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Catalysis of reactions of Si–H by titanocene and its derivatives

John F. Harrod *

Chemistry Department, McGill University, 801 Sherbrooke St. W, Montréal, Québec, Canada H3A 2K6

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* Tel.: + 1-514-3986911; fax: + 1-514-3983797.
E-mail address: harrod@chemistry.mcgill.ca (J.F. Harrod).

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Abstract

This review describes the remarkable ability of titanocene derivatives to catalyze reactions of Si–H compounds. These reactions involve addition of Si–H to unsaturated molecules, dehydrocoupling of Si–H with Si–H and with a variety of other E–H bonds, and redistribution of compounds containing the RO–Si–H bond system. The characterization of the many new titanocene complexes, which have been isolated as intermediates from these catalytic reactions, are also reviewed.

Keywords: Titanocene; Organosilanes; Hydrosilation; Dehydrocoupling; Redistribution; Catalysis; Enantioselection

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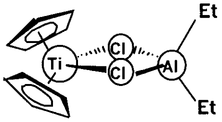
1. Historical introduction

The midpoint of the 20th century was punctuated by two remarkable discoveries that engendered the field of transition organometallic chemistry. These two discoveries were the synthesis of ferrocene [1] and the stereoselective polymerization of unsaturated hydrocarbons by Ziegler–Natta catalysts [2]. For 50 years these themes: coordination compounds with carbocyclic ligands and coordination catalysis of reactions of unsaturated molecules, have driven the burgeoning growth of research into the chemistry of transition metal organometallics. The first decade of research in Ziegler–Natta catalysis was dogged by an almost total lack of information regarding the fundamental chemical behavior of carbyls of the early transition metals. Key discoveries of the period 1950–1960 were the syntheses of $PhTi(OBu)_3$ [3], $MeTiCl_3$ [4], TiR_4 ($R = Me, PhCH_2, Ph$) [5]. These compounds served to reinforce the notion of the instability of the Group 4 carbyls, but added little to our understanding of catalysis.

Another important milestone in the development of this chemistry was the synthesis of the first titanocene derivative, Cp_2TiCl_2 [6]. This compound has since been the starting point for the synthesis of a large family of derivatives. One of the first such derivatives was compound **1**, reported by Natta et al. in 1958 [7]. This compound was isolated, and structurally characterized by single-crystal X-ray diffraction, from the reaction of Et_3Al with Cp_2TiCl_2 during attempts to isolate simple compounds capable of polymerizing olefins. Although **1** did polymerize ethylene, its activity was too low to be of interest and this avenue of research remained quiescent for three decades, until the discovery of alumoxane-promoted Cp_2MMe_2 ($M = Ti, Zr, Hf$) catalysts [8]. With the benefit of hindsight, it is interesting to note how close Natta came to discovering the single site catalysts that have revolutionized the low pressure polymerization of olefins in the final decade of the second millennium.



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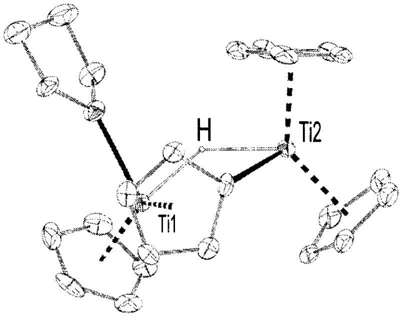
Cp_2TiCl_2 also served as a precursor for the synthesis of Cp_2TiMe_2 [9]. This fascinating compound is unexpectedly stable in the presence of O_2, or H_2O. Its synthesis, by metathetical replacement of Cl with MeLi, can be performed in air after completion of the MeLi addition and involves an aqueous wash during workup. Its solutions can be stored in air in the dark and at low temperature for long periods. Indeed, the presence of air is necessary for stabilization of the compound during storage and putting the crystalline solid under vacuum or Ar atmosphere leads to its rapid, and sometimes violent decomposition. The mechanism of this decomposition, and the nature of the brown–black product, remains unknown, but it is surely the key to many of the reactions of Cp_2TiMe_2 which will be described below. The initiation of decomposition appears to be photochemical, but once initiated, the reaction proceeds by a rapidly accelerating autocatalytic process. Oxygen appears to inhibit the decomposition by destroying the catalytic intermediate. The reactivity of Cp_2TiMe_2 is in marked contrast to that of the Zr and Hf analogs, which are extremely sensitive to air and moisture. The difference may be ascribed to low polarity of the Ti–C bond and the lower steric accessibility of the Ti.

2. Titanocene and the titanocene hydrides

In the present review, we will use the name titanocene in a number of different senses. If the molecule contains substituted Cp rings, the term 'substituted titanocene' will generally be used. If the titanocene molecule has additional ligands attached to the titanium, it will generally be called a 'titanocene derivative'. In many catalytic cycles, the key intermediate is not well defined and such cycles will usually be referred to as 'titanocene catalyzed'.

The synthesis of Cp_2TiCl_2 resulted from attempts to synthesize Cp_2Ti, titanocene [6]. Other attempts to synthesize titanocene have led to the discovery of a number of interesting compounds (mostly hydrides), but the synthesis of monomeric titanocene, or even its detection, has eluded us to this day. However, substituted derivatives have been reported [10]. One reason for the ephemeral nature of titanocene is its high reactivity, which in turn results from its unique, carbene-like electronic and orbital structure [11,12]. Its high propensity to insert into X–H bonds leads to the facile formation of the hydride species shown in Fig. 1. In the absence of a more reactive substrate, titanocene undergoes a self-insertion of one titanocene molecule into a C–H bond of a second molecule. This results in the titanocene(III) dimer **2**, originally



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isolated as the THF complex by Pez from a reaction of Cp_2TiCl_2 with (anthracene)$^{-\bullet}K^+$ [13]. A second insertion of the left side Ti of **2** (which would be highly unsaturated in the absence of the THF ligand), into one of the C–H bonds of the right side bis(η^5-cyclopentadienyl)Ti unit, would give rise to the bisfulvenyl hydride dimer **3**, originally identified by Bercaw and Brintzinger [14], and synthesized by reaction of solid Cp_2TiMe_2 with H_2. In solution Cp_2TiMe_2 reacts with H_2 to give **4** [14]. This reaction probably occurs by oxidative addition of H_2 to one molecule of Cp_2Ti, followed by conproportionation of the resulting $Cp_2Ti^{IV}H_2$ with a second molecule of Cp_2Ti to give **4**.

Although the structures of **3** and **4** were correctly assigned on the basis of a number of physical and chemical observations, the X-ray structure of **3** was only recently determined [15], whilst that of **4** still remains to be completed.

3. The transition metal–silicon bond

The first compound containing a M–Si bond (M = a transition metal), η^5-$CpFe(CO)_2SiMe_3$, was reported by Birmingham and Wilkinson in 1958 [16]. Little further interest was shown in such compounds until the importance of silyl metal intermediates in the hydrosilation of olefins and acetylenes, catalyzed by Group 18 complexes, was recognized in 1964 [17]. In the following two decades silyl complexes of most transition elements were reported. One notable exception was the elements of Group 4. In 1984, only four compounds had been reported to contain Ti–Si bonds and all were compounds of Ti^{IV} (two of these were subsequently shown to be erroneous). No compounds with Zr–Si or Hf–Si bonds were known.

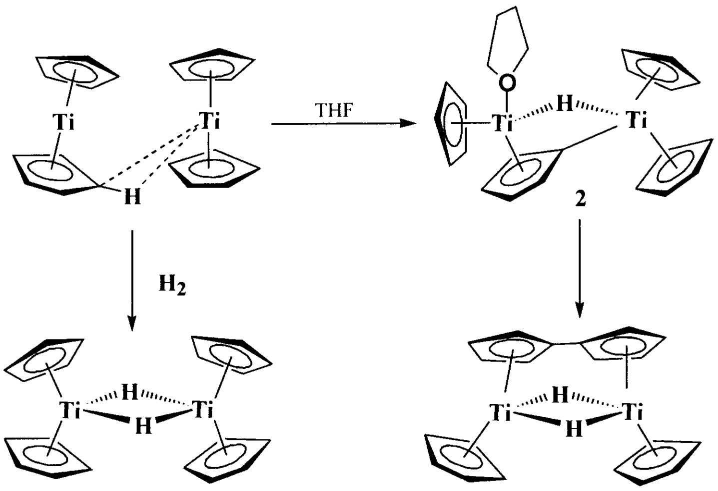
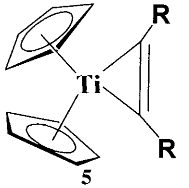


Fig. 1. Modes of reaction of titanocene.

In 1983 we began an attempt to synthesize titanocene silyl complexes by reaction of organosilanes with Cp_2TiMe_2. Since metathesis of organosilicon hydrides with transition metal alkyls was already established as a broadly applicable synthetic route to silyl complexes, and since Cp_2TiMe_2 was recognized to be metastable, we anticipated that compounds of the type $Cp_2TiMe_n(SiR_3)_{2-n}$ ($n = 0$, or 1) would result. Initial trials with common tertiary hydrides such as Ph_3SiH and Et_3SiH yielded only undefined products. However, after an induction period, $(RO)_3SiH$ (R = Me and Et) reacted with Cp_2TiMe_2 on exposure to sunlight or a tungsten lamp, to give a vivid transformation from the orange color of Cp_2TiMe_2 to a beautiful, intense navy–blue color. Soon after the color change, blue–black crystals deposited. Although the crystals seemed relatively well formed, and were easy to produce, they failed to be usable for X-ray diffraction despite the use of a wide variety of synthesis conditions. We therefore embarked on a search for a more suitable hydrosilane for the production of diffraction grade crystals. This search quickly led us to the primary and secondary silanes, exemplified by $Ph_{4-n}SiH_n$ ($n = 2$ or 3). Although these silanes appeared to give better quality crystals, these also failed to yield to X-ray analysis. They did, however, lead to the discovery of an important new reaction, the catalytic dehydrocoupling of organosilanes (see below) [18].

4. Catalytic hydrogenation of alkenes

The activity of a wide range of Ziegler-type catalysts for the catalysis of alkene hydrogenation was first demonstrated by Breslow et al. [19] $Cp_2Ti(CO)_2$ [20], $Cp_2Ti(CO)(C_2Ph_2)$ [21] and the titanacyclopropenes **5** [22] were all reported to be effective homogeneous hydrogenation precatalysts for a variety of alkenes and alkynes, as was a polystyrene supported Cp_2TiCl_2, activated with *n*-BuLi [23]. A catalytic system based on $Cp_2TiCl_2/(anthracene)^{-\bullet}K^+$ was reported by Pez et al. [24] and in a later study, Samuel reported that Cp_2TiMe_2 is active as a precatalyst for the hydrogenation of alkenes [25].



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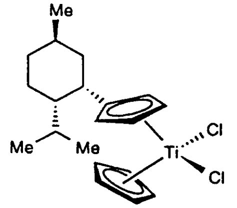
Harrod and Yun found that dimethyl titanocene activated by a silane is effective for the hydrogenation, as well as for the isomerization and hydrosilation of olefins [26]. Some substituted titanocene derivatives have also been activated and used for the hydrogenation of olefins [27,28].

Catalytic enantioselective hydrogenation of prochiral alkenes can be achieved with chiral titanocene catalysts [29]. Kagan reported low % *ee* values with complexes such as **6** [30]. The use of other more symmetrical titanocenes such as **7** [31,32] and **8** [33] bearing novel annulated Cp ligands led to improved enatioselectivities only in certain cases.



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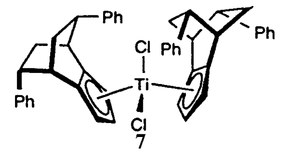

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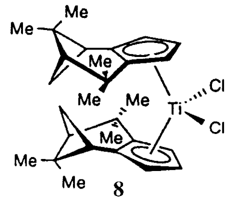

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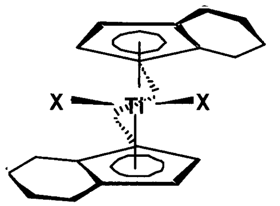
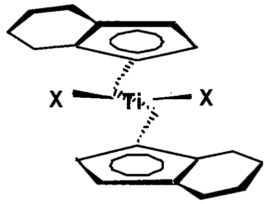
Buchwald et al. developed a very effective chiral titanocene catalyst by activating **9** and **10** with butyllithium. They obtained the corresponding Ti(III) hydride species which proved to be a highly enantioselective hydrogenation catalyst for unfunctionalized trisubstituted olefins, including acyclic and cyclic derivatives [34a]. With the same catalyst, high enantioselectivities were also obtained in the asymmetric hydrogenation of 1,1-disubstituted enamines to give the corresponding tertiary amines [34b].



(S,S,S)
9



(R,R,R)
10

(X_2 = 1.1' binaphthyl1-2,2'-diolate)

The active catalytic species for these hydrogenation reactions are believed to be $Cp_2Ti(III)$ hydrides, which can be produced by reduction of the corresponding dichlorides or dialkyl compounds [35]. The hydride species adds readily to alkenes to form titanocene alkyls, which can undergo hydrogenolysis to yield the alkanes and regenerate the catalyst. A simple catalytic loop for these processes is shown in Fig. 2. The hydrogenation of alkynes proceeds similarly.

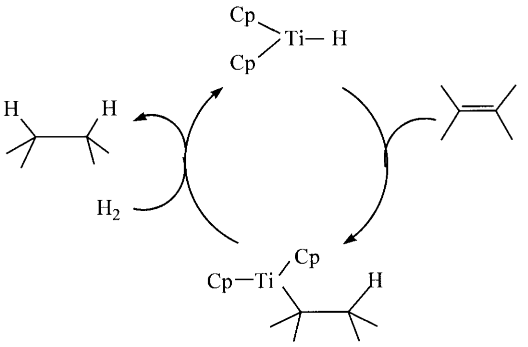


Fig. 2. A possible mechanism for the hydrogenation of alkenes with $Cp_2Ti(III)$ hydride.

