

Heterodehydrocoupling of Phosphines and Silanes Catalyzed by Titanocene: A Novel Route to the Formation of Si–P Bonds

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Received May 6, 1998

We report herein the first examples of catalytic heterodehydrocoupling between Si–H and P–H (eq 1).



Dehydrocoupling and heterodehydrocoupling reactions to form Sn–Te, Si–N, Si–C, Si–O, and B–N bonds have all been achieved using group 4 metallocenes as catalysts.¹ A notable absence from the above list is a heterodehydrocoupling reaction to form Si–P bonds. Catalytic dehydrocoupling has some advantages over currently available methods for the synthesis of Si–P bonds² in that it can be carried out as a one-pot reaction under mild conditions and it does not produce large amounts of waste products that may be difficult to dispose of.

Some results for the heterodehydrocoupling of silanes and phosphines with a Cp₂TiMe₂ precatalyst are shown in Table 1. These reactions exemplify the range of reactivities and selectivities that are achievable. A surprising feature is the much lower reactivity of the less sterically encumbered phosphines. Such behavior is counter to that expected for σ -bond metathesis chemistry where the larger groups should hinder the formation of the transition state.

Residual tertiary Si–H bonds are inactive toward coupling; hence, all of the final products contain a Si–H bond. Residual P–H bonds are more active, and although compounds with P–H bonds were detected in the slow CyPH₂ reactions, they undergo further coupling to give longer chains. An NMR experiment showed that, in the reaction of CyPH₂ with *p*-TolSiH₃, *p*-TolH₂-SiPHCy was the initial product, followed by CyP[SiH₂*p*-Tol]₂, **1**. Subsequently, as the *p*-TolSiH₃ concentration diminished relative to that of CyPH₂, *p*-TolHSi(PHCy)₂, **2**, and other higher, uncharacterized oligomers appeared. After 2 days, white crystals of 1,3,5-tri(cyclohexylphospha)-2,4,6-tri(*p*-tolylsila)cyclohexane, **3**, began to appear and continued to accumulate, eventually reaching a yield of 30% after several weeks.³ A similar reaction of PhSiH₃ and CyPH₂ gave the previously reported phenylsila

Table 1. Heterodehydrocoupling of Phosphines and Silanes^a

phosphine	silane	reaction time (h)	product	yield (%) ^b
Ph ₂ PH	<i>p</i> -TolSiH ₃	2	<i>p</i> -TolH ₂ SiPPh ₂	84
			<i>p</i> -TolHSi(PPh ₂) ₂	16
Ph ₂ PH	<i>p</i> -TolSiH ₃	9	<i>p</i> -TolHSi(PPh ₂) ₂	100 (75) ^c
Ph ₂ PH	CySiH ₃	2	CyH ₂ SiPPh ₂	100
Ph ₂ PH	Ph ₂ SiH ₂	2	Ph ₂ HSiPPh ₂	100
Ph ₂ PH	PhMeSiH ₂	2	PhMeHSiPPh ₂	100
Cy ₂ PH	<i>p</i> -TolSiH ₃	3	<i>p</i> -TolH ₂ SiPCy ₂	8.2
		24	<i>p</i> -TolH ₂ SiPCy ₂	24
Cy ₂ PH	PhSiH ₃	24	PhH ₂ SiPCy ₂	21
Cy ₂ PH	CySiH ₃	24	CyH ₂ SiPCy ₂	100
Cy ₂ PH	PhMeSiH ₂	24	PhMeHSiPCy ₂	100
PhPH ₂	<i>p</i> -TolSiH ₃	24	NR	
PhPH ₂	CySiH ₃	24	NR	
PhPH ₂	PhMeSiH ₂	24	NR	
CyPH ₂	<i>p</i> -TolSiH ₃	3	<i>p</i> -TolH ₂ SiPHCy	3.3
			<i>p</i> -TolHSi(PHCy) ₂	0.3
CyPH ₂	<i>p</i> -TolSiH ₃	650	<i>c</i> -[<i>p</i> -TolHSiPCy] ₃	(30)

