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Exploration of tin-catalyzed phosphine dehydrocoupling: Catalyst effects and observation of tin-catalyzed hydrophosphination

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Dedicated to Prof. T. Don Tilley on the occasion of his 60th birthday. We look forward to many more years of his scientific leadership, steadfast mentorship, and kind friendship

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ABSTRACT

The phosphine substrate scope in dehydrocoupling reactions catalyzed by $Cp^*_2SnCl_2$ (Cp^* = pentamethylcyclopentadienyl, **1**) have been explored. Catalyst variants R_2SnX_2 (R = Cp^*, Ph; X = Cl, Me, Ph) were also tested, which revealed that activity is dependent on the Cp^* ligands as well as more electron withdrawing X ligands. Steric factors at the phosphine substrate are also important. Compound **1** was found to be a catalyst for hydrophosphination of styrene, 2,3-dimethylbutadiene, and diphenylacetylene with phenylphosphine, which is the first example of a p-block catalyst for hydrophosphination.

1. Introduction

Transition-metal catalysts are responsible for many powerful reactions. However, due to increasing scarcity and price, main group catalysts have become appealing as potential alternatives. Main group catalysis is a burgeoning field that features several examples of transformations that are equally efficient as those with transition-metal complexes [1–4]. These are exciting developments as main group elements had been viewed as largely unsuited towards catalysis except as Lewis acids [2]. This view originates from the lack of readily accessible and reversible redox reactivity under mild conditions as is known for many transition-metal systems. For example, the d orbital energies of transition-metals allows for facile reductive elimination and oxidative addition reactions as well as potentially labile coordination of ligands. However, there are many powerful reactions that do not require changes in the oxidation state of the metal (e.g., σ-bond metathesis), and the possibility of using main group metals for these redox-neutral processes has fueled interest in main group catalysis [1,5,6]. Currently, there are many examples of main group compounds that engage in classically transition-metal-mediated catalysis [1–4], including hydrogenation [7], hydrophosphination [8–12], hydrosilylation [13], dehydrocoupling [14], heterodehydrocoupling [15–20], and hydroamination [21–24].

Recently, we reported on the dehydrogenation of amine boranes with tin catalysts, which exhibits an unusual dependence of mechanism on amine-borane substrate [17]. Those studies were prompted by Wright and coworkers' report of phosphine dehydrocoupling catalyzed by a tin(IV) complex, $Cp^*_2SnCl_2$ (Cp^* = pentamethylcyclopentadienyl, **1**), at 10 mol % catalyst loading (Table 1) [25].

Phosphine dehydrocoupling reactions have been rarely catalyzed by main group compounds [26], and a limited number of transition-metal catalysts have been reported for the transformation [27,28]. Stoichiometric main group-mediated phosphine dehydrocoupling is better known in the literature than catalytic examples, and tin has been implicated in both [29,30].

Tin-catalyzed dehydrogenative P–P bond formation was dependent on the oxidation state of tin. Only tin(IV) showed catalytic activity, whereas stoichiometric phosphine dehydrocoupling was observed in reactions with a tin(II) complex, Cp^*_2Sn. It was proposed that the redox instability of this and other Sn(II) complexes render them non-catalytic [1,29–31]. Further evidence from isolated crystalline byproducts indicated that Cp^* was subject to protonation by

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Table 1
Reported conversions of RPH_2 to dehydrocoupled products using **1** [25][a].

R	Conversion (%)
Cy	80
^{t}Bu	68
Fc[b]	82
$FcCH_2$	65

[a] Conditions: 60 °C for 4 d in THF.
[b] Fc = ferrocenyl, $(C_5H_5)Fe(C_5H_4)$.

substrate, and that Sn(IV) can be reduced to Sn(II), which is catalyst deactivating. The proposed mechanism for this transformation is similar to that hypothesized by Stephan for phosphine dehydrocoupling catalyzed by $Cp^*_2ZrH_3^-$ (Scheme 1) [32].

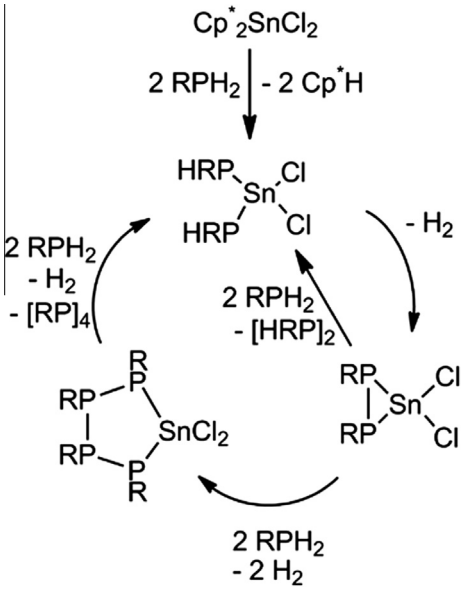
While the oxidation state of tin played a tremendous role in catalytic activity, ligand and substrate effects merited further study. Additionally, the facile P–H activation displayed by **1** suggested that further catalysis is possible, and hydrophosphination is a good initial target transformation owing to its broad utility [33–40]. Herein, both efforts are described.

