Titanocene-Catalyzed Dehydrocoupling of Silanes in the Presence of Phosphines. Probing a Complex Organometallic Catalysis by EPR Spectroscopy

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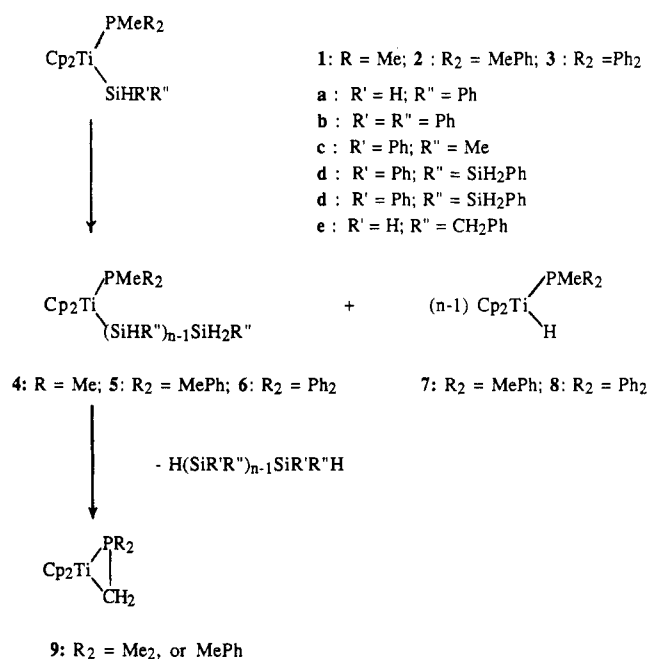
Summary: EPR spectroscopy shows that reactions of organosilanes with dimethyltitanocene in the presence of the phosphines PMe_nPh_{3-n} (n = 1-3) lead to a rich variety of products, including $Cp_2TiH(PMe_nPh_{3-n})$, $Cp_2TiSiRR'H(PMe_nPh_{3-n})$, $Cp_2Ti[(SiRR')_nSiRR'H]$- (PMe_nPh_{3-n}), and $Cp_2Ti(\eta^2\text{-}CH_2PMe_xPh_{2-x})$ (x = 1, 2).

We report an unusual example in which EPR spectroscopy provides essential insights into the mechanism of a complex catalytic system, a system in which the many species involved are extremely reactive, or ephemeral, and where it is most improbable that their presence could be established by other methods. The details of many complex organometallic catalytic cycles have been elucidated with the aid of NMR spectroscopy. In certain cases, such as organoactinide catalyses, this method can still be used to observe paramagnetic reactants and intermediates, since the effect of the paramagnetism is to cause large chemical shifts, with relatively little relaxation-induced line broadening.[1] With d-group elements, the line broadening due to paramagnetic relaxation is often so severe as to render the NMR method inapplicable. Although EPR spectroscopy can be very useful for identifying certain paramagnetic intermediates, its extreme sensitivity, and the more localized spin systems involved, greatly limit its usefulness compared to NMR. Nevertheless, EPR spectroscopy has proven to be indispensable for elucidating the mechanisms of some catalytically important Ti(III) reactions.[2-5] In the present paper, the method is used to illuminate some important steps in the titanocene-catalyzed dehydrocoupling of silanes.[6]

We reported earlier the synthesis and crystallographic characterization of the Ti(III) compounds 1 (see Scheme I).[5] The EPR spectra of these compounds (see Table I for all measured parameters) show the single unpaired electron of Ti(III) to be coupled to the phosphorus ($a_P \approx 30$ G) and to any hydrogens on the Si attached directly to Ti(III) ($a_H \approx 3$ G). The latter coupling permits the distinction between SiH_2R and $SiHRR'$ groups attached to Ti(III). In

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Scheme I

1: R = Me; 2 : R_2 = MePh; 3 : R_2 =Ph_2

a : R' = H; R" = Ph
b : R' = R" = Ph
c : R' = Ph; R" = Me
d : R' = Ph; R" = SiH_2Ph
d : R' = Ph; R" = SiH_2Ph
e : R' = H; R" = CH_2Ph

4: R = Me; 5: R_2 = MePh; 6: R_2 = Ph_2 7: R_2 = MePh; 8: R_2 = Ph_2

$- H(SiR'R")_{n-1}SiR'R"H$

9: R_2 = Me_2, or MePh

our earlier work, the 1,2-diphenyldisilyl complex **1d** was prepared from a reaction of 1,2-diphenyldisilane.[5] Compounds **1** can only be observed if their solutions are prepared and studied at temperatures of ≤-20 °C. At higher temperature, all of the PMe_3 complexes undergo rapid decomposition to a product which is stable in solution at room temperature and exhibits a simple doublet, due to coupling of a single unpaired electron to a single phosphorus atom; a_P = 20.0 G. The same product is observed independent of the starting silyl ligand and may also be generated by electrochemical reduction of Cp_2TiMe_2 in the presence of PMe_3. We believe this product to be the complex **9**.

