ligand set, since the hydrogen atom on the phosphine was not observed.

Reaction of *rac*-[(EBTHI)Ti(μ-H)]$_2$ (3) with $PhPH_2$. Synthesis and X-ray Structure of *rac*-[(EBTHI)TiP$_2$Ph$_2$] (4). In a previous report we showed that substituting the (η^5-Cp) ring with (η^5-indenyl) results in quite different chemistry,[13] producing a mixed valence Ti(III)/Ti(IV) hydride dimer that does not
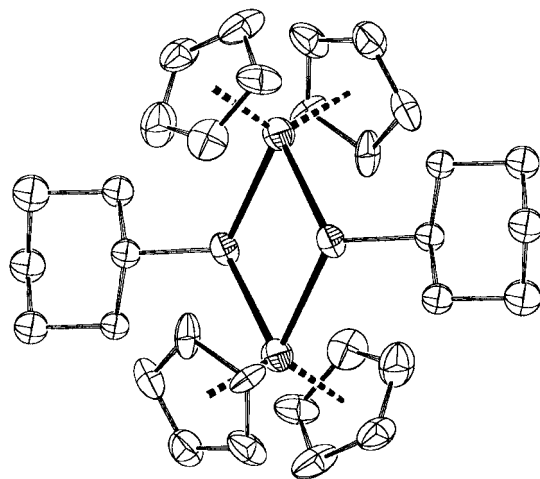
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(29) We have previously reported that triphenylgermane undergoes a slow σ-bond metathesis with DMT under certain conditions, to give a Ti(IV) germylmethyl complex. Under other conditions it undergoes the rapid branched chain reaction to produce reduced titanocene species. An equivalent of the methylgermane or the methylsilane is always produced when a titanocene(IV) is reduced by a germane or silane. Aitken, C.; Harrod, J. F.; Malek, A.; Samuel, E. *J. Organomet. Chem.* **1988**, *349*, 285. Harrod, J. F.; Malek. A.; Rochon, F. D.; Melanson, R. *Organometallics* **1987**, *6*, 2117.

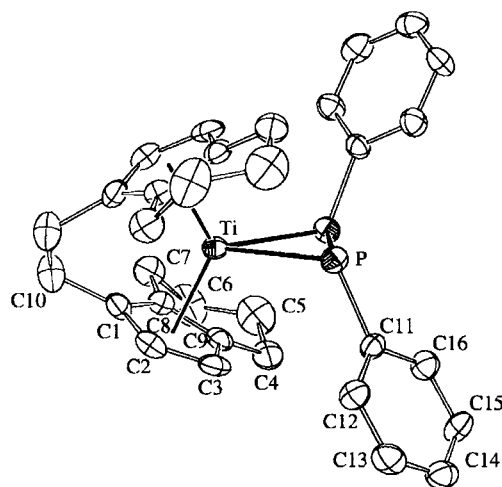**Figure 2.** Thermal ellipsoid plot of [$Cp_2Ti(\mu$-P(H)Cy)]$_2$ (**2**).

Figure 3. ORTEP diagram of a molecule of complex **4**, at 30% probability. Bond lengths (Å): Ti–P 2.525(2); P–P′ 2.174(3). Bond angles (deg): P–Ti–P′ 51.00(6); Ti–P–C(11) 117.8(2); Ti–P–P′ 64.50(3); P–P′–C(11) 107.2(2); C(11)–P–P′–C(11)′ 133.9(5).

contain a Ti–Si bond. Pursuing these investigations further, we also recently described the preparation of *rac*-[(EBTHI)-TiH]$_2$ (3; EBTHI = ethylene-1,2-bis(η^5-4,5,6,7-tetrahydro-1-indenyl), a paramagnetic dimer, by reaction of [EBTHI]TiMe$_2$ with primary and secondary silanes.[15] Similar reactions carried out in the presence of phosphines were not conclusive except for $PhPH_2$. Addition of 10 equiv of this phosphine to a freshly prepared solution of **3** in toluene at 40–50 °C gave well-formed, diamond-shaped, green crystals of *rac*-[ethylene-1,2-bis(η^5-4,5,6,7-tetrahydro-1-indenyl)(1,2-diphenyldiphosphene)titanium-(IV)] (**4**) in high yield. The product is diamagnetic and insoluble in the common nonhalogenated solvents, a factor that impeded the study of its NMR properties and its reactivity in solution. The absence of a vibrational band in the 2100–2350-cm^{-1} region in its FT-IR spectrum is indicative of the absence of a P–H or a Ti–H bond.