Early mechanistic studies of olefin polymerization by Natta et al. also implicated the involvement of hydrides via polymer chain termination by hydride transfer and subsequent reinitiation of chain growth by insertion of olefin into the resulting metal hydride bond [36]. It was also shown that H_2 terminated polymer chain growth, presumably by hydrogenolysis of the M–polymer bond, to regenerate an active metal hydride bond. These reactions are summarized in Fig. 3.

In this scheme, the average value of n in the absence of H_2 is determined by the lower loop, i.e. the intrinsic rate of the hydride transfer from polymer chain end to metal (or to in-coming monomer). With increasing concentration of H_2, the upper loop becomes progressively faster until it determines the value of n. In the extreme, at high H_2 concentrations, the value of n approaches 1 and the reaction becomes a hydrogenation rather than a polymerization reaction. This chemistry provided the standard means of controlling the molecular weights of polyolefins produced by polymerization with the first three generations of Ziegler–Natta catalysts. More recently, Marks and co-workers have extended these principles by showing that silicon hydrides can function in a similar way with lanthanide-based catalysts. In this case, the polymer chain is terminated by metathesis of the M–C bond with Si–H, as shown in Eq. (1) [37].

$$\text{M–C} + \text{S–H} \rightarrow \text{Si–C} + \text{M–H} \tag{1}$$

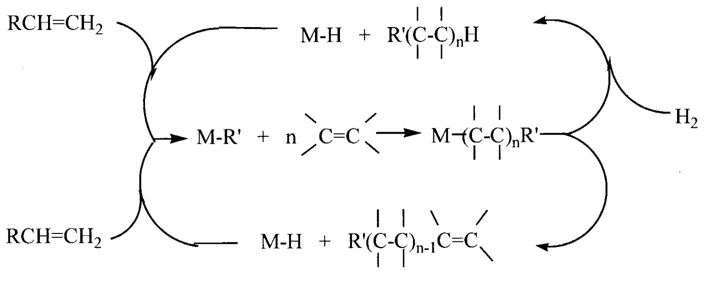
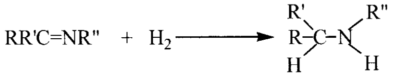


Fig. 3. Some hydride transfer reactions involved in Ziegler–Natta polymerization.

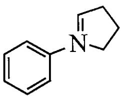
5. Catalytic hydrogenation of other substrates

A versatile and efficient titanocene catalyzed hydrogenation of ketimines has been reported by Willoughby and Buchwald (Eq. (2)) [38].



$$RR'C{=}NR'' + H_2 \longrightarrow RR'CH{-}NHR'' \qquad (2)$$

With a *R*,*R*,*R*-bis(tetrahydroindenylethane)titanium-1,1′-binaphth-2,2′-diolate/*n*-BuLi/$PhSiH_3$ catalyst ([BTHIE]Ti), a variety of ketimines were reduced to the corresponding amines in moderate to excellent enantioselectivities. The authors proposed a mechanism of insertion of the imine into a Ti–H bond, analogous to the olefin hydrogenation mechanism of Fig. 2. The enantioselectivity arises from the difference in energy between the two diastereomeric transition states **A** and **B**, Fig. 4. In **A** only one of the substituents of the imine is brought into close proximity to the phenylene rings of the C_2 symmetric bis-indenyl ligand, while in **B**, two of the imine substituents are in close proximity, leading to a preference for **A**. This model correctly predicts the absolute configuration of the product for an *anti*-ketimine (e.g. **11** and **12**) to be *R*, while that of a *syn*-ketimine (e.g. **13**) is *S*.



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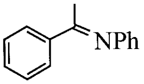

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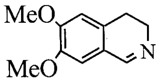

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6. Hydrosilation of alkenes and alkynes

Dimethyltitanocene is not an effective hydrosilation catalyst for simple alkenes. Simple linear and cyclic alkenes in fact promote catalytic dehydrocoupling of organosilanes by acting as hydrogen acceptors to produce alkanes [26]. With

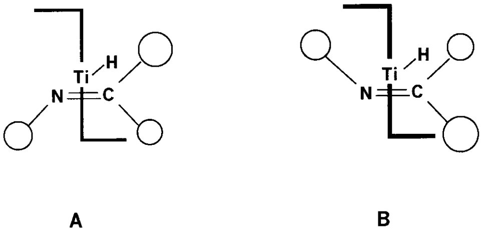
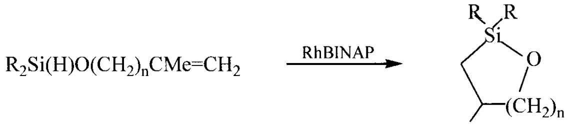


Fig. 4. Two diastereomeric transition states for a prochiral imine coordinated to a C_2 titanocene.

activated alkenes, such as styrenes, 1,3-dienes and norbornene, hydrosilation occurs with $PhSiH_3$, but the reactions are complicated by the simultaneous catalytic oligomerization of the silane. This contrasts with zirconocene-based catalysts, which efficiently catalyze hydrosilation of simple olefins [39].

Intramolecular hydrosilation has been extensively used to control regio- and enantioselectivity [40]. Bosnich et al. used this strategy (with homogeneous rhodium-based catalysts) to synthesize chiral diols by catalytic intramolecular hydrosilation of alkenyl silyl ethers [41] (Eqs. (3) and (4)).

$$R_2SiHCl + HO(CH_2)_nCMe{=}CH_2 \rightarrow R_2Si(H)O(CH_2)_nCMe{=}CH_2 + HCl$$
$$n = 1 \text{ or } 2 \qquad (3)$$



(4)

Xin and Harrod carried out similar reactions as a one-pot reaction using the titanocene catalyzed dehydrocoupling of the alcohol with a diorganosilane to generate the intermediate silyl ether, Eq. (5) [42]. The titanocene-based catalysts are of little synthetic utility since they give both intra- and intermolecular hydrosilation products, as well as products resulting from hydrogenation and redistribution reactions. The one-pot dehydrocoupling/hydrosilation strategy has more recently been shown to work to better effect with a rhodium-based catalyst [43]. In this case, although an unspecified amount of hydrogenation was reported to take place, it was very minor compared to the hydrogenation and other side reactions observed with the titanocene catalysts. A comparison of the two catalyst systems is presented in Table 1. The prevalence of the bis(alkenyloxy)silane products in the titanocene catalyzed reactions is due to the high activity of these catalysts for redistributing the mono(alkenyloxy)silanes, rather than to a competitive second dehydrocoupling reaction. In the case of the last entry of Table 1, the hydrosilation reaction occurs at a negligible rate compared to the first dehydrocoupling step and the subsequent redistribution.

$$R_2SiH_2 + HO(CH_2)_nCMe{=}CH_2 \xrightarrow{Cp_2TiMe_2} R_2Si(H)O(CH_2)_nCMe{=}CH_2 \qquad (5)$$

7. Hydrosilation of ketones

Nakano and Nagai first reported the use of diphenyltitanocene as a precatalyst for the hydrosilation of ketones [44]. The reactivity of this system is not very high

Table 1
Comparison of catalytic dehydrocondensation/hydrosilation reactions of $CH_2{=}C(Me)CH_2OH$ in the presence of Rh and Ti based catalysts

Catalyst	Silane	Time	Yield (**a**+**b**+**c**)[a] (%)	**a**:**b**:**c**	Ref.
$[Rh(diphos)(solv)_2]^+$ [b]	Ph_2SiH_2	<10 min	>95	95:5:0	[41]
$[Rh(diphos)(solv)_2]^+$ [b]	Et_2SiH_2	<10 min	>95	95:5:0	[41]
Cp_2TiMe_2 [c]	Ph_2SiH_2	49 h	90	29:24:35	[42]
Cp_2TiMe_2 [c]	$PhMeSiH_2$	19 h	93	68:5:20	[42]
rac-[BTHIE]$TiMe_2$ [c,d]	Ph_2SiH_2	24 h	82	26:28:28	[42]
rac-[BTHIE]$TiMe_2$ [c]	$PhMeSiH_2$	6 h	99	0:65:34	[42]

[a] **a** = cyclosiloxane, **b** = mono(alkenyloxy)silane, **c** = bis(alkenyloxy)silane.
[b] Catalyst concentration 2–4%.
[c] Catalyst concentration 1 mol % based on substrate.
[d] BTHIE = bis(1,2-tetrahydroindenyl)ethane.

owing to the stability of Cp_2TiPh_2. Dimethyltitanocene gives much higher reactivity, selectivity and yields. A considerable body of work has been reported on the use of C_2-symmetric *ansa*-titanocenes for the enantioselective hydrosilation of prochiral ketones. The performance of such reactions is highly variable and can depend sensitively on the structures of the catalyst, the silane, the ketone and the solvent. Buchwald and co-workers have obtained the most outstanding results. They have reported excellent enantioselectivity for the hydrosilation of acetophenones with PMHS as the hydrosilylating agent and a [BTHIE]titanium-based catalysts [45]. High enantioselectivity requires α-unsaturation and selectivities for dialkylketones are much lower. Buchwald has attributed this to the coplanarity of the carbonyl group and the aromatic ring, resulting from conjugation, which greatly favors one transition state diastereomer over the other [45].

Although the enantioselectivity is much lower in the case of dialkyketones, it can be varied significantly by sterically biasing the substrate [46]. The steric constraints within the intra-annular cleft of metallocenes plays an important role in this as in many other catalytic reactions of metallocenes.

The participation of a Ti–H intermediate in the catalytic cycle is strongly supported by the isolation of the hydride $[(BTHIE])TiH]_2$ from reactions of $[BTHIE]TiMe_2$ with silanes, both in the presence and absence of ketones [47]. Once again, we cannot be sure whether it is the Ti(III) hydride, or the Ti(IV) hydride, $[BTHIE]TiH_2$, produced together with [BTHIE]Ti, by disproportionation of the Ti(III) hydride.

8. Hydrosilation of other carbonyl compounds

Titanocene catalyzed hydrosilation of esters was achieved a decade later than the first report of their titanocene-catalyzed hydrogenation [48].

Buchwald and co-workers developed several procedures for the overall reduction of esters to primary alcohols via titanocene catalyzed hydrosilation [49]. The air stable system of the combination of Ti(O-*i*-Pr)$_4$ with (EtO)$_3$SiH converts esters to alcohols in excellent yield and with a high level of functional group compatibility [49c,d]. Another system for the conversion of esters to primary alcohols was also developed with a titanocene-based catalytic system employing (EtO)$_3$SiH as the stoichiometric reductant (Fig. 5) [50].

Catalyst generation was effected by the addition of *n*-BuLi to Cp$_2$TiCl$_2$. The system was found to be relatively insensitive to the presence of adventitious moisture or small amounts of oxygen, and was active for the reduction of a great variety of ester substrates. A high degree of selectivity was reported. For example, ethyl 6-bromohexanoate is cleanly converted to 6-bromo-1-hexanol. Likewise, α,β-unsaturated esters and esters containing phenolic, amino, or cyclopropyl groups, as well as di- and trisubstituted olefins, are efficiently transformed into the corresponding primary alcohols. A methyl ester can even be selectively reduced in the presence of a *tert*-butyl ester. However, the more hindered titanocene dichloride species, [BTHIE]titanium dichloride, **14**, is required for the selective hydrosilation of an ester in the presence of a ketone, or a terminal olefin, or an epoxide.

It is known that (EtO)$_3$SiH undergoes rapid redistribution to yield SiH$_4$ in the presence of titanocene catalysts [51]. To avoid the danger of SiH$_4$ and reduce the cost, two modifications have been introduced to the Cp$_2$TiCl$_2$/*n*-BuLi/(EtO)$_3$SiH system: (a) the use of PMHS instead of (EtO)$_3$SiH to eliminate the generation of SiH$_4$, (b) the use of EtMgBr instead of *n*-BuLi to generate an active catalyst system [50b]. The conversion of esters to the corresponding alcohols was accomplished in good to excellent yield using this system.

The catalytic reduction of five- and six-membered ring lactones to the corresponding lactols can also be accomplished using titanocene-based catalytic systems. Buchwald et al. reported the convenient method for the conversion of lactones to lactols via hydrosilation shown in Fig. 6 [52]. The hydrosilation to lactols was carried out via air-stable titanocene difluoride, or a titanocene diphenoxide precatalyst using PMHS as the stoichiometric reductant. The catalyst can be activated by reaction with phenylsilane or with tetrabutylammonium fluoride (TBAF). The

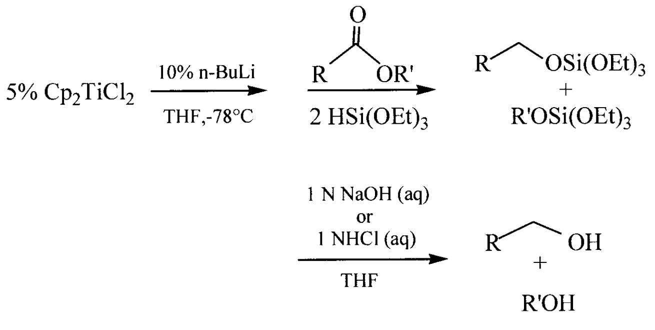


Fig. 5. Scheme for the reduction of esters to alcohols via hydrosilation.

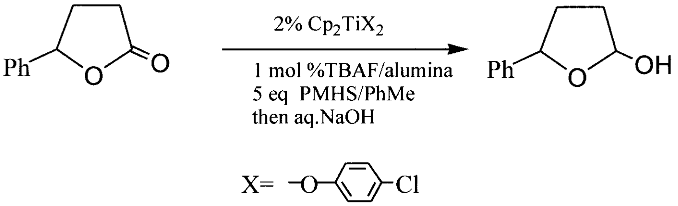


Fig. 6. Reduction of a γ-lactone catalyzed by a titanocene-based catalyst.

amount of titanocene catalyst can be as low as 0.5% relative to lactone substrate without any decrease in yield. Aromatic halides and α-substituted lactones can also be reduced to the corresponding lactols without any epimerization.