2. Results and discussion

2.1. Catalyst effects on phosphine dehydrocoupling

In the initial report of phosphine dehydrocoupling using $Cp^*_2SnCl_2$ (**1**), the substrate scope consisted of primary alkyl phosphines. Here, the activity of **1** towards other phosphine substrates was explored with primary aryl phosphines, $PhPH_2$ and $dmpPH_2$, (dmp = 2,6-dimesitylphenyl) as well as secondary aryl and alkyl phosphines (R_2PH, R = Ph, Cy (cyclohexyl), and Mes (mesityl). These substrates were treated with **1** under reaction conditions similar to those reported, which all resulted in H_2 evolution, and the results are summarized in Table 2.

Combination of the reagents in deuterated solvent resulted in bright yellow solutions, which gradually became colorless as products formed. A fine colorless precipitate was also observed in all reactions that could not be definitively identified. The progress of



Scheme 1. Proposed catalytic cycle for phosphine dehydrocoupling using **1** adapted from reference 30.

Table 2
Results of the catalytic dehydrocoupling of new substrates, RR′PH, using **1**[a].

Entry	R	R′	Conversion (%)	Major product (%)
1	Ph	H	80	PhPH–PHPh
2	dmp	H	47	dmpPH–PHdmp
3	Ph	Ph	41	$Ph_2P–PPh_2$
4	Cy[b]	Cy	40	$Cy_2P–PCy_2$
5	Mes	Mes	34	$Mes_2P–PMes_2$

[a] Conditions: 60 °C for 3 d in benzene-d_6 10 mol % catalyst loading. Percent conversion was determined through integration of an external standard (a glass capillary solution of PPh_3 in benzene-d_6) by $^{31}P\{^1H\}$ NMR spectroscopy.
[b] Cy = cyclohexyl.

these reactions were monitored by $^{31}P\{^1H\}$ NMR spectroscopy, and percent conversions were calculated by integration against an external standard. These results display a similar trend to those previously reported in that increased steric bulk of substrate leads to decreased conversion [25]. For example, the dehydrocoupling of $PhPH_2$ goes further to completion than $dmpPH_2$ under the same conditions (Table 2, Entries 1 and 2). In the dehydrocoupling of $PhPH_2$ both diastereomers (rac and meso) are formed in almost equal amounts. However, in the dehydrocoupling of $dmpPH_2$ only one diastereomer is observed (*vide infra*).

The activity of **1** towards secondary phosphines was probed, and it was found that **1** gave lowered conversions as compared to reactions with primary phosphines (Table 2, Entries 4–6). There is no strong trend here. Lowered conversion to product is observed with more sterically encumbered but electron rich Mes_2PH (Mes = 2,4,6-trimethylphenyl) in comparison to Ph_2PH and Cy_2PH. The dialkylphosphine Cy_2PH gives similar conversion to products as Ph_2PH. An apparent electronic dependence is inconsistent with σ-bond metathesis [5]. though a trend has not truly been identified based on two substrates (Ph, Mes) alone. Likewise, the products of the dehydrocoupling of secondary phosphines (e.g., $R_2P–PR_2$) appear to discount an α-phosphinidene elimination pathway [6].

This supposition was buttressed through the dehydrocoupling of $dmpPH_2$. In some stoichiometric systems, the formation of dmpP = Pdmp has been considered indicative of the condensation of two phosphinidene fragments [40,41]. Here, it appears that α-phosphinidene elimination does not occur. No products of an apparent phosphinidene elimination such as a diphosphine are observed, and instead, a resonance in the $^{31}P\{^1H\}$ NMR spectra at $\delta = -101$ ppm with $J_{PH} = 227$ Hz is observed that is tentatively assigned as dmpPH–PHdmp based on similarity to Mes*PH–PHMes* and MesPH–PHMes [42–44].

This broader scope of phosphine substrates indicates that steric factors play a role in the efficiency of the catalysis. A second area of investigation was ligand effects at the catalyst. Three other Sn(IV)

Table 3
The effect of catalyst, $L_2SnL'_2$, on phosphine dehydrocoupling to products (% conversion)[a].

Compound	L	L′	Conversion (%)
1	Cp*	Cl	80
2	Cp*	Me	33
3	Cp*	Ph	73
4[b]	Ph	Cl	1
4[c]	Ph	Cl	2

[a] Conditions: 10 equiv. $PhPH_2$ in benzene-d_6 at 60 °C. Percent conversion was determined through integration of an external standard (a glass capillary solution of PPh_3 in benzene-d_6) by $^{31}P\{^1H\}$ NMR spectroscopy.
[b] ~20 equiv ^{t}BuPH$_2$ in THF.
[c] ~12 equiv. *o*-$(PH_2)_2C_6H_4$.