Single-crystal X-ray structural analysis confirmed that **4** is a C_2-symmetric molecule with one 1,2-diphenyldiphosphene ligand coordinated to an [EBTHI]Ti unit. The unit cell contains two pairs of racemic molecules. The molecular structure of **4** (Figure 3) shows that the [EBTHI]Ti fragment retains the same structure as the precursor molecule **3**.[15] The most notable feature of the structure is the opposite configurations at the C(1) and P atoms of each molecule, i.e., an *R,R* (EBTHI)Ti unit is bound to an *S,S* diphenyldiphosphene ligand, and vice versa. The molecule shown in Figure 4 is the *R,R,S,S* molecule.
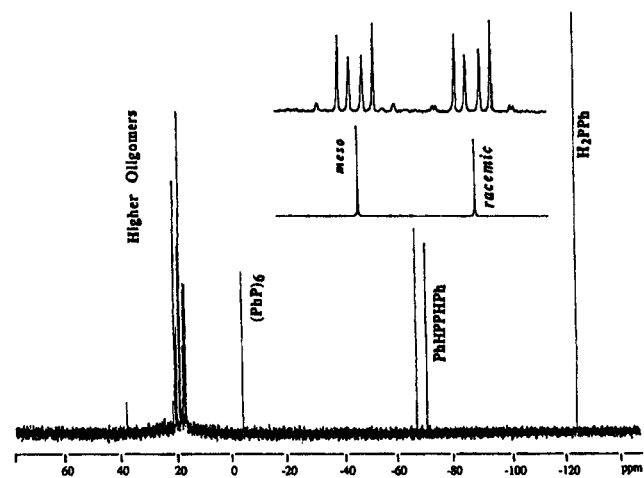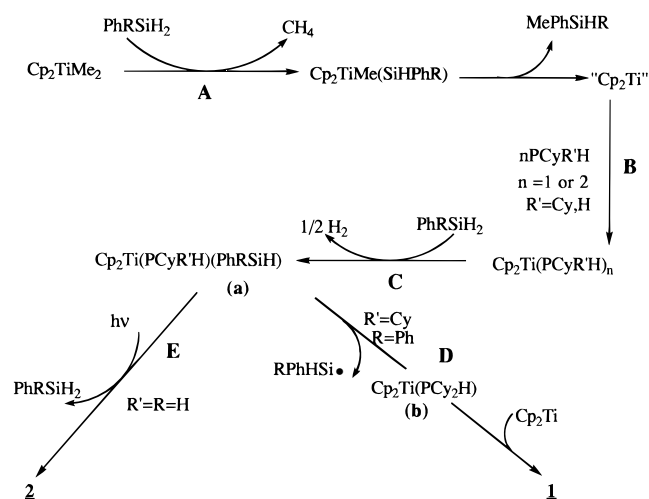
Figure 4. $^{31}P\{H\}$ NMR spectrum of the mother liquor from the reaction of **3** with phenylphosphine. Inset: Proton-coupled ^{31}P NMR spectrum of the diphenyldiphosphine.