9. Hydrosilation of imines and pyridines

In an elegant series of studies, Buchwald et al. have also developed titanocene-type catalyst systems that are effective for hydrosilation of prochiral imines with very high enantioselectivity [53]. The most effective catalyst systems use the pre-catalyst **9**(**10**) with $X = F$. The pre-catalyst is activated by a remarkably facile reaction with $PhSiH_3$ at room temperature (r.t.), presumably with the generation of a titanium hydride. This reaction of the strong Ti–F bond is a prime example of how the similarity of Ti–X and Si–X bond strengths allow easy transfer of groups between the two elements, the key reason for the particular efficacy of titanocene catalysts for reactions of silanes (see also Si–O bond redistribution reactions discussed below).

The authors proposed that the chiral center is created through the same type of transition state (**A** or **B**, vide supra) as proposed for the analogous hydrogenation of imines. In the case of hydrosilation, displacement of the chiral amido ligand occurs by transfer of a silyl group to N via σ-bond metathesis between Si–H and Ti–N, with concurrent regeneration of the Ti–H bond.

The effectiveness of this catalyst system was extended for use with more sterically encumbered imine substrates by using a base-activation procedure [53b]. In this procedure a moderately bulky primary amine, such as $i\text{-BuNH}_2$, is added slowly over the course of the reaction. It is believed that the added amine promoter functions by rapid metathetical displacement of the bulkier chiral secondary amide ligand (Eq. (6)). Some results using this amine promotion effect are shown in Table 2.

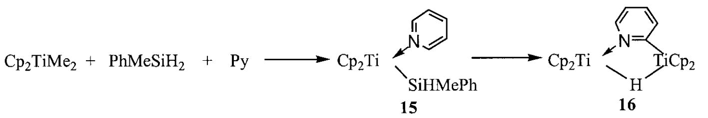
$$\text{Ti–NRR}' + \text{R}''\text{NH}_2 \rightarrow \text{Ti–NHR}'' + \text{RR}'\text{NH} \qquad (6)$$

A special case of imine hydrosilation, that of pyridines, was reported by Hao et al. [54]. Titanocenes are the only known homogeneous catalysts to effect the hydrosilation of pyridines and this reaction is also the only known example of hydrosilation of a highly aromatic molecule. The hydrosilation of pyridine with

Me_3SiH has been achieved in low yields using noble metal catalysts [55]. The titanocene-catalyzed hydrosilation of pyridines is also often accompanied by hydrogenation of one of the residual double bonds, as shown in Table 3.

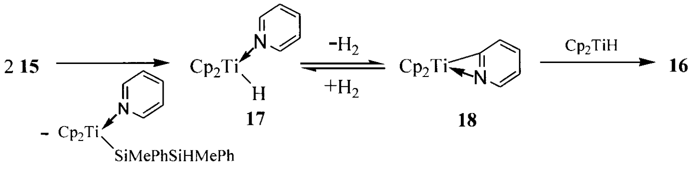
Although the dihydro- and tetra-hydropyridine products resist further reduction, even in the presence of a large excess of silane, they can be completely reduced by application of a moderate pressure of H_2. Pyridines with substituents in the 2-, or 6-positions are generally unreactive, but quinoline is an exception to this rule.

Stoichiometric reactions of Cp_2TiMe_2 with a variety of silanes and pyridines yield products such as **15** and **16** (Eq. (7)) [54]. Depending on the reaction conditions and the reactants, either **15** or **16** may crystallize from the reaction mixture and the structures of both types of compound have been established by single-crystal X-ray analysis.



(7)

A suggested mechanism for the transformation of **15** into **17** is shown in Eq. (8). A similar decomposition to the first step of (8) has been observed with titanocenesilyl phosphine complexes [56]. Klei and Teuben have previously proposed the species **18** [57a]. Although this compound has yet to be isolated and fully characterized in crystalline form, analogous acyclic complexes have been fully structurally characterized [57b].



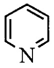
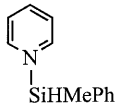
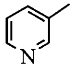
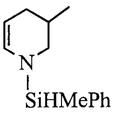
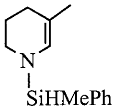
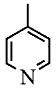
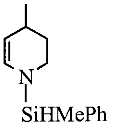
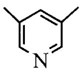
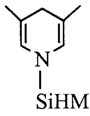
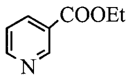
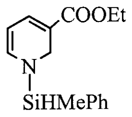
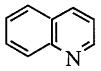
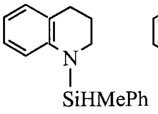
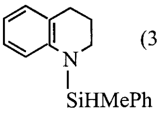
(8)

Table 2
Effect of added base on rate and *ee* in catalytic hydrosilation of imines [53b]

Entry[a]	Amine additive	*t* (h)	Conversion (%)	*ee* (%)
1	None	24	5	–
2	*n*-$HexNH_2$	2	100	85
3	*t*-$BuNH_2$	24	39	–
4	Pyrrolidine	24	4	–
5	*i*-$BuNH_2$	2	100	92
6	(±)-*s*-$BuNH_2$	2	75	78
7	None	12	94	97

[a] All entries except 7 used *N*-benzyl-1-indanimine and poly(methylhydrosiloxane) as the substrate. Entry 7 is the result obtained with 1(-phenylethylidene)methylamine and $PhSiH_3$ as substrates. Entries 1–6 were run at 60°C with 5 mol % catalyst. Entry 7 was run at r.t. with 1 mol % catalyst.

Table 3
Titanocene catalyzed hydrosilation/hydrogenation of pyridines [54][a]

Entry	Pyridine	Product		Yield (%)[b]
1				94
2		 	(3:2; 80°C) (1:2; 20°C)	85
3				83
4				70
5				100
6		 	(3:1)	74

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[a] All reactions were carried out neat at 80°C using 10 mol % Cp_2TiMe_2 (based on pyridine). Silane–pyridine ratio = 1.5:1.

[b] Based on integrals of ^{29}Si spectra.

A series of experiments using $PhMeSiD_2$ and C_5H_5N, or $PhMeSiH_2$ and C_5D_5N as substrates gave products in which much more extensive H/D exchange was evident at the 2- and 6-positions than in the other positions of the product and of the unreacted pyridine. Complete H/D exchange at the 2- and 6-positions of C_5D_5N also occurred under 15 atm of H_2 in the presence of a catalytic amount of $[Cp_2TiH]_2$. Of particular significance is the fact that 2-picoline undergoes neither hydrosilation nor hydrogenation, but complete exchange of the 6-proton occurs under catalytic conditions.

The products of reactions (7) and (8) and the H/D exchange results can be rationalized by the mechanism shown in Fig. 7 This scheme is essentially that

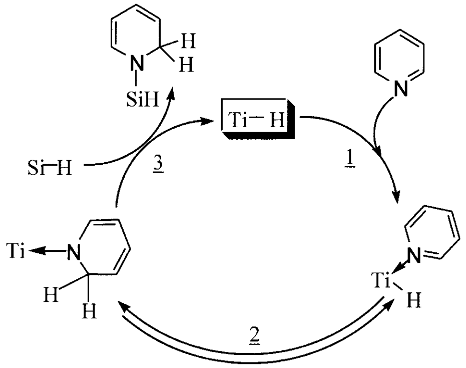


Fig. 7. A catalytic loop for hydrosilation of pyridine with a Ti–H intermediate.

proposed by Buchwald for the hydrosilation of imines, and the key catalytic intermediate is the titanocene hydride [53]. The H/D exchange results can be easily rationalized by the reversibility of step 2 in this cycle. The alternative cycle of Fig. 8, in which the titanocene silyl complex is the key catalytic intermediate cannot be excluded at the present time. However, this scheme requires another cycle to account for the H/D exchange results. Such a cycle is readily provided by the reversible *o*-metalation step of Eq. (8).

A result which supports the Ti–Si route is the distribution of isomers produced from 3-picoline. At 80°C the 1,2,3,4- and the 1,4,5,6-tetrahydropicolines are produced in a ratio of 3:2 (entry 2, Table 3), but at 25°C this ratio is $<0.05:1$. The strong preference for the 1,4,5,6-isomer at low temperature supports the case for insertion into a Ti–Si bond rather than a Ti–H bond. In the case of the Ti–Si bond, a preference for primary attack of the Si on the N moves the bulky Cp_2Ti group to either the 2- (pathway A, Fig. 9) or the 6-position (pathway B, Fig. 9) of the ring.

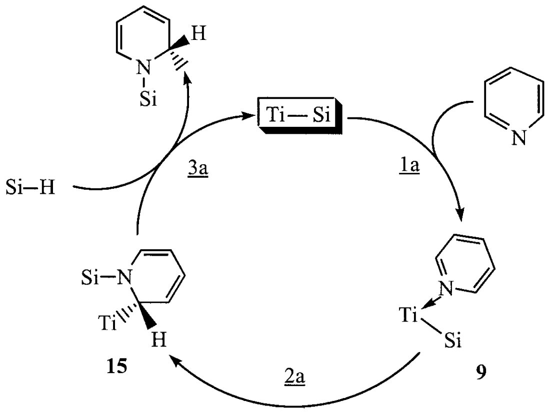


Fig. 8. A catalytic loop for hydrosilation of pyridine with a Ti–Si intermediate.

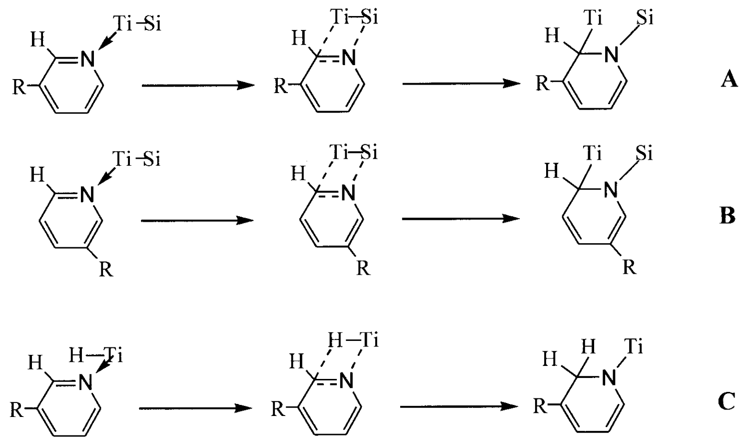


Fig. 9. Some possible reaction coordinates for the insertions of N=C of pyridine into Ti–Si and Ti–H bonds.

Clearly the steric repulsion of the Me group favors the shift to the 6-position to give eventually the 1,4,5,6-tetrahydropicoline isomer. In the case of Ti–H, attack of Ti at N occurs (pathway C, Fig. 9) and not much steric preference for the H to move to either the 2- or 6-position is expected. In this case, little regioselectivity is expected with respect to the two pathways and the regioselectivity would be relatively temperature independent.

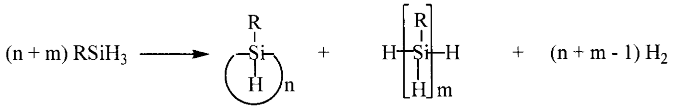
Since many substituted pyridines are prochiral, this reaction will no doubt be further developed for enantioselective hydrosilation of such pyridines.

10. Catalytic dehydrocoupling of silanes

Dehydrocoupling is the process of forming an element–element bond by the elimination of H_2 between two E–H bonds, thus in Eq. (9):

$$\mathrm{E}\boxed{\mathrm{H} \;+\; \mathrm{H}}\mathrm{E} \longrightarrow \mathrm{E}_2 + \mathrm{H}_2 \qquad (9)$$

The metallocenes of Group 4 are uniquely active for the formation of Si–Si bonds by dehydrocoupling [58]. Primary organosilanes undergo the reactions shown in Eq. (10), giving linear polymers with average values of *m* approaching 100 with the better catalysts. Other catalysts yield mainly cyclic oligosilanes with *n* values of ca.



(10)

6. With the exception of methylsilane [59], there is no evidence that the third hydrogen reacts at all and it is this lack of reactivity, which leads to the formation

of a linear polymer. In the case of methylsilane polymerization, gelation occurs after complete consumption of monomer owing to coupling of backbone Si–H groups [59].

Although most organometallics of the transition elements seem to show some activity, only the Group 4 metallocenes have so far been shown to catalyze the reaction rapidly, under ambient conditions, to give polymers. Even with Group 4 metallocenes, only the primary organosilanes react in this manner. Secondary silanes only give dimers, or oligomers with a few Si atoms, and tertiary silanes do not react to give disilanes at all [60]. It has been amply demonstrated that reactions catalyzed by metallocenes are typically very sensitive to steric effects due to the space limitations in the coordination cleft of the metallocene unit, so the dramatic decline in activity with increasing substitution at the silicon is not surprising. Despite many attempts by several different groups, number average molecular weights above ca. 10^4 have not yet been achieved.

Although electronic and optical properties have reached a plateau at molecular weights of ca. 10^4, desirable engineering properties require an increase of another order of magnitude. It seems probable that the limitation on molecular weight is purely a rate problem, since polystannanes of much higher molecular weight can be synthesized by similar dehydrocoupling chemistry [61].

11. The mechanism of the Cp_2TiMe_2 catalyzed dehydrocoupling of silanes

When Cp_2TiMe_2 is used to catalyze dehydrocoupling, the reaction occurs in two stages. Firstly, there is an induction period followed by a rapid, autocatalytic reaction which transforms Cp_2TiMe_2 into the active catalyst [35b,62]. This stage always produces one equivalent each of Si–Me and CH_4. We have speculated that this reaction is as depicted in Eq. (11), although the titanocene is not observed (however, see below).

$$Cp_2TiMe_2 + R_2SiH_2 \rightarrow R_2MeSiH_2 + CH_4 + Cp_2Ti \tag{11}$$

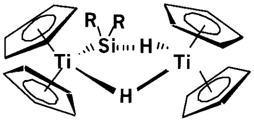
The autoacceleration is believed to arise from a catalysis of the reaction by Cp_2Ti. A catalytic loop illustrating such a process is shown in Fig. 10.

The steps in this cycle are conproportionation of Cp_2Ti^{II} with $Cp_2Ti^{IV}Me_2$ to give $[Cp_2Ti^{III}Me]_2$ (**a**), dissociation of $[Cp_2Ti^{III}Me]_2$ (**b**), σ-bond metathesis between Si–H and Ti^{III}–Me to give Si–Me and Ti^{III}–H (**c**) and reaction of Ti^{III}–Me and Ti^{III}–H to give two equivalents of Cp_2Ti and one of CH_4 (**c**′ + **d**). Through the agency of this loop, one molecule of Cp_2Ti doubles itself with each cycle, leading to a geometrical growth in the rate of the cycle and of the overall rate of decomposition of $Cp_2Ti^{IV}Me_2$.