After many unsuccessful efforts to grow good-quality single crystals of **9**, it was decided to replace methyl groups on the phosphine; since it is well-known that aryl substitution on the phosphine often facilitates crystallization, the reactions were repeated using $PPhMe_2$ and PPh_2Me.

Reactions of Cp_2TiMe_2 with various silanes in the presence of 1 equiv of either $PPhMe_2$ or PPh_2Me, under the same conditions as described previously for the PMe_3 compounds,[5] lead generally to precipitation of microcrystalline products which can be redissolved in toluene at -20 °C for measurement of their EPR spectra. The results obtained with $PhSiH_3$ were unusual in that, rather

Table I.   Summary of EPR Parameters for Products Described in the Text[a]

silane	phosphine	product 223 K	product 290 K
PhSiH$_3$	Me$_2$PhP	5a: a_P = 29.4; a_H = 3.3	7: a_P = 28.5; a_H = 10.7; g = 1.9931
MePhSiH$_2$	Me$_2$PhP	2c: a_P = 30.0; a_H = 3.2	7 + other species
Ph$_2$SiH$_2$	MePh$_2$P	5b: transient	7 + Ph$_2$SiD$_2$
	MePh$_2$P	d-5b: a_P = 30.0	h-8 and d-8 mixture
[PhSiH$_2$]$_2$	Me$_2$PhP	2d (not measd) + 9	2a + 9
PhCH$_2$SiH$_3$	Me$_2$PhP	2e: a_P = 28.2; a_H = 2.6; a_{Ti} = 11.3	9: a_P = 20.0; g = 1.9867
PhCH$_2$SiH$_3$	MePh$_2$P	6e: a_P = 27.9; a_H = 3.9	8: a_P = 26.3; a_H = 9.7; g = 1.9932
Ph$_2$SiH$_2$	MePh$_2$P	complex mixture	8
Ph$_2$SiD$_2$	MePh$_2$P	8	unchanged
PhSiH$_3$	MePh$_2$P	6a: a_P = 29.4; a_H = 4.8	8

[a] All parameters are measured in gauss.

than the very characteristic doublet of triplets of **2a** and **3a**, PMe$_2$Ph and PMePH$_2$ gave a doublet of doublets, typical of a secondary silyl ligand. These spectra were essentially identical with that of **1d**[5] and can be assigned to species **5a** and **6a**. Since the unpaired spin only couples measurably to the Si–H proton of the Si attached to Ti-(III), it is not possible to distinguish between the different species with $n \geq 1$. Warming these solutions to room temperature resulted in rapid decay of **5a** and **6a**, with the appearance of new species, characterized by coupling of the Ti(III) electron to a phosphorus $a_P \approx 27$ G) and to another $S = {}^1/_2$ nucleus, assumed to be H ($a_H \approx 10$ G).[7] These new species are believed to be **7** and **8**.

A reaction of 1,2-diphenyldisilane with Cp$_2$TiMe$_2$ in the presence of PPhMe$_2$ gave the spectrum expected for **2d** (or **5d**) at −20 °C, but as the mixture was warmed to room temperature, this species decayed and was replaced by the doublet of triplets expected for Cp$_2$Ti(SiH$_2$Ph)PPhMe$_2$ (**2a**). This result strongly suggests the presence of the redistribution reaction shown in (1). Although **7** is not

$$nCp_2Ti \Big\langle{}^{PPhMe_2}_{SiHPhSiH_2Ph} \quad \rightleftharpoons$$

2d

$$(n-1)Cp_2Ti \Big\langle{}^{PPhMe_2}_{SiH_2Ph} \quad + \quad Cp_2Ti \Big\langle{}^{PPhMe_2}_{(SiHPh)_nSiH_2Ph} \qquad (1)$$

2a   **5d**
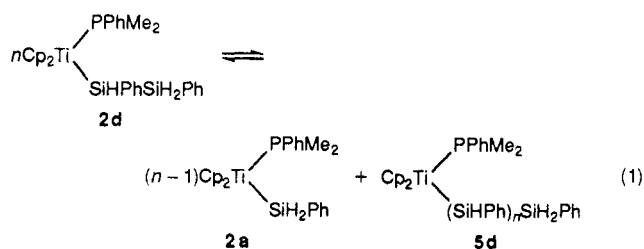
observed in this reaction, it is unlikely that it is not formed. More probably, it reacts rapidly with the disilyl complex, cleaving the Si–Si bond to give **2a** and PhSiH$_3$. The resulting free PhSiH$_3$ will then undergo methathesis with the disilyl ligand to give **7** and 1,2,3-triphenyltrisilane.