Scheme 1 Proposed Mechanism for the Formation of **1** and **2**

The Ti−P bond distance of 2.525(2) Å is shorter than those seen in related Ti(III) species $[Cp_2Ti(\mu\text{-}PR_2)]_2$ (Ti−P_{av} = 2.618(3) Å, R = Me,[18] Et[25a]), $Cp_2Ti(PPh_2)(PMe_3)$ (Ti−P = 2.658(3) Å)[23b] or $[Cp_2Ti(PPh_2)]^-$ (Ti−P_{av} = 2.69(1) Å),[25b] but it is similar to the fulvalene-bridged Ti(III) dimer $[CpTi(\mu\text{-}PH_2)]_2(\mu\text{-}C_{10}H_8)$ (Ti_{av} = 2.513 (5) Å).[17b] This is consistent with its Ti(IV) character. The P−P bond distance is 2.174(3) Å, which is longer than in the anionic complex $[Cp_2Zr(PPh)_2Br]^-$ (**5**, P−P = 2.145(3) Å),[17c] and slightly longer than in the vanadium complex $Cp_2V(PPh)_2$ (**6**, P−P = 2.160(4) Å).[17c] These data suggest a stronger Ti−P bond and a weaker P−P bond compared to those in the related $Zr^{IV}P_2$ and $V^{IV}P_2$ complexes, and are consistent with the 16-electron count about Ti in **4** compared to the 18-electron Zr in **5** and 17-electron V in **6**. The P−Ti−P bond angle of 51.00(6)° in **4** is similar to the P−V−P angle in **6** (50.3(1)°) and the P−Mo−P angle (49.9-(2)°) in $Cp_2Mo(PH)_2$,[30] but larger than the P−Zr−P in **5** (46.6°),[17c] typical of such MP_2 three-membered rings. The P−P−C(11) bond angle of 107.2(2)° and the C(11)−P−P′−C(11)′ torsion angle of 133.6(3)° in **4** are consistent with a cyclopropane-type, rather than a cyclopropene-type, bonding mode.

The structure of **4** is unique for a number of reasons: (i) it is the first example of a $Ti^{IV}P_2$ three-membered-ring complex and the first diphosphanato complex possessing a chiral *ansa* ligand; (ii) the highly strained three-membered P−P−Ti ring is normally not expected to be preferred over the less strained four-membered, bimetallic ring product in this type of reaction; and (iii) a ligand-directed chirality induction is clearly indicated on the configuration of the diphosphanato ligand. Although polyphosphanato ligands usually adopt the trans orientation of their organic substituents to minimize their mutual repulsion, the dependence of the absolute configuration of the ligand on the configuration of the [EBTHI]Ti fragment is a prominent feature of **4**. A similar effect has recently been observed in the structure of (EBTHI)ZrBz₂ (Bz = benzyl).[31]

Reaction Mechanisms. Formation of 1 and 2. In earlier publications we have discussed at some length the kinds of species that are generated when dimethyltitanocene is reacted with organosilanes, either in the presence or absence of phosphines.[26,28] Based on the present and earlier results it is reasonable to assume that the initial reaction of Cp_2TiMe_2 with

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silanes is the formation of a Cp_2Ti^{IV}(silylmethyl) complex,[29] which then forms titanocene(II) as a reactive intermediate, possibly by reductive elimination of Si−Me. Moreover, in the course of the present work it has been shown that $Cp_2Ti(PMe_3)_2$ reacts cleanly with phenylsilane to give $Cp_2Ti(SiH_2Ph)(PMe_3)$, detected by its characteristic EPR spectrum.[14] With this experimental evidence in mind, a mechanism for the formation of the products observed in the reactions of $PhSiH_3$ and Ph_2SiH_2 with DMT in the presence of Cy_2PH is shown in Scheme 1. The silylphosphine complex **a** is formed through steps A, B, and C. When R = H, the reaction does not go beyond step C and **a** is the only product identified. On the other hand, when R = Ph, **a** is unstable and the reaction proceeds further through sequence D. A plausible explanation is that excessive steric encumbrance, resulting from the presence of a second phenyl group on the silicon, facilitates decomposition of the silylphosphine complex **a**, possibly by homolysis of the Ti−Si bond. This homolysis gives $Cp_2Ti^{II}(PCy_2H)$, which then undergoes intramolecular oxidative addition to produce the titanocene(IV) complex, **b**. The latter then captures a titanocene(II) molecule to give the observed product, **1**.