Since none of the species have been directly detected in the course of a reaction, Fig. 10 is largely speculative. As will be seen below, the Cp_2TiH moiety recurrently appears in products from reactions of silanes with Cp_2TiMe_2 in the presence of a variety of other substrates. We have also recently isolated the THF coordinated titanocene dimer, **2**, from reactions of Cp_2TiMe_2 with lactones and $PhMeSiH_2$, providing fairly direct evidence for the participation of titanocene. (We have re-determined the structure of this compound and located the bridging hydride which Pez was not able to locate in the original structure determination [13]. The presence of the hydride confirms the structure as a true dimer of titanocene, stabilized by coordination of a THF molecule). Finally, we have also demonstrated the general tendency of Cp_2Ti^{II} and $Cp_2Ti^{IV}X_2$ to conproportionate to $Cp_2Ti^{III}X$ [63]. Of particular relevance was the reaction shown in Eq. (12). In this reaction $Cp_2Ti(PMe_3)_2$ is a source of Cp_2Ti^{II}.

$$Cp_2Ti(PMe_3)_2 + Cp_2TiMe_2 \rightarrow 2Cp_2TiMe(PMe_3) \tag{12}$$

The second stage of the reaction of an excess of R_2SiH_2 with Cp_2TiMe_2 is the formation of the titanocene(III) silyl complexes **21** and **22** through reactions of titanocene with the Si–H [58,64]. The dimetallic **21**, which is formally a combination of $Cp_2Ti^{IV}H(SiHR_2)$ with Cp_2Ti^{II}, or of $Cp_2Ti^{III}(SiHR_2)$ with $Cp_2Ti^{III}H$, appears first and is then converted to **22**, the dimer of $Cp_2Ti^{III}(SiHR_2)$, by reaction with silane. In the case of $PhSiH_3$, both of these compounds have been isolated pure and characterized by single-crystal X-ray diffraction. Although **22** is moderately stable in the solid state, it slowly reverts to **21** in solution, with the production of polyphenylsilane. A series of reactions which explains how **21** and **22** may be



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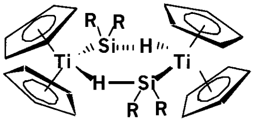

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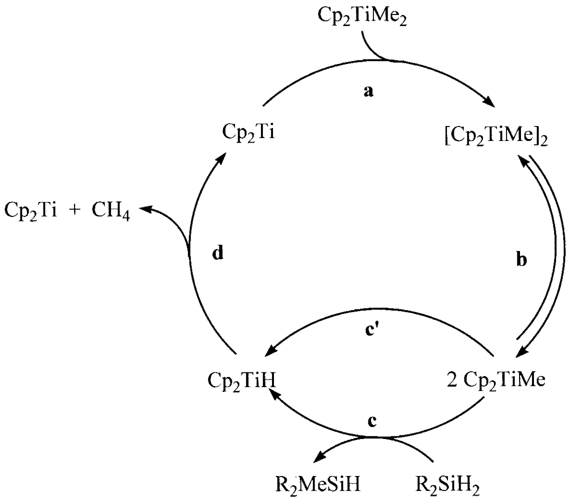
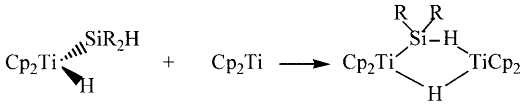


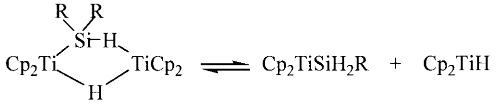
Fig. 10. A proposed catalytic loop for the autoacceleration of decomposition of Cp_2TiMe_2 in the presence of silanes.

formed is shown in Eqs. (13–18). There is no direct experimental observation of (14) and (15), but (13) is inferred from the reactions of $Cp_2Ti(PMe_3)_2$ with phosphines (see Section 15), while (16), (17) and (18) may be inferred from the results of some reactions of **22** with phosphines (see Section 13). The precise manner in which reaction (18) occurs is not clear, but an understanding of its mechanism is the key to understanding the mechanism of silane polymerization.

(13)

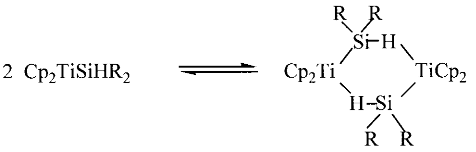


(14)

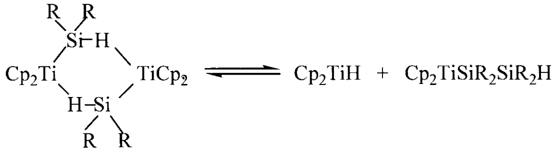


(15)

$$Cp_2TiH + R_2SiH_2 \rightarrow Cp_2TiSiHR_2 + H_2 \qquad (16)$$



(17)

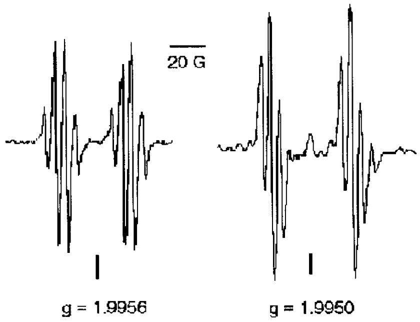


(18)

At the time the structures of **21** and **22** were determined, the intermetallic η^2-Si–H bonding seemed quite unusual. However, there were some precedents in the literature for metals other than Ti [65]. Subsequently, many examples of both intra- and intermetallic η^2-Si–H bonds have been reported [66].

12. Catalytic dehydrocoupling of other Group 14 hydrides

Organogermanes can also be polymerized by dehydrocoupling in the presence of titanocene [67] and zirconocene [68] catalysts. Reactivities of Ge–H bonds seem to be higher than Si–H, which leads to cross-linking of poly(phenylgermane). Diphenyl germane also undergoes rapid reaction, but only oligomers with ca. Ge_4 are produced.



(a) (b)

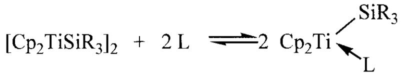
Fig. 11. EPR spectra of (a) $Cp_2Ti(SiH_3)(PMe_3)$ and (b) $Cp_2Ti(SiH_2Ph)(PMe_3)$ showing characteristic couplings to ^{31}P and Si–^1H.

$PhGeH_3$ and Ph_2GeH_2 undergo catalytic and stoichiometric reactions with Cp_2TiMe_2 which are very similar to those of $PhSiH_3$ and Ph_2SiH_2. It appears that the mechanisms of the germane reactions parallel those of the silanes [67].

Although polystannanes can be produced readily by dehydrocoupling with zirconocene catalysts, there has been no report of successful polymerization to linear polymers with titanocene catalysts [61].

13. Phosphine complexes of titanocene(III) silyls

The dimer **22** reacts with donor ligands (L) to give classical monomeric complexes, **23**, as depicted in Eq. (19). These complexes are readily detected in solution by their simple EPR spectra, especially in cases where there are other nuclear spins

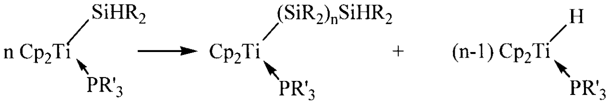


$$[Cp_2TiSiR_3]_2 + 2\,L \rightleftharpoons 2\ \underset{\mathbf{23}}{Cp_2Ti(SiR_3)(L)} \qquad (19)$$

bonded to, or close to the Ti^{III}. This is particularly important in the case of coupling to the ^1H of Si–H bonds since it provides a means of identifying the number of protons attached to the Si of the silyl ligand.

Phosphines readily form complexes **23** which, because of their relative insolubility in the hydrocarbon solvents used as the reaction medium, give nicely crystalline products directly [69]. This is fortunate since many of these complexes are quite unstable in solution, but relatively stable in the solid state. The structures of a number of R_3P (R = Me or Et) R'_3Si complexes ($R'_3 = PhH_2$, Ph_2H, PhMeH) have been confirmed by single-crystal X-ray diffraction [69a,c,70]. The EPR spectra of two of these complexes in solution are shown in Fig. 11. These illustrate the usefulness of such spectra in assigning the structures of titanocene(III) species in solution. The spectra are relatively simple due to the absence of resolvable coupling to the protons on the Cp rings, or to protons not directly attached to the Si and P atoms. The larger coupling constant is due to coupling of the unpaired electron to ^{31}P (ca. 28 G) and the smaller to coupling to the ^{1}H of the Si–H bonds (ca. 4 G). In the case of spectrum (a), the silyl ligand is SiH_3, which gives a doublet of quartets, while the $PhSiH_2$ ligand of spectrum (b) gives doublet of triplets.

As part of a search for better quality crystals, complexes **23** with the phosphine ligands $Ph_nMe_{3-n}P$, $n = 1$ or 2, were prepared [69b]. Analysis of the products by solution EPR gave surprising results. In some cases, the spectrum corresponded to the expected complex **23**, in others an apparent complex **23** was observed with one less Si–H than expected, in yet others a hydride $Cp_2TiH(PR'_3)$ was the principal species observed. The origin of these confusing results was traced to the decomposition of complexes **23** according to Eq. (20).



23 **24** **25** (20)

The EPR spectra of a sample of $Cp_2Ti(SiH_2Me)PMe_3$, prepared and measured at 223 K, and then remeasured after allowing the solution to warm up to r.t., are shown in Fig. 12. As the average chain length of the polysilyl ligand increases, the concentrations of **23** and **24** decrease relative to **25**, asymptotically approaching zero at high conversions. In addition, since the EPR spectrum only detects the Si–H bonds on the Si bonded directly to the Ti, the spectrum of **24** manifests coupling of the unpaired electron to one less proton than that of **23**.

Although the mechanism by which reaction (20) occurs is still not understood, it is clearly the key to fully understanding the mechanism of titanocene catalyzed silane dehydrocoupling. A catalytic loop for dehydrocoupling of silanes, which incorporates the concepts developed above is illustrated in Fig. 13.

14. Some other reactions of phosphines with Cp_2TiMe_2 in the presence of silanes

Complexes **22** react rapidly and cleanly with phosphines, either following preparation in solution without isolation, or following isolation and redissolution. Addition of a phosphine to Cp_2TiMe_2 before reaction with a silane suppresses the autocatalytic cycle shown in Fig. 10, probably by trapping the Cp_2Ti. In the case of tertiary phosphines this leads to a slowing down of the production of titanocene(III) complexes, but the isolated product is still **23**. With primary and secondary phosphines the results are more complicated.

A photo-initiated reaction of Cp_2TiMe_2 with $PhSiH_3$ in the presence of Cy_2PH (Cy = cyclohexyl) produces $Cp_2Ti(SiH_2Ph)(PHCy_2)$ [71]. Although the product is detectable in solution by EPR spectroscopy, no crystalline product is obtained,

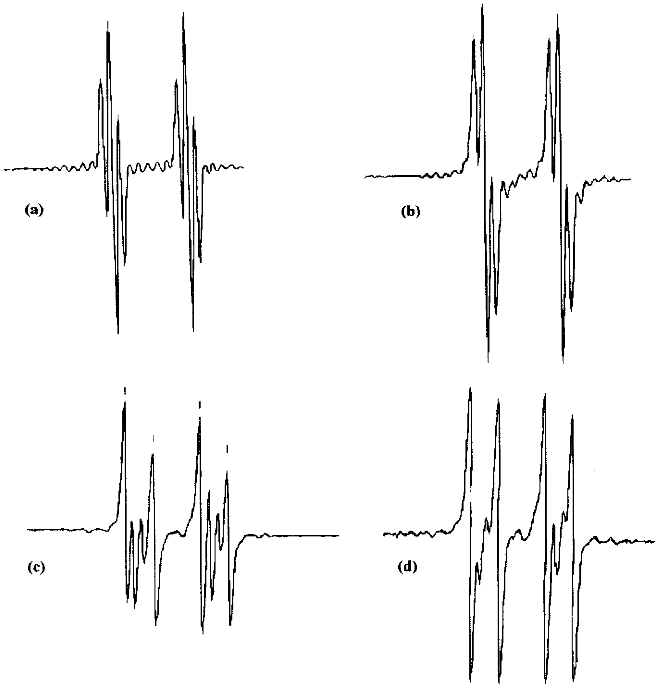


Fig. 12. Decomposition of $Cp_2Ti(SiH_2Me)PMe_3$ in solution followed by EPR spectroscopy. (a) Initial $Cp_2Ti(SiH_2Me)PMe_3$ in toluene at 233 K. A doublet of triplets characteristic of a $Cp_2Ti(SiH_2R)(PMe_3)$ complex. (b) After 20 min at 293 K. The triplets have given way to doublets, indicating the change from SiH_2Me to $(SiHMe)_nSiH_2Me$. (c) After 6 days at 293 K. The doublet of doublets due to $Cp_2TiH(PMe_3)$ is apparent (d) After 14 days at 293 K. The doublet of doublets shows that the hydride is now the dominant species.

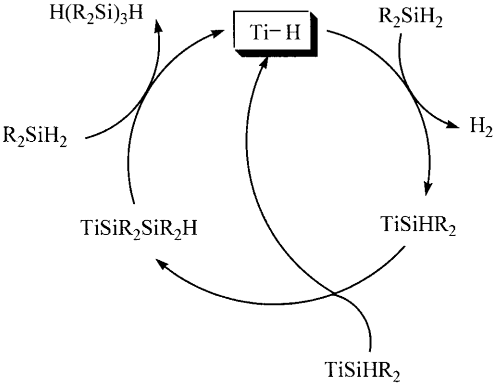


Fig. 13. A proposed catalytic loop for the titanocene hydride catalyzed dehydrocoupling of silanes.