^a Reactions were run at room temperature, without solvent, using 3–5 mol % Cp₂TiMe₂ based on silane. Phosphine/silane ratio = 1:1.2 unless otherwise noted. All compounds were characterized by ¹H, ³¹P, and ²⁹Si NMR. NR: no cross-coupling observed; Tol = tolyl, Cy = cyclohexyl. ^b Based on integration of ³¹P NMR. Figures in parentheses are isolated yields. ^c Phosphine/silane ratio = 2.1.

analogue of **3** in an isolated yield of 53%.⁴ These six-membered rings could either result from coupling of **1** and **2**, or from redistribution reactions. In either case their isolation is due to their low solubilities in the reaction medium.

Some steps in the mechanism of titanocene-catalyzed SiH/PH cross-dehydrocoupling are suggested by the catalytic and stoichiometric reactions of Cp₂Ti(PMe₃)₂, **4**, with RR'PH (R = Ph, R' = Ph or H; R = Cy, R' = H). Although the presence of the PMe₃ reduces the catalytic activity of **4** relative to that of Cp₂TiMe₂, it greatly facilitates the observation of intermediate titanocene(III) species by EPR spectroscopy. A series of experiments was performed which demonstrated the occurrence of the reactions shown in Scheme 1. A reaction of **4** with Ph₂PH (1:1 molar ratio) at room temperature gave the known phosphido compound **5a** as dark green crystals in 86% isolated yield.⁵ With a 2:1 molar ratio of **4** to Ph₂PH, EPR spectroscopy showed **5a** and the hydride **6** to be formed in a 1:1 ratio.⁶ These compounds could result from the oxidative addition of a P–H bond to **1** (or, more likely, one of its phosphine dissociation products) to give the intermediate **7**. This intermediate could transfer a hydrogen atom to a second molecule of **4** to give an equal mixture of **5a** and **6**. **7** was not observed, even at low temperatures, presumably because of its rapid reaction with **4**.⁷

(3) NMR in C₆D₆ at 25 °C: $\delta(^1H) = 0.7\text{--}2.2$ (m, C₆H₁₁), 2.01 (s, *p*-CH₃), 6.0 (m, 3 H, Si-H), 7.04, 7.95 (m, m, 12 H, CH₂C₆H₄); $\delta(^{31}P) = -160.0$ (br); $\delta(^{29}Si) = -15.0$ (br); IR (KBr pellet): $\nu(SiH) = 2104$ (s) cm⁻¹; FAB-MS (*m*-nitrobenzyl alcohol matrix) *m/z*(%) 703 (M + 1), 3), 619 (M - C₆H₁₁), 9). Anal. Calcd for C₃₉H₅₇P₃Si₃: C, 66.63; H, 8.17; P, 13.22. Found C, 66.38; H, 8.40; P, 13.02. The spectra data are comparable to the reported analogous compounds.¹⁷

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(7) The reaction between Ph₂PH and **4** occurred at and above -60 °C (monitored by variable temperature ¹H and ³¹P NMR spectroscopy, which showed a gradual decrease in the peak intensity of **1** and Ph₂PH and an increase in the peak intensity of the free PMe₃ in the ¹H and ³¹P NMR spectra. No resonances due to **4** were detected.