The role of light is an important factor in all of the reactions reported in this study. The reaction with Cy_2PH described above, in common with most reactions of DMT with silanes, requires photoinitiation, which leads to the rapid, autocatalytic reduction of DMT to lower oxidation states. In contrast, the necessity for continuous photolysis in the reaction with $CyPH_2$, and the different product obtained, suggests that a different mechanism is operating in this case. In a complex, multi−step reaction of this kind, photochemistry may intervene at various stages. But given our present ignorance of many details of the overall reaction process, other more complex pathways could very likely be involved. However, we suggest that compound **a** is formed in the same manner (R′ = H), which then undergoes a photoinduced dehydrosilation, sequence E, and dimerization to give **2**.

The Catalytic Dehydrocoupling of $PhPH_2$ and the Formation of 4. Previous reports describing the formation of $Cp_2M^{IV}P_n$ complexes (M = Zr, Hf, V; $n = 1$−3) involved the intramolecular elimination of PH_2R from a $Cp_2M^{IV}(PRH)_2$ complex, with the concurrent formation of a metal phosphinidene as the key intermediate.[25] A Ti(IV) phosphinidene species was also suggested in the formation of a fulvalene-bridged Ti-(III) phosphide dimer.[25b] Unlike their zirconocene analogs, such Ti(IV) phosphinidene species have never been detected. If **2** is a phosphide dimer, one may ask why there is no further

Scheme 2 Proposed Mechanism for the Formation of **4** and the Catalytic Dehydrocoupling of PhPH₂

4
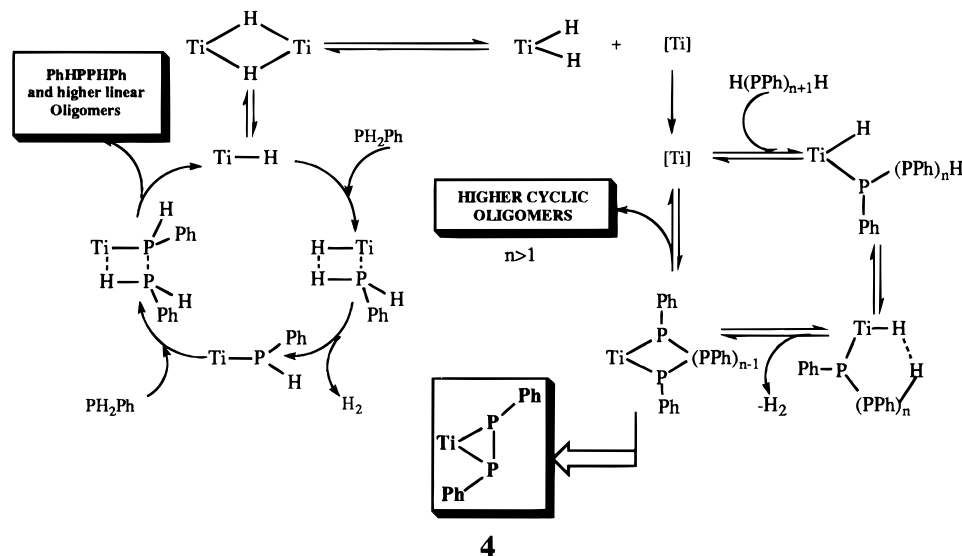
dehydrogenation of the CyPH bridging ligand to give either the phosphinidine dimer or its decomposition products. This, or some similar process, clearly occurs in the reaction of PhPH₂ with **3**. Analogs of **4**, with less sterically demanding Cp ligands, should presumably be able to capture a Cp_2Ti^{II} moiety to give a bridged phosphinidene dimer, but this apparently does not occur.