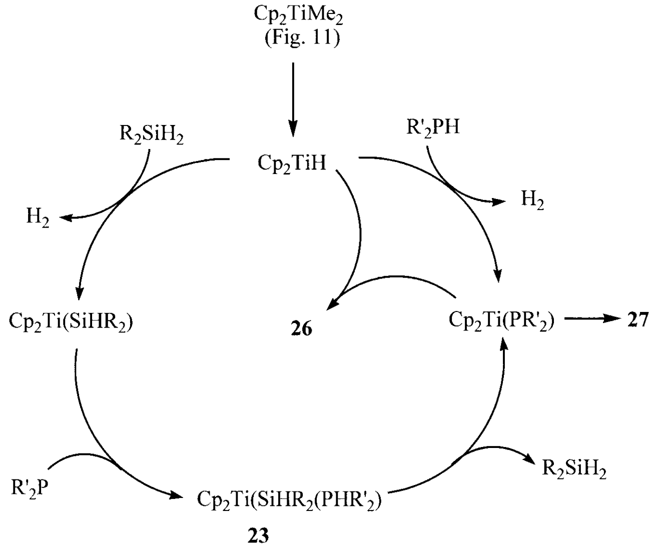
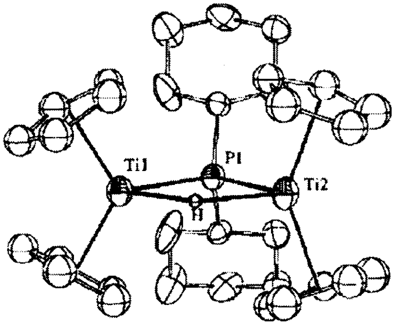


Fig. 14. A reaction scheme to show possible reactions forming **21**, **24** and **25**.

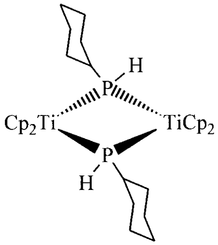
presumably due to the effect of Cy groups on its solubility. A similar reaction with Ph_2SiH_2 in place of $PhSiH_3$ gave a crystalline product, which X-ray analysis showed to be **26**, formally composed of $Cp_2Ti^{III}H$ and $Cp_2Ti^{III}PCy_2$ and isoelectronic with **21**. It is assumed that **26** forms by reactions analogous to (13) and (14) and is the isolated product by virtue of its being the least soluble species in the mixture of products. It is important to note that, in this case, photolysis in the absence of silane does not result in any identifiable reaction.



26

A similar reaction using $CyPH_2$ (with either Ph_2SiH_2 or $PhSiH_3$) behaves quite differently. No reaction occurs without continuous photolysis and no $Cp_2Ti(SiH_2R)(PH_2Cy)$ is detected. However, extended photolysis with a low pressure Hg lamp source yields the titanocene(III) phosphide dimer, **27**. In contrast to the case of **26**, a number of analogs of **27**, prepared by classical metathesis methods, had already been reported [72].

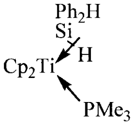
Fig. 14 shows some reactions which account for the observed behavior of the $Cp_2TiMe_2/R_2SiH_2/R'_2PH$ systems. Whether the observed product is **23**, **26**, or **27** depends on the steric demands of both the silyl and the phosphine ligands. Excessive steric encumbrance renders **23** unstable, which accounts for the fact that it is observed as a fairly stable species in solution when $R_2 = PhH$, and $R'_2 = CyH$, but not when $R_2 = Ph_2$ and $R'_2 = Cy_2$. The isolated product of the decomposition in the latter case is **26**, whose preferential formation may either be due to the fact that it is the least soluble species in the product mixture, or because the formation of **27** is precluded by the excessive steric hindrance of two Cy groups on the phosphide. With only a single Cy group on the phosphide, the solubility and steric factors favor formation of **27**.



27

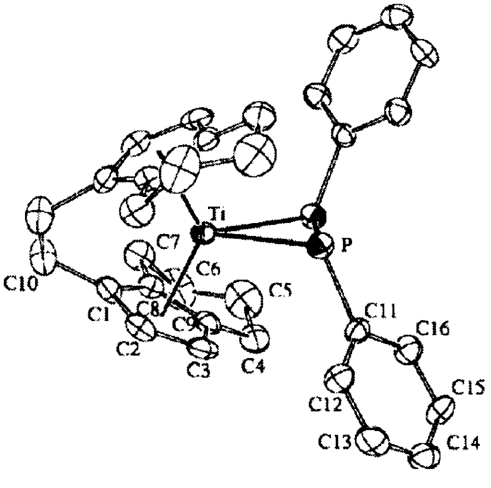
15. Catalytic dehydrocoupling of phosphines

Although organophosphines are isoelectronic with organosilanes, the reactivity of R_nPH_{3-n} ($n = 1$ or 2) is clearly quite different from that of the analogous R_nSiH_{4-n}. Despite the formal analogy of compounds **26** and **27** to **21** and **22**, their rates and mechanisms of formation from Cp_2TiMe_2 are quite different. This difference is largely due to the much greater ability of phosphines to form strong dative bonds to metals. However, although silanes do not form dative bonds, they do form η^2-bonds, as for example in **28**, which results from reaction of $Cp_2Ti(PMe_3)_2$ with Ph_2SiH_2 [71].



28

None of the reactions described in the previous section gave any indication of catalytic dehydrocoupling of P–H bonds. On the other hand, $[(BTHIE)TiH]_2$ does catalyze the oligomerization of $PhPH_2$ to a mixture of linear and cyclic oligophosphanes [71]. The catalytic reaction slows and eventually stops due to precipitation of the very insoluble complex **29**. The isolation and characterization of this complex



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provides a clue to the possible mechanism of the reaction, shown in Fig. 15. This scheme raises a question which recurs in much of the catalytic chemistry of titanocene and its derivatives, namely: what is the oxidation state of the active species? In this particular reaction, the catalyst, $[(BTHIE)TiH]_2$, is formally a Ti^{III} complex, while the isolated Ti-containing product is either a Ti^{IV} (assuming a cyclodiphosphane structure) or a Ti^{II} (diphosphene π-complex). In fact, the NMR parameters favor the former assignment. On the other hand, most of the previously described catalytic reactions start with Cp_2TiMe_2 (formally a Ti^{IV} complex) and most of the isolated Ti-containing products are formally Ti^{III} compounds. This behavior arises from the facile disproportionation/comproportionation of these three oxidation states of titanocene, as depicted in Eq. (21).

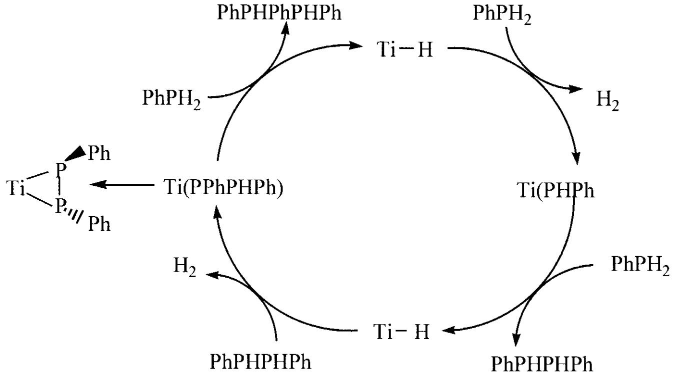


Fig. 15. Reactions proposed to explain the formation of **28** and the dehydrocoupling of $PhPH_2$.

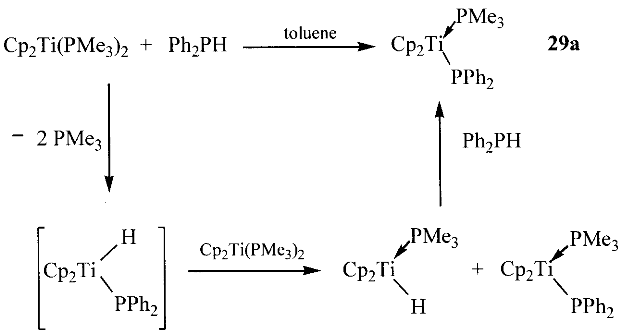


Fig. 16. Proposed sequence of reactions leading to formation of **29a**.

$$2Cp_2TiX \rightleftharpoons Cp_2Ti^{II} + Cp_2Ti^{IV}X_2 \qquad (21)$$

Reaction (21) has been shown to lie to the left for a broad range of ligands X in the presence of Me_3P [63]. There are also some examples of the reaction moving to the right. Notably the reaction where X = Cl lies to the right in the presence of CO to give Cp_2TiCl_2 and $Cp_2Ti(CO)_2$ [74].

To date there have been no follow-up studies of phosphine dehydrocoupling with titanocene-based catalysts. However, some very interesting reactions have been reported using a zirconocene-based catalyst, which seems to be more active than titanocene [75].

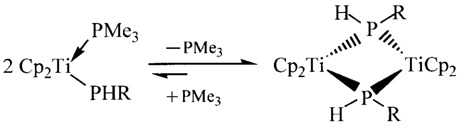
16. Catalytic cross-dehydrocoupling of phosphines with silanes

Both Cp_2TiMe_2 and $Cp_2Ti(PMe_3)_2$ are effective catalysts for the cross-coupling of P–H with Si–H [76]. In a typical catalytic reaction, depicted in Eq. (22), equimolar amounts of $PhSiH_3$ and Ph_2PH in the presence of 5 mol % of $Cp_2Ti(PMe_3)_2$ gave

$$PhSiH_3 + Ph_2PH \xrightarrow[\text{toluene, 25°C}]{Cp_2Ti(PMe_3)_2\ 3-10\ \text{mol}\ \%} PhH_2SiPPh_2 + (Ph_2P)SiHPh + H_2 \qquad (22)$$

the products Ph_2PSiH_2Ph and $(Ph_2P)_2SiHPh$ in a molar ratio of 5:1 with 100% consumption of Ph_2PH in 24 h at ambient temperature. The reaction proceeds in a stepwise manner with Ph_2PSiH_2Ph produced first, followed by reaction with a second molecule of phosphine. The reaction of $PhSiH_3$ with $CyPH_2$ was slower, but produced the same type of products. Prolonged reaction (14 days) resulted in the eventual formation of the known compound, 1,3,5-tri(phenylsila)-2,4,6-tri(cyclohexylphospha)-cyclohexane, in 65% yield [77]. $PhSiH_3$ and $PhPH_2$, or $PhSiH_3$ and Cy_2PH, did not react under similar conditions.

A series of experiments demonstrated the occurrence of the reactions shown in Fig. 16. A reaction of equimolar amounts of $Cp_2Ti(PMe_3)_2$ and Ph_2PH at r.t. gave $Cp_2Ti(PPh_2)(PMe_3)$, **29a**. With a 2:1 molar ratio of $Cp_2Ti(PMe_3)_2$ to Ph_2PH, $Cp_2Ti(PPh_2)(PMe_3)$ and the hydride $Cp_2TiH(PMe_3)$ were formed in a 1:1 ratio, as shown by EPR spectroscopy. The intermediate $Cp_2TiH(PPh_2)$ was not observed, even at low temperatures, presumably due to its rapid reaction with $Cp_2Ti(PMe_3)_2$. A similar sequence to that shown in Fig. 16 occurred in the reactions of $Cp_2Ti(PMe_3)_2$ with primary phosphines RPH_2 (R = Ph, Cy), to yield the phosphido compounds $Cp_2Ti(PHR)(PMe_3)$ (**29b**, R = Ph; **29c**, R = Cy). **29b** and **29c** lose PMe_3 easily to form the phosphide bridged dimers $[Cp_2Ti(\mu\text{-}PHR)]_2$, cf. **27** shown below. The poor solubility of these dimers pulls the PMe_3 dissociation equilibrium in the direction of **27** by precipitation (see Eq. (23)). On the other hand, **29a** can be isolated, either as a consequence of tighter binding of the PMe_3, or due to its more sterically demanding phosphido ligand destabilizing the dimer. Addition of PMe_3 to toluene solutions of the phosphide bridged dimers regenerated **29b** and **29c**, respectively, proving the reversibility of Eq. (23). No reaction occurred between $Cp_2Ti(PMe_3)_2$ and Cy_2PH, presumably because of steric hindrance. The rates of the reactions of $Cp_2Ti(PMe_3)_2$ with phosphines to give **27** follow the order $PhPH_2 > Ph_2PH \sim CyPH_2$.



29 **27**

29b R = Ph
29c R = Cy

27b R = Ph
27c R = Cy

(23)

Treatment of **29a** with $PhSiH_3$ (two equivalents) led to its complete conversion to $Cp_2Ti(PhSiH_2)(PMe_3)$, **23**, in about 2 h. Addition of Ph_2PH (two equivalents) to this solution regenerated **29a** fully in 1 h, showing that the conversion of **23** to **29a** is about twice as fast as that of **29a** to **23**. A solution of **23**, prepared independently from Cp_2TiMe_2 and $PhSiH_3$ in the presence of Me_3P, also reacted completely with Ph_2PH to give **29a** and Ph_2PSiH_2Ph in 1 h. It was concluded from these results that the key catalytic intermediate is most likely $Cp_2TiH(PMe_3)$, even though it was not observed by EPR spectroscopy in the course of the reaction.

A sample of $Cp_2TiH(PMe_3)$, prepared independently, reacted cleanly with Ph_2PH, or $PhSiH_3$ to give $Cp_2Ti(PPh_2)(PMe_3)$, or $Cp_2Ti(PhSiH_2)(PMe_3)$, respectively. These reactions were very fast at r.t., in contrast to the much slower reactions of $Cp_2Ti(PPh_2)(PMe_3)$ with $PhSiH_3$, or $Cp_2Ti(PhSiH_2)(PMe_3)$ with phosphine, which took place in the order of hours. This difference in reactivity accounts for the extremely low steady state concentration of $Cp_2TiH(PMe_3)$ and the failure to detect it by EPR in the course of the catalytic reaction.