For the cases of Ph$_2$SiH$_2$ and PhMeSiH$_2$ with PPhMe$_2$, the spectra observed at −20 °C are those of **5b** and **2c**, respectively. Replacement of the silane hydrogens with deuterium gives spectra in which the hydrogen coupling is no longer evident, as expected. Warming the solutions to room temperature does not give **9**, but as the spectra of complexes **5b** and **2c** disappear, they are replaced, in

both cases, by the doublet of doublets characteristic of **7**. Attempts to do the same experiments with **3b** and **3c** were unsuccessful, apparently due to the tendency of these compounds to decompose in the solid state. Solutions of the products of reactions of Ph$_2$SiH$_2$, and PhMeSiH$_2$, with Cp$_2$TiMe$_2$ and PPh$_2$Me showed only the spectrum of **8**, even at low temperature.

The extreme sensitivity of these reactions to the nature of the reactants is also illustrated by the results obtained from reactions of PhCH$_2$SiH$_3$ with Cp$_2$TiMe$_2$, in the presence of PPhMe$_2$ or PPh$_2$Me. In the case of PPhMe$_2$, the initial product is **2e**, which, as it is warmed to room temperature, gives **9**. On the other hand, PPh$_2$Me gives initially **6e**, which, as it is warmed to room temperature, gives **8**.

All of the above observations can be accommodated within the reactions of Scheme I and eq 1. At low temperature, all of the silanes give **1** as the primary product when the phosphine is PMe$_3$. This is the most basic of the phosphines used, and it is the least likely to dissociate significantly. It would therefore be expected to form relatively stable silyl complexes which do not lead easily to coupled products. However, at higher temperatures these silyl/phosphine complexes can lose silane by deprotonation of the phosphine methyl group, to form **9**. With increasing phenyl substitution on the phosphine, it is likely that the reduced basicity leads to weaker binding of the phosphine ligand to Ti(III), resulting in easier formation of the phosphine-free species that is responsible for the catalytic dehydrocoupling. Consequently, with these systems, it is the catenated species **5** and **6** that are observed in the low-temperature regime, rather than **1**. At room temperature, the value of n (Scheme I) increases progressively, leading to a corresponding decrease in the ratios of **5**, or **6**, to **7** or **8**. The persistence of **7** and **8** in these cases indicates that they are not an efficient source of **9** via H$_2$ loss.

An alternative explanation of the failure of **9** to form with the phenylphosphines is that the phenyl group inhibits rotation about the Ti–C bond and prevents the methyl group from achieving the optimum conformation necessary for the abstraction of a hydrogen atom by the adjacent silyl ligand. We have reported elsewhere on the tendency of phenylsilyl ligands to have their conformation determined by the presence of phenyl substituents.[5]

The above results, and the conclusions derived therefrom, closely parallel similar results and conclusions based on zirconocene and hafnocene-derived catalysts.[8,9] However, in the case of zirconocene and hafnocene, virtually all of the catalysts and their precursors appear to be in oxidation state IV and are observable by NMR methods.[8,9] The key outstanding question in the titanocene-based system is whether the polymerization reaction takes place at a Ti(III) or a Ti(IV) center. Our earlier tentative conclusion, based on kinetic results,[10] that the true catalyst is a Cp$_2$Ti^{IV}(SiHR'R'')(H) complex (**10**) resulting from the disproportionation of the bimetallic Cp$_2$Ti(μ-H)(μ-HSiR-

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'R'')TiCp$_2$ (11), is fully consistent with the new observations. If the phosphine complexes are all in equilibrium with their phosphine-free antecedents, as we have previously proposed for the silyl species 1, then 11 results from the combination of the phosphine-free Ti(III) hydride, derived from 7 or 8, with the appropriate Ti(III) silyl.

We are continuing to search for isolable analogues of 7, 8, and 9 by modifying the ligand environment and using alternative syntheses.

Supplementary Material Available: Text giving representative examples of experimental details (1 page). Ordering information is given on any current masthead page.

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