An equilibrium between the dimer and monomer of **3** has been observed in its EPR spectra both at room temperature and in frozen toluene.[15] Slow decomposition of **3** to liberate hydrogen gas when it is dissolved in organic solvents has also been observed at room temperature. These observations suggest the possibility of disproportionation of **3** to $(EBTHI)Ti^{II}$ and $(EBTHI)Ti^{IV}H_2$, and the latter may further reductively eliminate dihydrogen to generate more of the former. In the presence of PhPH₂, any, or all, of the three possible oxidation states of titanium in this system may catalyze the dehydrocoupling reaction to give the observed cyclic and linear oligophosphines.

The reaction of **3** with an excess of PhPH₂ to form **4** is accompanied by a steady evolution of H₂. The ³¹P NMR spectrum of the reaction mother liquor is shown in Figure 4. In addition to the peaks due to the starting material, PhPH₂ (−123 ppm), some new peaks appear in the spectrum. The ³¹P{¹H} spectrum shows two signals which exhibit symmetrical AA′XX′ coupling patterns in the corresponding proton-coupled spectrum. These two signals of nearly equal intensity are the *meso* (−66 ppm) and *rac* (−70 ppm) diastereomers of 1,2-diphenyldiphosphine (PhHPPHPh).[32] A sharp peak at −3.5 ppm in the ³¹P-{¹H} spectrum shows no change in the proton-coupled spectrum, suggesting a cyclic phosphine with an even number of P atoms and the phenyl groups in the all-trans configuration. A likely candidate is all trans (PhP)₆, which has previously been synthesized by noncatalytic methods, which also give the all-trans isomer.[33] This result appears to conflict with the recent report of catalytic dehydrocoupling of primary phosphines by an anionic hydridozirconocene complex, where the reported products were cyclopentaphosphines.[34] However, the latter reactions were carried out at much higher temperature (120 °C) in dioxane. The disproportionation of oligophosphines and the

formation of the highly insoluble (RP)₅ are known to occur spontaneously under these conditions.

A group of signals located in the region of +17 to +22 ppm which are further complicated in the proton-coupled spectrum are suggestive of some higher oligophosphines with P−H end groups, but an attempt to separate the products by GC was not successful. This is not surprising given the tendency of oligophenylphosphines to disproportionate and undergo oxidation. However, the high yield and low solubility of **4**, together with the ³¹P NMR data, suggest that the reaction of PhPH₂ with **3** initially proceeds via a catalytic dehydrocoupling pathway to give **4** and higher phenylphosphines. The catalytic reaction eventually ceases due to loss of catalyst through precipitation of the highly insoluble complex **4**.

Scheme 2 accounts for the experimental observations by using a conventional intermolecular σ-bond metathesis loop for the dehydrocoupling process and an intramolecular loop for production of cyclophosphanes and **4**. A σ-bond metathesis reaction could occur with either a Ti(IV) or a Ti(III) hydride, while a classic oxidative addition/reductive elimination process could involve Ti(II) and Ti(IV) species. Such a mechanism can also explain the production of a nearly equal distribution of *meso*- and *rac*-1,2-diphenyldiphosphine. In the σ-bond metathesis process, a free PhPH₂ can approach a Ti−P bond from either side. If the phosphine approaches the Ti−P bond from one side it will give *rac* diphosphine, while a *meso* diphosphine is produced if the PhPH₂ approaches the Ti−P bond from the other side. Spontaneous racemization of either diphosphine is very unlikely under the present reaction conditions because of the high inversion energy ($\Delta G^* \sim 22$ kcal/mol).[33b]

It is not unexpected that $(EBTHI)Ti^{II}$ would have a different reactivity from Cp_2Ti^{II}, in view of the radically altered steric and electronic properties of EBTHI compared to the Cp ligand. It is believed that the reason for the phosphine dehydrocoupling activity of the EBTHI complex and the absence of observable activity for the simple titanocenes probably lies in its lesser tendency to form an inactive bridged dimer. The enhancement of catalytic activity for analogous silane dehydrocoupling reactions by increasing the steric bulk of the Cp ligand has also been attributed to suppression of inactive dimer formation.[4b]