The proposed mechanism for the catalytic heterodehydrocoupling reactions, involving a sequence of σ-bond metatheses between substrates and Ti(III)–X species, where X = silyl, phosphide or H is shown in Fig. 17 [76]. The surprising fact that primary phosphines are much less reactive than secondary phosphines is explained by the excessive stability of their complexes **29**. In stoichiometric reac-

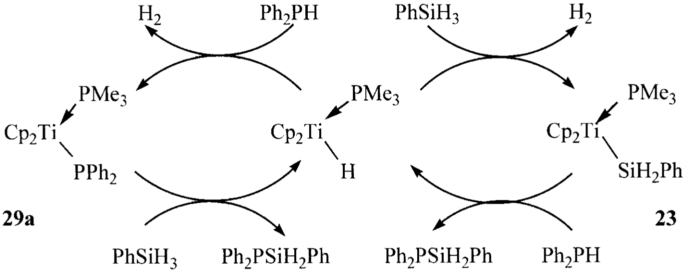


Fig. 17. The two reaction loops involved in the cross dehydrocoupling of Si–H/P–H.

tions **29b** does react with $PhSiH_3$ to give **23b** at a similar rate to **29a**, while treating **23b** with $PhPH_2$ regenerates **29b**. However, under catalytic conditions, the phosphine reactant is present at a much higher concentration than the Me_3P introduced with the catalyst. Among the phosphines studied in these reactions, $PhPH_2$ was the least basic, but also the least sterically demanding ligand. If the steric factor predominates, then the formation constant for $Cp_2TiPHPh(PH_2Ph)$ could be high compared to its analogs $Cp_2TiPPh_2(PHPh_2)$ and $Cp_2TiPHCy(PHCy_2)$. This in turn could lead to depletion of the reactive intermediates in the catalytic cycle, as shown in Fig. 18.

No homodehydrocoupling reaction of $PhSiH_3$ or of RR′PH occurred in any of the reactions described above. Reaction of $Cp_2Ti(PMe_3)_2$ with excess $PhSiH_3$ gave first the η-^{2}Si–H complex, $Cp_2Ti(\eta^2\text{-}HSiH_2Ph)PMe_3$ [73], which slowly decomposed to give **23** with evolution of H_2. No Si–Si coupling products were detected over a period of weeks. The presence of phosphine suppresses the homodehydrocoupling reactions, either through formation of **23** (silane-coupling), or **29** (phosphine-coupling).

17. Other cross-dehydrocoupling reactions

The subject of other SiH/HE coupling reactions has been thoroughly reviewed recently and it will only be mentioned briefly here [58a,d].

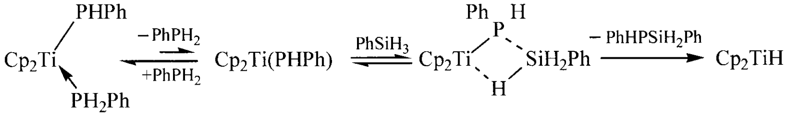


Fig. 18. Scheme showing how high stability of **29b** removes essential catalytic intermediates.

17.1. SiH/HO coupling

A wide range of catalysts has been reported for dehydrocoupling of OH-containing compounds with silanes. These include acids and bases and both homogeneous and heterogeneous transition metal catalysts. Such reactions can be useful in organic synthesis (protection of OH groups), in organosilicon synthesis (alkoxysilanes) and in sol–gel chemistry (direct reaction of silanes with H_2O). Bedard and Corey carried out a detailed survey of the dehydrocoupling of a range of organosilanes and alcohols under the influence of Cp_2TiCl_2/n-BuLi [77]. This catalyst is effective under mild conditions (ambient temperature for $t \leq 1$ h). EtOH and ^{i}PrOH react with primary and secondary organosilanes to give, in most cases, near quantitative yields of the corresponding alkoxysilanes. With secondary and tertiary alcohols, more forcing conditions (higher reaction temperatures and/or longer reaction times, $t =$ several hours) are necessary.

Partial replacement of the SiH occurs in the more sterically hindered combinations, but complete substitution is only observed with the less hindered silanes, even when reactions are carried out with sub-stoichiometric amounts of alcohol and at low temperatures [77]. It was suggested that rapid redistribution of the hydroalkoxysilane intermediates might account for this behavior. This suggestion seems reasonable since we have observed that the rates of dimethyltitanocene-catalyzed redistributions also follow the degree of steric encumbrance on the silicon.

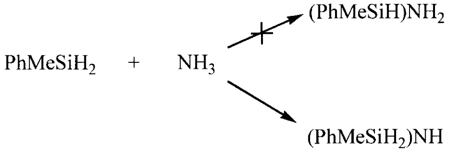
A variety of diols also react with secondary silanes to give the 1,3-dioxa-2-silacycles in excellent yields [77]. This method is superior to the alcoholysis of the dichlorosilanes, particularly with respect to the absence of polymeric products in the dehydrocoupling reactions. The diol reactions do not work well with primary silanes owing to formation of oligomeric products. Attempts to react all three OH groups of *cis*,*cis*-1,3,5-cyclohexanetriol, or glycerol, intramolecularly with primary silanes were also unsuccessful. However, high yields of the silatrane were obtained from triethanolamine.

The reaction of H_2O with hydrosilanes is of interest as an approach to sol–gel materials [78,79]. Alkyl and aryl hydrosilanes do not react at a significant rate with neutral water, but are hydrolyzed by aqueous acid or base. Catalytic hydrolysis offers the prospect of control of the outcome of the reaction, particularly with respect to the formation of silanols, or siloxanes. Bedard and Corey briefly studied the reactions of $PhMeSiH_2$ and Ph_2SiH_2 with H_2O using the Cp_2TiCl_2/n-BuLi catalyst [77]. The Ph_2SiH_2 reaction gave the disiloxane, $(Ph_2SiH)_2O$ in quantitative yield, presumably via the silanol. The $PhMeSiH_2$ reaction gave a complicated mixture of oligo(methylphenylsiloxanes), some of which carried PhMe(OH)Si- and/or PhMe(H)Si-end groups.

17.2. SiH/NH cross-dehydrocoupling

The only homogeneous catalyst that has been systematically studied for the reaction of silanes with ammonia is Cp_2TiMe_2 [80]. This catalyst is effective for primary, secondary and tertiary organosilanes, but the products from primary and secondary organosilanes are complex mixtures whose compositions depend strongly on the reaction conditions. Reasonable rates were achieved at temperatures of 70–100°C, at partial pressures of 1–2 atm of NH_3 and at a catalyst concentration of ca. 1 mol % relative to silane. At long reaction times, both Si–H bonds of $PhMeSiH_2$ react to give products of greater complexity than the disilazane. However, no replacement of the third N–H bond was observed under any circumstances.

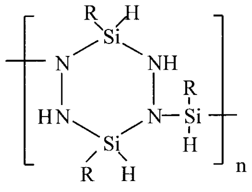
The initially observed products in the reactions of $PhMe_2SiH$ and $PhMeSiH_2$ with NH_3 are the disilazanes, Eq. (24). No monosilazane is observed under any conditions.



(24)

An unexpected feature of the Cp_2TiMe_2 catalyzed cross coupling of silanes with NH_3 is the sequence of reactivity with respect to the substitution on the reactant silane [80]. Organosilanes normally show a sequence of reactivity: $1° > 2° > 3°$. In the present case the order is dramatically reversed. The anomaly was attributed to an antagonistic competition between the homo- and heterodehydrocoupling reactions [80]. The Cp_2TiMe_2-catalyzed homodehydrocoupling of silanes follows the normal reactivity sequence, with the 1° silanes reacting very rapidly and the 3° silanes, not at all. In the presence of ammonia, the homodehydrocoupling of phenylsilane occurs more rapidly than heterodehydrocoupling and the N-containing products result mainly from amination of oligo(phenylsilanes). However, the rate of homocoupling is still very much lower than in the absence of NH_3.

Reactions of hydrazines with hydrosilanes provide a novel synthesis of silylhydrazines [81]. N_2H_4 and substituted hydrazines are more reactive towards hydrosilanes than are NH_3 and amines. Primary silanes react spontaneously with hydrazine to give soluble polymers of ill-defined composition, in which most of the Si–H functions have reacted [82]. Model compound studies on cyclic and acyclic dimethylhydrazinosilanes indicate that a dominant motif in the polymer chain is **30**:



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In the presence of a 1% Cp_2TiMe_2 catalyst, $PhSiH_3$ reacts violently with N_2H_4 to give an insoluble, crosslinked polymer, presumably of a similar structure to that produced in the absence of catalyst, but with a higher cross link density resulting from more complete reaction of Si–H functions [82].

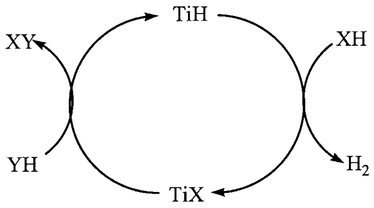
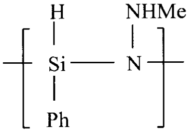


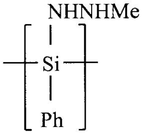
Fig. 19. Generalized catalytic loop for heterodehydrocoupling.

Methyl-substituted hydrazines react at best very slowly with silanes in the absence of catalysts, but they are reactive with primary and secondary silanes in the presence of a Cp_2TiMe_2 catalyst. Even in the presence of catalyst, they react progressively more slowly with increasing methyl substitution. $PhSiH_3$ reacts with $MeNHNH_2$ to give a mixture of oligomers with two types of chain unit, **31** and **32**. As in the case of reactions of primary silanes with NH_3 described above, the units **31** arise from direct heterodehydrocoupling of $PhSiH_3$ with $MeNHNH_2$ while units **32** arise from competing homodehydrocoupling of $PhSiH_3$, followed by amination of the backbone Si–H units. With unsubstituted NH_2NH_2, the homocoupling of $PhSiH_3$ cannot compete with the faster heterocoupling reaction. With Me_2NNH_2, the rate of heterocoupling is comparable to that of homocoupling of $PhSiH_3$ and a mixture of oligomers with units analogous to **31** and **32** is obtained. With MeNHNHMe, the heterocoupling reaction of the first NH group is faster than the rate of homocoupling of $PhSiH_3$, and a relatively clean reaction occurs to give a mixture of $PhSiH_2(NMeNHMe)$ and $PhSiH(NMeNHMe)_2$.



$$-\left[\overset{\mathrm{H}}{\underset{\mathrm{Ph}}{\mathrm{Si}}}-\overset{\mathrm{NHMe}}{\mathrm{N}}\right]-$$

and



$$-\left[\overset{\mathrm{NHNHMe}}{\underset{\mathrm{Ph}}{\mathrm{Si}}}\right]-$$

31 **32**

Ph_2SiH_2 does not react spontaneously with hydrazine, or its methylated derivatives, at temperatures below 100°C. In the presence of 1% Cp_2TiMe_2 these reactions all take place slowly; the reaction rate sequence being $NH_2NH_2 > MeNHNH_2 > Me_2NNH_2$. Products of the $MeNHNH_2$ reactions were obtained directly as crystalline solids from the cooled reaction mixtures. The rate of heterodehydrocoupling with Me_2NNH_2 is so slow that the major product is the product of silane homodehydrocoupling.

No significant mechanistic work has been carried out on SiH/OH and Si/NH systems and little can be said with confidence about how they occur. It is most likely that they all take place by a sequence of σ-bond metathesis steps analogous to those shown in Fig. 19. In this scheme, it is not known for any particular case whether the metal is Ti^{III} or Ti^{IV}, or whether X is Si or the other element, or whether both TiX and TiY loops are occurring.

Titanocene catalyzed coupling of Si–H with NH_3 or N_2H_4 have both been used to incorporate N into SiC, or to make polymeric precursors for Si_3N_4 synthesis [82a,83].

17.3. Cross-dehydrocoupling with heavier elements

The hydrides of the heavier congeners of the Group 14–16 elements have weak E–H bonds and they undergo spontaneous thermal decomposition under relatively mild conditions to yield the pure element, or a low oxidation state hydride (in many cases of ill-defined chemical composition and structure). There is still, however, a need for catalysts, particularly to control the specificity of dehydrocoupling. For example, the ability to make rings of a particular size or isomeric composition, or the ability to avoid cyclic products altogether. In addition, it is desirable to control homo- versus heterodehydrocoupling selectivity, something difficult to do by non-catalytic methods.

Fisher and co-workers recently reported a nice example of the kind of reaction that can be achieved [84]. The authors' goal was to produce an MOCVD (metallorganic chemical vapor deposition) reagent and they were successful in achieving the reaction shown in Eq. (25).

$$2\ Bu_3SnH + Bu_3P{=}Te \xrightarrow[-\ Bu_3P,\ 25°C]{Cp^*_2TiH} (Bu_3Sn)_2Te + H_2 \qquad (25)$$

Although at first sight this reaction does not appear to be a formal dehydrocoupling process, the analogy to heterodehydrocoupling can be seen if it is imagined as a reaction between Bu_3SnH and Bu_3SnTeH. Detecting and isolating several of the key intermediates elucidated many of the details of the catalytic cycle. The proposed cycles are shown in Fig. 20.

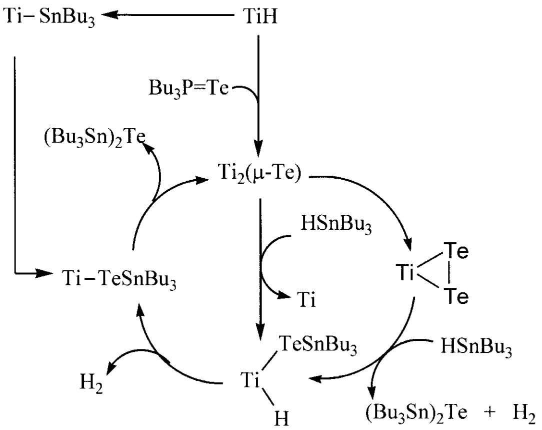


Fig. 20. The mechanism proposed for Cp^*_2TiH catalyzed dehydrocoupling of Bu_3SnH and $Ph_3P{=}Te$ (in the scheme $Ti{=}Cp^*_2Ti$).

Despite the complexity of Fig. 20, it is still a considerable over-simplification of the full mechanism and most of the steps depicted must occur by several discrete reactions. This example is a foretaste of the rich chemistry that waits to be uncovered with these heavier element reactions.