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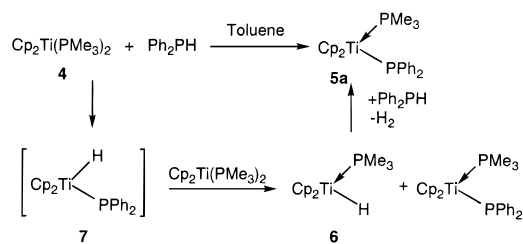
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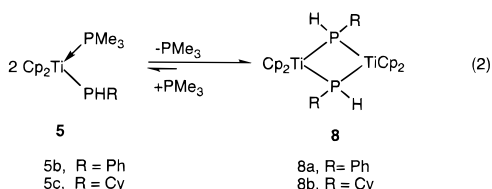
(1) For reviews see: (a) Harrod, J. F. In *Progress in Catalysis*; Smith, K. J., Sanford, E. C., Eds.; Elsevier: Amsterdam, 1992; p 147. (b) Corey, J. Y. *Silicon Chem.* **1991**, *1*, 327. (c) Tilley, T. D. *Acc. Chem. Res.* **1993**, *26*, 22 and references therein. (d) Gauvin, F.; Harrod, J. F.; Woo, H. G. *Adv. Organomet. Chem.* **1998**, *42*, 363.

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Scheme 1



A similar sequence to that shown in Scheme 1 occurred in the reactions of **4** with primary phosphines RPH₂ (R = Ph, Cy), to yield the phosphido compounds Cp₂Ti(PHR)(PMe₃) (**5b**, R = Ph; **5c**, R = Cy), as shown by the EPR spectroscopy.⁸ **5b** and **5c** lose PMe₃ easily to form the phosphide-bridged dimers [Cp₂Ti(μ-PHR)]₂ (**8a**, R = Ph; **8b**, R = Cy). In concentrated solutions the poor solubility of these dimers pulls the PMe₃ dissociation equilibrium in the direction of **8** by precipitation of the dark purple crystals in high yield (82% for **8b** and 81% for **8c**) (see eq 2).



On the other hand, **5a** can be isolated either as a consequence of tighter binding of the PMe₃ or because its more sterically demanding phosphido ligand destabilizes the dimer.⁵ Addition of PMe₃ to a toluene solution of **8b** or **8c** regenerated **5b** and **5c**, respectively, proving the reversibility of eq 2.⁹ No reaction occurred between **4** and Cy₂PH, presumably because of steric hindrance. The rates of the reactions of **4** with phosphines to give **5** follow the order PhPH₂ > Ph₂PH ≈ CyPH₂ ≫ Cy₂PH.

Reaction of a toluene solution of **5a** with PhSiH₃ (2 equiv) for 2 h converted it completely to Cp₂Ti(PhSiH₂)(PMe₃), **9**,¹⁰ with the production of Ph₂PSiH₂Ph and a minor amount of (Ph₂P)₂-SiHPh. Addition of Ph₂PH (2 equiv) to this purple solution regenerated **5a** fully in 1 h, showing that the conversion of **9** to **5a** is about twice as fast as that of **5a** to **9**. An isolated sample of **9**¹⁰ reacted similarly with Ph₂PH to give **5a** and Ph₂PSiH₂Ph.

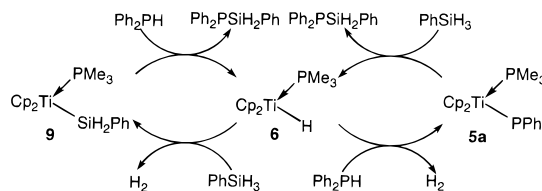
A solution of **6** was prepared by reaction of titanocene(III) hydride with PMe₃¹⁰ and converted cleanly to **5a** or **9** by adding Ph₂PH or PhSiH₃, respectively. EPR spectroscopy showed these

(8) EPR data in toluene at 25 °C for **5b**: $g = 1.9902$, $a(^{31}\text{P}) = 25.3$ G, $a(^{31}\text{P}) = 8.0$ G, $a(^1\text{H}) = 5.0$ G; for the PhPD analogue of **5b**: $g = 1.9902$, $a(^{31}\text{P}) = 25.3$ G, $a(^{31}\text{P}) = 8.0$ G, $a(^{47/49}\text{Ti}) = 9.8$ G; for **5c**: $g = 1.9895$, $a(^{31}\text{P}) = 25.3$ G, $a(^{31}\text{P}) = 8.4$ G, $a(^1\text{H}) = 2.8$ G; for **10**: $g = 1.9728$, $a(^{31}\text{P}) = 4.66$ G, $a(^{47/49}\text{Ti}) = 13.20$ G; the same EPR spectrum as **10** was observed for Cp₂Ti(PDPh)(PD₂Ph).