Attempts at dehydrogenative cross-coupling of Ph₂PH, or PhPH₂, with PhSiH₃ mediated by Cp₂TiMe₂ were unsuccessful. After 24 h the ¹H NMR spectra only showed resonances assignable to unreacted PhSiH₃ and Ph₂PH, or PhPH₂ with a

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Table 1. Crystallographic Information

	1	**2**	**4**
chemical formula	$C_{32}H_{43}Ti_2P$	$C_{32}H_{44}Ti_2P_2$	$C_{32}H_{34}TiP_2$
formula wt	554.43	586.41	528.47
cryst system	orthorhombic	monoclinic	orthorhombic
space group	*Pnma*	*P2₁/c*	*Pbcn*
Z	4	2	4
F(000)	1176	620	1112
a (Å)	10.130(2)	10.329(5)	9.796(4)
b (Å)	16.290(4)	16.871(9)	15.829(6)
c (Å)	16.902(6)	8.382(4)	16.757(6)
b deg		102.44(2)	
V (Å³)	2788.9(14)	1426.4(12)	2598(2)
d_{calc}	1.320		1.351
wavelength (Å)	1.54178	0.71073	0.71073
m (cm⁻¹)	55.34	6.84	1.90
trans. range	0.37−1.00	0.8329−1.00	0.90−1.00
cryst size (mm)	0.50, 0.30, 0.25	0.40, 0.21, 0.02	0.50, 0.28, 0.15
max 2θ (deg)	120	45	50
R	0.139	0.076	0.1546
R_w	0.233	0.140[a]	0.1313
S	1.050	1.009	0.901
no. of reflcns measd	8408		5214
no. of unique reflcns (R_{int})	2335 (0.139)	1790 (0.056)	2614 (0.119)
no. used in LS	2110	1762	2287
observation criteria (s)	3	2	3
no. of variables	156	220	160
no. of restraints	21	255	0
last D F map (e/Å³)	1.078; −0.397	0.24; −0.23	0.282; −0.300

[a] Value based on F^2.

small amount of PhMeSiH$_2$. P−Si cross-coupling products were not observed. It is probable that in these reactions, no catalytic chemistry is observed due to the formation of stable, unreactive titanocene(III) phosphide products.

Conclusion

In this work we show that the reactions of dimethyltitanocene with secondary and primary organophosphines resemble in many respects those of the isoelectronic silanes. These reactivity studies led to the isolation and structural characterization of several novel Ti−P complexes. Two major differences between silanes and phosphines are the inability of the phosphines to effect the rapid reduction of titanocene(IV) and the failure of the phosphines to undergo facile catalytic dehydrocoupling under most circumstances. Both of these effects are likely due to the ability of the phosphines to coordinate to key intermediates, thus blocking further reaction. The absence of nonbonding electron pairs from silanes (or other group 4 hydrides) precludes these inhibitory effects. However, prereduction of the Cp$_2$TiMe$_2$ by a silane permits reactions of the phosphines, leading to products (compounds **1** and **2**) that are isostructural and isoelectronic with those previously isolated from Cp$_2$TiMe$_2$/ silane reactions.

The diphosphene complex **4**, although without precedent in titanocene chemistry, is analogous to similar compounds that have been characterized for zirconocene and other early transition metal metallocene derivatives. The silicon analogues are unknown, for early transition metals, although disilenes are known for later transition metals.[35] The discovery of **4**, as an apparent participant in a dehydrocoupling cycle, keeps open the possibility that, under the right conditions, a silicon analogue might be isolated. We are continuing our explorations in this direction.

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Experimental Section

All reactions were performed under argon with use of conventional Schlenk apparatus and methods. Manipulation of air-sensitive crystals was performed in a Braun Lab-Master 130 glovebox with O$_2$ and H$_2$O maintained at less than 0.5 ppm. Solvents were dried and purged of oxygen by standard methods. Cp$_2$TiMe$_2$[36] and compound **3**[15] were prepared by methods described in the literature. All phosphines were purchased from the Aldrich Chemical Co. and used as received. Organosilanes were prepared by reduction of the corresponding chlorosilanes, purchased from Hüls America, with LiAlH$_4$.[37]

Combustion analyses were performed by Oneida Research Services, Whitesboro, NY. NMR spectra were recorded on a Varian Unity 500 FT spectrometer, operating at 200.33 MHz for ^{31}P. EPR experiments were recorded on a Bruker ER 220D spectrometer. Mass spectra were recorded on a KRATOS MS25RFA spectrometer equipped with a KRATOS DS90 data system. Photolyses were performed with a HANAU low-pressure mercury-vapor lamp cooled inside a Pyrex cooling jacket.