18. Redistribution of alkoxysilanes and siloxanes

Curtis and Epstein have reviewed the redistribution of hydrosilanes catalyzed by later transition metal complexes [85]. Dimethyltitanocene was subsequently found to be a very effective catalyst for the rapid redistribution of alkoxyhydrosilanes and alkylhydrosiloxanes [86]. A generalized equation for the redistribution of monohydroalkylalkoxysilanes is shown in Eq. (26)

$$n(\mathrm{RO})_{n-1}\mathrm{R}'_{4-n}\mathrm{SiH} \rightarrow (n-1)(\mathrm{RO})_n\mathrm{R}'_{4-n}\mathrm{Si} + \mathrm{R}'_{4-n}\mathrm{SiH}_n \qquad (26)$$

and some specific examples are shown in Eqs. (27)–(29). All of these reactions take place with catalyst loadings of ca. 1–2 mol % at room or slightly elevated temperatures and they are essentially quantitative.

$$4(\mathrm{MeO})_3\mathrm{SiH} \rightarrow 3(\mathrm{MeO})_4\mathrm{Si} + \mathrm{SiH}_4 \qquad (27)$$

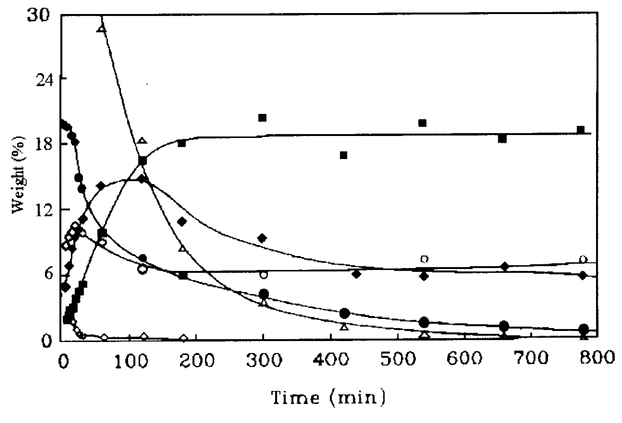
$$3\mathrm{Me(EtO)}_2\mathrm{SiH} \rightarrow 2\mathrm{Me(EtO)}_3\mathrm{Si} + \mathrm{MeSiH}_3 \qquad (28)$$

$$n\mathrm{HMe}_2\mathrm{SiOSiMe}_2\mathrm{H} \rightarrow \mathrm{HMe}_2\mathrm{SiO[SiMe}_2\mathrm{O]}n\mathrm{H} + (n-1)\mathrm{Me}_2\mathrm{SiH}_2 \qquad (29)$$

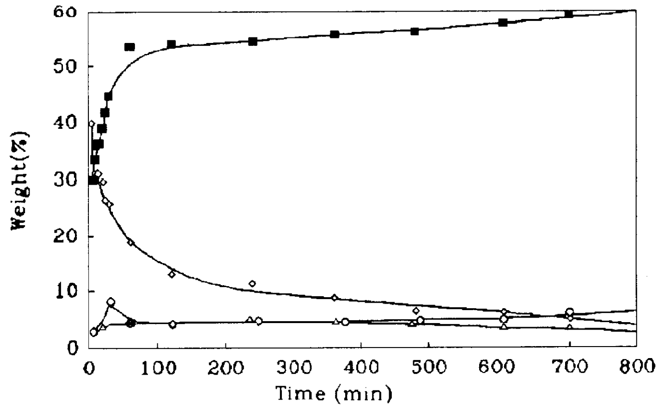
Reaction (27) is potentially dangerous, as are other disproportionation reactions of silanes, owing to the spontaneously explosive character of SiH_4 in air. However, used properly it is a convenient way of making small amounts of SiH_4 on a laboratory scale and with a minimum of danger. The reaction can serve a similar purpose to the small-scale generation of BH_3 by the reaction of $NaBH_4$ with a strong Lewis acid for hydroboration reactions. This source of SiH_4 has been used to prepare $[Cp_2Ti(SiH_3)]_2$ [87a] and $Cp_2Ti(SiH_3)PMe_3$ [87b].

Reaction (29) produces a mixture of linear and cyclic polysiloxanes (the latter require removal of an additional molecule of Me_2SiH_2). Detailed product distribution analyses of Eq. (29) and similar reactions of $HMe_2SiO(SiMe_2O)_xSiMe_2H$ ($x = 1$ and 2) showed that linear higher molecular weight products arise from intermolecular redistributions of linear molecules while the cyclics arise from intramolecular redistribution [86]. The latter is dramatically evident in the fact that $HMe_2SiO(SiMe_2O)_2SiMe_2H$ gives hexamethylcyclotrisiloxane as virtually the only product. The reaction profiles for the reactions of $HMe_2SiOSiMe_2H$ and $HMe_2SiO(SiMe_2O)_2SiMe_2H$ are shown in Fig. 21.

Stoichiometric reactions of alkoxysilanes or hydrosiloxanes with Cp_2TiMe_2 produce mixtures of $[Cp_2Ti(OR')]_2$ and $[Cp_2TiSiR_{3-n}H]_2$ ($n = 1$ or 2) in proportions depending on the ratio of Cp_2TiMe_2 to silane reactant. Such reactions can be used to synthesize pure, crystalline $[Cp_2Ti(OR)]_2$ ($R = Me$ and Et) [88], or the $Cp_2Ti(SiH_3)$ complexes mentioned above.



(a)



(b)

Fig. 21. (a) Reaction profiles for the catalytic redistribution of $HMe_2SiOSiMe_2H$. $[Cp_2TiMe_2] = 0.05$ M in neat $HMe_2SiOSiMe_2H$. ◇: $HMe_2SiOSiMe_2H$; △: $HMe_2SiO(SiMe_2O)SiMe_2H$; ●: $HMe_2SiO(SiMe_2O)_2SiMe_2H$; ◆: $(SiMe_2O)_3$; ■: $(SiMe_2O)_4$; ○: $(SiMe_2O)_5$. (b) Catalytic cyclization of $HMe_2SiO(SiMe_2O)_2SiMe_2H$. $[Cp_2TiMe_2] = 0.05$ M in neat reactant. ◇: $HMe_2SiO(SiMe_2O)_2SiMe_2H$; ■: $(SiMe_2O)_3$; ○: $(SiMe_2O)_4$; △: $(SiMe_2O)_6$.

A catalytic loop explaining the experimental results is shown in Fig. 22. This loop is preferred over others involving σ-bond metatheses or silanone intermediates since it provides a more ready explanation of Eq. (30). This reaction produces only the products shown, and no siloxanes containing HMe_2Si units.

$$Me_3SiOSiMe_2H \xrightarrow{Cp_2TiMe_2} Me_3Si(OSiMe_2)SiMe_3 + Me_2SiH_2 \tag{30}$$

For reaction (30), X and R of Fig. 22 are Me and Me_3Si, respectively. The metathesis between Si–OR and Ti–H may occur within an actual hydride-bridged bimetallic intermediate, or simply by a bimolecular encounter to produce a four-center transition state. There is ample precedent for this type of metathesis from the catalytic hydrosilations of carbonyl compounds (Sections 7 and 8). When X and R of Fig. 22 are alkoxy and Me groups respectively, we have the case of alkoxysilane redistribution. When X = Me and R = $SiMe_2H$ we have the tetramethyldisiloxane case. Although all of the experimental observations can be accounted for by Fig. 22, there is clearly still much to be understood about these fascinating reactions.

The production of polydimethylsiloxanes by disproportionation of hydrosiloxanes is of no practical interest in itself. However, the possible stereo- and enantioselective catalysis of the redistribution of prochiral disiloxanes, such as HPhMeSiOSiMePhH is of interest since the control of tacticity in potentially stereoregular polysiloxanes remains an unsolved challenge in silicones technology. The titanocene-catalyzed redistribution of poly(methylhydrosiloxanes) has also been used as a 'dry' route to poly(methylsilsequioxane) ceramics [89], and for the production of polymethylsilsesquioxane/polyacetylene composites [90].

19. Conclusions

Titanocene-based catalysts are remarkable for the range of reactions of Si–H containing compounds for which they are active. This broad range of activity is no doubt due to a close correspondence between the bond energies of Ti–X and Si–X bonds, which leads to more or less thermally neutral reactions within the catalytic loop. In addition, both reactants and catalysts have available low lying orbitals which allow expansion of the coordination spheres of both Si and Ti with relatively little sacrifice in energy along the pathways to transition states. Hence, facile shuttling of groups X can occur with elements at both extremes of the range of electronegativity (viz. H, O and F).

In the coming millenium, it is likely that the restrictions on the disposal of halogen-containing wastes will maintain pressure on industrial main-group chemistry to move away from its dependence on element chlorides as raw materials. A natural direction to move would be towards the use of hydrides, many of which can be produced without generating halide wastes. The catalytic chemistry of main

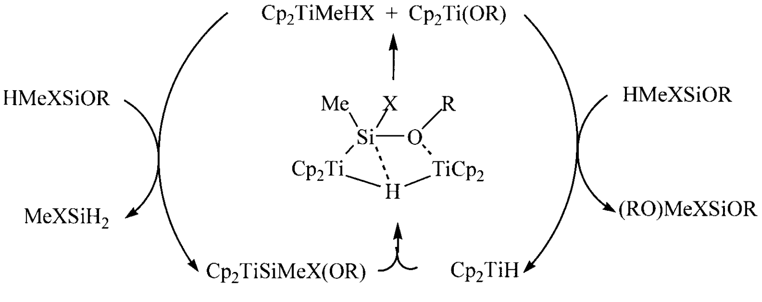


Fig. 22. A catalytic cycle for the Cp_2TiMe_2 catalyzed redistribution of oxyhydrosilanes.

group hydrides will therefore remain an important research area for the foreseeable future.

One particular group of reactions, which will receive attention, is that of Si–H with C–X compounds (particularly those where X = H or C). This problem is a subclass of the more general problem of useful catalytic activation of C–H or C–C by any type of coordination catalysis. In particular, it would be very interesting to be able to dehydrocouple Si–H with C–H to give the basic raw materials of the silicones industry. The recent successful hydrosilation of pyridines points the way to the possibility that one day we may be able to hydrosilate benzene, which, if accompanied by a facile re-aromatization, could form the basis for making arylsilanes.

Another very obvious direction for the continued development of the chemistry described in this review is the exploitation of the existence of stable chiral catalysts. The number of possible catalysts is very large and very little is understood of the factors controlling rates and selectivities. A number of reactions catalyzed by titanocene derivatives occur with very impressive turnover rates. However, rates tend to fall dramatically with increased steric bulk of reactants, a tendency that is particularly evident with chiral *ansa*-metallocenes.

Finally, the metallocenes have provided a unique platform for beginning the exploration of the catalytic chemistry of the early transition elements. This is due in no small measure to their ability to yield isolable and characterizable intermediates, and hence some understanding of the pathways involved. However, as is already evident in the evolution of homogeneous, early transition element olefin polymerization catalysts, there is nothing unique about the metallocenes and a whole universe of non-metallocene early transition element systems remains to be explored.

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References

[1] (a) P.L. Pauson, T.L. Kealy, Nature 168 (1951) 1039. (b) S.A. Miller, T.A. Tebboth, J.F. Tremaine, J. Chem. Soc. (1952) 632.
[2] (a) K. Ziegler, Angew. Chem. 16 (1955) 424. (b) G. Natta, J. Polym. Sci. 16 (1955) 143.
[3] D.F. Hermann, W.K. Nelson, J. Am. Chem. Soc. 75 (1953) 3877.
[4] C. Beerman, R. Graf, H. Bestian, German Patent 1,023,766 (1956).