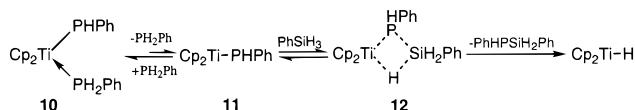
(9) The assignments of the structures of **8** are based on this reaction since **8** shows no structurally informative resonances in their EPR, ¹H or ³¹P NMR spectra. **8b** was characterized earlier by a single-crystal X-ray structure analysis and was shown to undergo the reaction shown in eq 2.¹

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Scheme 2



Scheme 3



reactions to be complete immediately following mixing at room temperature, in contrast to the much slower reactions of **5a** with PhSiH₃ or that of **9** with phosphine. This accounts for the low steady-state concentration of **6** and our failure to detect it by EPR, even at temperatures down to -50 °C.

A set of reactions which conforms to the observed results is shown in Scheme 2. This scheme involves a sequence of σ-bond metatheses occurring between substrates and Ti(III)-X species, where X = silyl, phosphide, or H.¹¹ It is likely that the σ-bond metatheses are preceded by PMe₃ dissociation from the EPR-observed titanocene species, although there is no direct evidence of this.

A contributing factor to the low reactivity of primary relative to that of secondary phosphines (in addition to the insolubility of the phosphide dimers, referred to above) is the high stability of their complexes **10**. **5b** does react with PhSiH₃ (2 equiv) at a similar rate to **5a** to give **9**, and **5b** is regenerated by treating **9** with PhPH₂ (2 equiv). However, under catalytic conditions, the phosphine substrate is present at a much higher concentration than the catalyst. Measurements under catalytic conditions clearly show that the excess substrate phosphine ligand completely converts **5b** to **10b** as the only EPR-observable product.⁸ On the other hand, a mixture of paramagnetic species is observed with Ph₂-PH, or CyPH₂, even at phosphine concentrations of >10:1 relative to the catalyst.

No homodehydrocoupling reaction of PhSiH₃ or of RR'PH occurred in any of the reactions described above. Reaction of **4** with excess PhSiH₃ first gives the η²-Si-H complex, Cp₂Ti(η²-HSiH₂Ph)PMe₃,^{12,13} which slowly decomposes to give **9** with evolution of H₂. No Si-Si coupling products were detected over a period of weeks. Thus, the presence of phosphine suppresses the homodehydrocoupling reactions, either through formation of **9** (silane coupling), or **5** (phosphine coupling). This also leads to the conclusion that all of the σ-bond metatheses of the catalytic cycle shown in Scheme 2 require predissociation of the phosphine ligand.

Acknowledgment. We thank the NSERC of Canada and the Fonds FCAR du Québec for financial support.

Supporting Information Available: ¹H, ²⁹Si, and ³¹P NMR assignments for all of the compounds in Table 1, EPR spectra of **5a-c**, **6**, **9**, and **10b**, and experimental details for syntheses (6 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(11) We agree with the suggestion of a reviewer that a reaction of **9** with phosphine to give **6** directly is less likely than its reaction to give **5** and silane.

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(13) NMR data for Cp₂Ti(η²-HSiH₂Ph)PMe₃ in toluene-d₆ at -55 °C: δ (¹H) = 5.70 (s, br, 2H, SiH₂), -4.02 (d, 1H, ²J_{PH} = 77.7 Hz, TiHSi); δ (³¹P) = 23.9 (d, 1P, ²J_{PH} = 77.7 Hz), -61.5 (free PMe₃).