Reaction of Cp$_2$TiMe$_2$ and Cy$_2$PH in the Presence of PhSiH$_3$. Cp$_2$TiMe$_2$ (50 mg; 0.25 mmol) was dissolved in 4 mL of hexane and 0.12 mL (1 mmol) of PhSiH$_3$ and 0.1 mL (0.5 mmol) of PCy$_2$H was added. The light-orange solution was photolyzed for a period of 5 min until it suddenly darkened in color to become deep violet. This color change was accompanied by vigorous gas evolution that lasted for about 15 min. No crystals separated, even after a long time at 20 or −30 °C. The EPR spectrum at room temperature exhibited a strong signal consisting of a doublet of pseudo-triplets (see text), strongly indicating the formation of Cp$_2$Ti^{III}(SiH$_2$Ph)(PCy$_2$H). The same reaction performed with PhSiD$_3$ instead of PhSiH$_3$ gave an EPR signal consisting of a doublet of doublets indicating the formation of Cp$_2$-Ti^{III}(PCy$_2$H)(PhSiD$_2$) (see text).

Reaction of Cp$_2$TiMe$_2$ and Cy$_2$PH in the Presence of Ph$_2$SiH$_2$. The reaction was conducted under exactly the same conditions as above, but with Ph$_2$SiH$_2$ instead of PhSiH$_3$ (same molar ratios of reactants). Shortly after gas evolution had ceased, a dark-violet crystalline compound began to settle. After 2 h, the solution was decanted and the crystals were washed twice with hexane and dried to yield 30 mg

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(25%) of **1**. Anal. Found: C, 66.56; H, 7.60; P, 5.70; Ti, 16.45. Calcd: C, 69.33; H, 7.76; P, 5.59; Ti, 17.29.

Reaction of Cp₂TiMe₂ and CyPH₂ in the Presence of PhSiH₃. Cp₂TiMe₂ (50 mg; 0.25 mmol) was dissolved in 4 mL of hexane and 0.12 mL (1 mmol) of PhSiH₃ and 0.1 mL (0.8 mmol) of CyPH₂ was added. The light-orange solution was photolyzed. The color gradually changed to light brown and became darker, without appreciable gas evolution. After a period of 30 min, dark crystals began to deposit on the wall of the Schlenk tube facing the light source. The solution was decanted and the crystals collected. Submitting the supernatant solution to a second photolysis resulted in the deposition of a new crop of crystals. Three such operations yielded 30 mg of **2**. Yield: 40%. Microanalysis did not give satisfactory results. Attempts at purification of the compound by recrystallization were unsuccessful due to its rapid decomposition in solution. However, some of the directly obtained crystals appeared to be suitable for X-ray diffraction studies, and a structure determination was undertaken (vide infra).

Synthesis of 4. (a) In Situ Preparation. A solution of MeLi (0.40 mL of 1.4 M; 0.56 mmol) was added to a solution of *rac*-[EBTHI]-TiCl₂ (96 mg; 0.25 mmol) dissolved in 2 mL of dry THF in a 15-mL Schlenk tube under argon. The mixture was stirred for 12 h, and the solvent was removed *in vacuo*. The residue was extracted with dry hexanes until the extract was practically colorless (5 × 1 mL) and was cannula-filtered under argon to another 15-mL Schlenk tube. The combined extract was evaporated to dryness under reduced pressure, and 5 mL of dry toluene was added to dissolve the yellow residue. Phenylmethylsilane (0.070 mL; 0.50 mmol) was added to the toluene solution, and after the solution changed color to dark green or blue, phenylphosphine (0.27 mL, 2.5 mmol) was syringed in and the mixture was heated to 40−50 °C for 7 h until the gas evolution stopped. The mixture was then left at room temperature for another 40 h. The colorless supernatant liquid was decanted, and the green crystalline material was washed with cold toluene (2 × 3 mL) and dried under vacuum (127.6 mg; yield 86%).