[5] (a) K.S. Boustany, B. Tabacchi, A. Jacot-Guillarmod, Chimia 24 (1971) 326. (b) K.S. Boustany, K. Bernauer, A. Jacot-Guillarmod, Helv. Chim. Acta 50 (1967) 1305.
[6] J.M. Birmingham, G. Wilkinson, J. Am. Chem. Soc. 76 (1954) 4281.
[7] G. Natta, P. Corradini, J. Am. Chem. Soc. 80 (1958) 755.
[8] (a) A. Andresen, H. Cordes, J. Herwig, W. Kaminsky, A. Merck, R. Mottweiler, J. Pein, H. Vollmer, Angew. Chem. Int. Ed. Engl. 15 (1976) 630. (b) H. Sinn, W. Kaminsky, Adv. Organomet. Chem. 18 (1980) 99.
[9] K. Clauss, H. Bestian, Liebigs Ann. Chem. 654 (1962) 8.
[10] J. Bercaw, J. Am. Chem. Soc. 96 (1974) 5087.
[11] P.B. Hitchcock, F.M. Kerton, G.A. Lawless, J. Am. Chem. Soc. 120 (1998) 10 264.
[12] J.W. Lauher, R. Hoffmann, J. Am. Chem. Soc. 98 (1976) 1729.
[13] G.P. Pez, J. Am. Chem. Soc. 98 (1976) 8072.
[14] (a) J. Bercaw, H.H. Brintzinger, J. Am. Chem. Soc. 91 (1969) 7301. (b) H.H. Brintzinger, J. Bercaw, J. Am. Chem. Soc. 92 (1970) 6182.
[15] S.I. Troyanov, H. Antropiusová, K.J. Mach, J. Organomet. Chem. 427 (1992) 49.
[16] T.S. Piper, D. Lemal, G. Wilkinson, Naturwissenschaften 43 (1956) 129.
[17] (a) A.J. Chalk, J.F. Harrod, J. Am. Chem. Soc. 87 (1965) 16. (b) J.F. Harrod, A.J. Chalk, Hydrosilation catalysed by Group VIII complexes, in: I. Wender, P. Pino (Eds.), Organic Syntheses via Metal Carbonyls, vol. II, Wiley, New York, 1977, pp. 673–704. (c) J. Speier, Adv. Organomet. Chem. 17 (1979) 407.
[18] C. Aitken, J.F. Harrod, E. Samuel, J. Organomet. Chem. 279 (1985) C11.
[19] (a) D.S. Breslow, N.R. Newburg, J. Am. Chem. Soc. 81 (1959) 81. (b) M.F. Sloan, A.S. Matlock, D.S. Breslow, J. Am. Chem. Soc. 85 (1963) 4014.
[20] K. Sonogoshira, N. Hagihara, Bull. Chem. Soc. Jpn. 39 (1966) 1178.
[21] C. Floriani, G. Fachinetti, US Patent 3,920,745 (1975).
[22] V.B. Shur, V.V. Burlakov, M.E. Vol'pin, J. Organomet. Chem. 439 (1992) 303.
[23] W.D. Bonds Jr., C.H. Brubaker Jr., E.S. Chandrasekaran, C. Gibbons, R.H. Grubbs, L.C. Kroll, J. Am. Chem. Soc. 97 (1975) 2128.
[24] G.P. Pez, S.C. Kwan, J. Am. Chem. Soc. 98 (1976) 8079.
[25] E. Samuel, J. Organomet. Chem. 198 (1980) C65.
[26] J.F. Harrod, S.S. Yun, Organometallics 6 (1987) 1381.
[27] J. Cermak, M. Kvicalova, V. Blechta, M. Capka, Z. Bastl, J. Organomet. Chem. 509 (1996) 77.
[28] T. Cuenca, J.C. Flores, P. Royo, J. Organomet. Chem. 462 (1993) 191.
[29] For a review see: R.L. Halterman, Chem. Rev. 92 (1992) 965.
[30] (a) E. Cesarrotti, R. Ugo, H.B. Kagan, Angew. Chem. Int. Ed. Engl. 18 (1979) 779. (b) E. Cesarotti, R. Ugo, J. Mol. Catal. 12 (1981) 63.
[31] R.L. Halterman, K.P.C. Vollhardt, Organometallics 7 (1988) 883.
[32] R.L. Halterman, K.P.C. Vollhardt, M.E. Welker, D. Bläser, R. Boesse, J. Am. Chem. Soc. 109 (1987) 8105.
[33] K.M. Doxsee, J.B. Farahi, H. Hope, J. Am. Chem. Soc. 113 (1991) 8889.
[34] (a) R.D. Broene, S.L. Buchwald, J. Am. Chem. Soc. 115 (1993) 12 569. (b) N.E. Lee, S.L. Buchwald, J. Am. Chem. Soc. 116 (1994) 5985.
[35] (a) J.E. Bercaw, R.H. Marvich, L.G. Bell, H.H. Brintzinger, J. Am. Chem. Soc. 94 (1972) 1219. (b) J.F. Harrod, S.S. Yun, Organometallics 6 (1987) 1381 (c) L.A. Paquette, S.M. Rivik, E.I. Bzowej, K.J. Stanton, Organometallics 14 (1995) 4865.
[36] G. Natta, Makromol. Chem. 24 (1957) 258.
[37] (a) P.-F. Fu, T.J. Marks, J. Am. Chem. Soc. 117 (1995) 10 747. (b) K. Koo, T.J. Marks, J. Am. Chem. Soc. 120 (1998) 4019.
[38] (a) C.A. Willoughby, S.L. Buchwald, J. Am. Chem. Soc. 114 (1992) 7562. (b) N.E. Lee, S.L. Buchwald, J. Am. Chem. Soc. 116 (1994) 5985.
[39] M.R. Kesti, R.M. Waymouth, Organometallics 11 (1992) 1095.
[40] (a) K. Tamao, T. Tanaka, T. Nakajima, R. Sumiya, H. Arai, Y. Ito, Tetrahedron Lett. 27 (1986) 3377. (b) K. Tamao, T. Nakajima, R. Sumiya, H. Arai, N. Higuchi, Y. Ito, J. Am. Chem. Soc. 108 (1986) 6090. (c) K. Tamao, T. Yamauchi, Y. Ito, Chem. Lett. (1987) 171. (d) K. Tamao, Y.

Nakagawa, Y. Ito, J. Org. Chem. 55 (1990) 3438. (e) M.S. Buck, J.E. Feaster, Tetrahedron Lett. 33 (1992) 2099.
[41] S.H. Bergens, P. Noheda, J. Whelan, B. Bosnich, J. Am. Chem. Soc. 114 (1992) 2121 and 2128.
[42] S. Xin, J.F. Harrod, J. Organomet. Chem. 499 (1995) 181.
[43] X. Wang, W.W. Ellis, B. Bosnich, Chem. Commun. (1996) 2561.
[44] T. Nakano, Y. Nagai, Chem. Lett. (1988) 481.
[45] M.B. Carter, B. Schiøtt, A. Gutiérrez, S.L. Buchwald, J. Am. Chem. Soc. 116 (1994) 11 667.
[46] (a) S.-X. Xin, J.F. Harrod, Can. J. Chem. 73 (1995) 999. (b) K. Rahimian, J.F. Harrod, Inorg. Chim. Acta 279 (1998) 330.
[47] S. Xin, J.F. Harrod, E. Samuel, J. Am. Chem. Soc. 116 (1994) 11 562.
[48] (a) F. Sato, T. Jinbo, M. Sato, Tetrahedron Lett. 21 (1980) 2175. (b) F. Sato, T. Jinbo, M. Sato, Synthesis (1981) 871.
[49] (a) S.C. Berk, K.A. Kreutzer, S.L. Buchwald, J. Am. Chem. Soc. 113 (1991) 5093. (b) S.C. Berk, S.L. Buchwald, J. Org. Chem. 57 (1992) 3751. (c) K.J. Barr, S.C. Berk, S.L. Buchwald, J. Org. Chem. 59 (1994) 4323. (d) M.T. Reding, S.L. Buchwald, J. Org. Chem. 60 (1995) 7884.
[50] K.J. Barr, S.C. Berk, S.L. Buchwald, J. Org. Chem. 59 (1994) 4323.
[51] S. Xin, C. Aitken, J.F. Harrod, Y. Mu, E. Samuel, Can. J. Chem. 68 (1990) 471.
[52] (a) X. Verdaguer, S.C. Berk, S.L. Buchwald, J. Am. Chem. Soc. 117 (1995) 12 641. (b) X. Verdaguer, M.C. Hansen, S.C. Berk, S.L. Buchwald, J. Org. Chem. 63 (1998) 8522.
[53] (a) X. Verdaguer, U.E.W. Lange, M.T. Reding, S.L. Buchwald, J. Am. Chem. Soc. 118 (1996) 7684. (b) X. Verdaguer, U.E.W. Lange, S.L. Buchwald, Angew. Chem. Int. Ed. Engl. 37 (1998) 1103.
[54] L. Hao, J.F. Harrod, A.-M. Lebuis, Y. Mu, R. Shu, E. Samuel, H.-G. Woo, Angew. Chem. Int. Ed. Engl. 37 (1998) 3126.
[55] N.C. Cook, J.E. Lyons, J. Am. Chem. Soc. 88 (1966) 3396.
[56] (a) L. Hao, A.-M. Lebuis, J.F. Harrod, Chem. Commun. (1998) 1089. (b) H.G. Woo, J.F. Harrod, J. Hénique, E. Samuel, Organometallics 12 (1993) 2883.
[57] (a) E. Klei, J.H. Teuben, J. Organomet. Chem. 214 (1981) 53. (b) E. Klei, J.H. Teuben, J. Chem. Soc. Chem. Commun. (1978) 659.
[58] (a) F. Gauvin, J.F. Harrod, H.G. Woo, Adv. Organomet. Chem. 42 (1998) 363. (b) T.D. Tilley, Comments Inorg. Chem. 10 (1990) 37. (c) T.D. Tilley, Acc. Chem. Res. 26 (1993) 22. (d) J.Y. Corey, Adv. Silicon Chem. 1 (1991) 327.
[59] (a) Z.-F. Zhang, F. Babonneau, R.M. Laine, Y. Mu, J.F. Harrod, J.A. Rahn, J. Am. Ceram. Soc. 74 (1991) 670. (b) Y. Mu, J.F. Harrod, in: J.F. Harrod, R.M. Laine (Eds.), Proceedings of the Symposium on Inorganic Polymers and Oligomers, 33rd International Symposium on Macromolecules, Montreal, July 1990, Kluwer, Dordrecht, 1991, p. 23.
[60] J.Y. Corey, X.-H. Zhu, J. Organomet. Chem. 439 (1992) 1.
[61] (a) T. Imori, T.D. Tilley, J. Chem. Soc. Chem. Commun. (1993) 1607. (b) T. Imori, V. Lu, H. Cai, T.D. Tilley, J. Am. Chem. Soc. 117 (1995) 9931.
[62] C. Aitken, J.F. Harrod, E. Samuel, J. Am. Chem. Soc. 108 (1986) 4059.
[63] L. Hao, J.F. Harrod, Inorg. Chem. Commun. 2 (1999) 191.
[64] J.F. Harrod, Y. Mu, E. Samuel, Can. J. Chem. 70 (1992) 2980.
[65] (a) J.K. Hoyano, W.A.G. Graham, J. Am. Chem. Soc. 300 (1969) 4569. (b) M.J. Bennett, K.A. Simpson, J. Am. Chem. Soc. 93 (1971) 7156. (c) W.A.G. Graham, J. Organomet. Chem. 300 (1986) 81.
[66] J.Y. Corey, J. Braddock-Wilking, Chem. Rev. 99 (1999) 175.
[67] C. Aitken, J.F. Harrod, A. Malek, E. Samuel, J. Organomet. Chem. 349 (1988) 285.
[68] N. Choi, M. Tanaka, J. Organomet. Chem. 564 (1998) 81.
[69] (a) E. Samuel, Y. Mu, J.F. Harrod, Y. Dromzee, Y. Jeannin, J. Am. Chem. Soc. 112 (1990) 3435. (b) H.G. Woo, J.F. Harrod, J. Hénique, E. Samuel, Organometallics 12 (1993) 2883. (c) S. Xin, H.-G. Woo, J.F. Harrod, E. Samuel, A.-M. Lebuis, J. Am Chem. Soc. 119 (1997) 5307.
[70] J. Britten, Y. Mu, J.F. Harrod, J. Polowin, M.C. Baird, E. Samuel, Organometallics 12 (1993) 2672.
[71] S. Xin, H.-G. Woo, J.F. Harrod, E. Samuel, A.-M. Lebuis, J. Am Chem. Soc. 119 (1997) 5307.
[72] (a) K. Isslieb, H. Hackert, Z. Naturforsch. Teil B 21 (1966) 519. (b) J. Hachgenei, G. Fritz, D. Fenske, Z. Naturforsch. Teil B 41 (1986) 1535. (c) J. Ho, Z. Hou, R.J. Draqke, D.W. Stephan, Organometallics 12 (1993) 3145. (d) E. Hey, S.G. Bott, J.L. Atwood, Chem. Ber. 121 (1988) 561.

[73] E. Spaltenstein, P. Palma, K.A. Kreutzer, C.A. Willoughby, W.M. Davis, S.L. Buchwald, J. Am. Chem. Soc. 116 (1994) 10 308.

[74] L.P. Battaglia, M. Nardelli, C. Pelizzi, G. Predieri, G.P. Chiusoli, J. Organomet. Chem. 259 (1983) 301.

[75] M. Fermin, D.W. Stephan, J. Am. Chem. Soc. 117 (1995) 12 645.

[76] R. Shu, L. Hao, J.F. Harrod, H.-G. Woo, E. Samuel, J. Am. Chem. Soc. 120 (1998) 12 988.

[77] T.C. Bedard, J.Y. Corey, J. Organomet. Chem. 428 (1992) 315.

[78] M. Driess, M. Reisgys, H. Prizkow, Angew. Chem. Int. Ed. Engl. 31 (1992) 1510.

[79] (a) R.J.P. Corriu, J.J. Moreau, M.J. Wong Chi Man, J. Sol–Gel Sci. Technol. 2 (1994) 87. (b) U. Schubert, C. Lorenz, Inorg. Chem. 36 (1997) 1258.

[80] J. He, H.Q. Liu, J.F. Harrod, R. Hynes, Organometallics 13 (1994) 36.

[81] U. Wannegat, Adv. Inorg. Radiochem. 6 (1964) 225.

[82] (a) J. He, J.F. Harrod, J. Am. Ceram. Soc. 78 (1995) 3009. (b) J. He, J.F. Harrod, Phosphorus Sulfur Silicon 93 (1994) 349.

[83] (a) M. Scarlete, Y. Mu, J.F. Harrod, I.S. Butler, Chem. Mater. 7 (1995) 1214. (b) M. Scarlete, J.F. Harrod, I.S. Butler, Polymethylsilane and poly(hydrazine-methylsilane) as precursors for silicon containing ceramics, in: J.F. Harrod, R. Laine (Eds.), Applications of Organometallic and Related Chemistry to the Synthesis and Processing of Advanced Materials, NATO ARW Series E, Kluwer, Dordrecht, 1995, p. 125.

[84] J.M. Fisher, W.E. Piers, S.D. Pearce Batchilder, M. Zaworotko, J. Am. Chem. Soc. 118 (1996) 283.

[85] M.D. Curtis, P.S. Epstein, Adv. Organomet. Chem. 19 (1981) 213.

[86] S. Xin, C. Aitken, J.F. Harrod, Y. Mu, E. Samuel, Can. J. Chem. 68 (1990) 471.

[87] (a) L. Hao, A.-M. Lebuis, J.F. Harrod. E. Samuel, Chem. Commun. (1997) 2193. (b) L. Hao, A.-M. Lebuis, J.F. Harrod, Chem. Commun. (1998) 1089.

[88] E. Samuel, J.F. Harrod, D. Gourier, Y. Dromzee, F. Robert, Y. Jeannin, Inorg. Chem. 31 (1992) 3252.

[89] R.M. Laine, J.A. Rahn, K.A. Youngdahl, J.F. Harrod, Catalytic synthesis of polymethylsilsesquioxanes, in: D. Slocum, W.R. Moser (Eds.), New Science in Transition Metal Catalyzed Reactions, vol. 230, Am. Chem. Soc. Adv. Chem. Series, 1992, p. 553.

[90] T. Grasczyk, J.F. Harrod, J. Polym. Sci. A 32 (1994) 3183.