(b) By Reaction of Phenylphosphine with 3. Complex **4** can also be synthesized by dissolving **3** in benzene at 40−50 °C followed by addition of 10 equiv of phenylphosphine. This method gave **4** in isolated yields ranging from 90 to 95%. Anal. Calcd for C₃₂H₃₄P₂Ti: C, 72.73; H, 6.49; P, 11.72. Found: C, 72.87; H, 6.06; P, 11.90. MW calcd for C₃₂H₃₄P₂Ti: 528.47. Measured: MS (CI) 529 (M⁺ + H); MS (EI) 528 (M⁺°). IR (KBr pellet): 3073 m, 3044 m, 2921 vs 2853 s, 1635 br w, 1575 s, 1560 w, 1472 s, 1438 vs, 1439 s, 1419 m, 1375 w, 1261 s, 1240 m, 1112 br vs, 1026 s, 902 w, 804 vs, 738 vs, 697 vs, 567 w, 481 s cm⁻¹.

Attempted dehydrogenative Cross-Coupling Reaction of Ph₂PH and PhSiH₃ in the Presence of Cp₂TiMe₂. PhSiH₃ (0.25 mL, 2.0 mmol) and Ph₂PH (0.28 mL, 1.6 mmol) were added to Cp₂TiMe₂ (42 mg, 0.2 mmol). The mixture was allowed to stir under ambient fluorescent room lighting. After 24 h, the solution turned brown-purple. The ¹H NMR spectrum showed resonances assignable to unreacted PhSiH₃ and Ph₂PH with a small amount of PhMeSiH₂. P−Si cross-

coupling products were not observed. This reaction was repeated with other phosphines and silanes with the same result.

Crystal Structures. The crystallographic data for compounds **1**, **2**, and **4** are listed in Table 1. For **1** and **4**, data sets were collected on a Rigaku AFC6S diffractometer. The structures were solved by direct methods and refined by full-matrix least-squares with use of SHELX93.[38] Data reduction was performed by using the NRCVAX system of crystallographic software for structure **1**,[39] SHELX for **2**, and the TEXSAN crystallographic software package of Molecular Structure Corporation for **4**.[40] For **1**, the molecule sits on a mirror plane passing through both Ti atoms and the bridging P atom plane. The Cp rings on both titaniums were found to be disordered over two orientations at 0.60 and 0.40 occupancies. These were modeled by using rigid C₅H₅ groups with independent isotropic thermal parameters for carbons. The remaining non-H atoms were refined anisotropically. The bridging hydride H was located on a difference map and held fixed. Other hydrogen atoms were introduced at their ideal positions.

For **4**, the molecule sits on a 2-fold axis. Non-hydrogen atoms were refined anisotropically, except the phenyl ring on phosphorus, which was refined as a rigid C₆H₅ group with independent isotropic thermal parameters for carbons. Hydrogen atoms were introduced at their ideal positions. Refinement was based on |*F*|.

Compound **2** diffracted very poorly. Data were collected on a Siemens P4 diffractometer equipped with a rotating anode generator. The compound is a dimer about an inversion center. All atoms except Ti are conformationally disordered, occupancies for each orientation are 50%. This amount of disorder explains the weak diffraction. The Cp rings were defined as rigid groups. Isotropic thermal parameters were restrained to be equal within standard uncertainties. The two P−C₆H₁₁ fragments were restrained to have similar geometries.

Supporting Information Available: Tables of crystallographic data for compounds **1**, **2**, and **4** (34 pages). See any current masthead page for ordering and Internet access instructions.

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