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ARTICLE

Tin-Catalyzed Hydrophosphination of Alkenes

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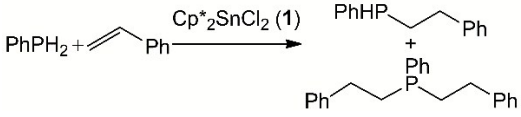
Simple tin derivatives, $Cp^*_2SnCl_2$ (**1**) and Ph_2SnCl_2 (**2**), catalyze the hydrophosphination of alkene substrates with diphenylphosphine. Competitive dehydrocoupling to give Ph_4P_2 was observed, but this side reaction can be mitigated when the catalysis is conducted under an H_2 atmosphere. Efforts to prepare stable tin bis(phosphido) compounds commonly resulted in decomposition to Ph_4P_2. Lewis acidic inorganic tin compounds do not show dehydrocoupling reactivity. It was found that the Lewis acid, $B(C_6F_5)_3$, is able to engage in the hydrophosphination of styrene, but it is poorly effective under the conditions tested.

Introduction

Main group catalysis has grown explosively over the last decade, driven by three main areas of interest: Frustrated Lewis pairs (FLP),[1-3] s-block metals,[4, 5] and p-block elements. Though there have been tremendous advances in p-block systems that engage in transition-metal–like reactivity,[6-9] non-Lewis acid catalysis[10] (e.g., redox or cooperative) from p-block elements has lagged behind developments with s-block metals and FLP systems.[11-14] As part of broader studies of dehydrocoupling reactions of phosphine substrates,[15-17] we have investigated tin compound catalysts,[18, 19] originally reported by Wright and coworkers.[20] In the course of those studies, it was found that $Cp^*_2SnCl_2$ (**1**) is an active catalyst for the hydrophosphination of alkene substrates (eqn 1).[18] That study surveyed the hydrophosphination reactivity of **1** with primary phosphines because that substrate type has been of increased interest in recent years as compared to historical interest.[18, 21-29] Herein, we report investigation of tin compounds as catalysts for hydrophosphination catalysis, focusing on a more classical diphenylphosphine substrate, Ph_2PH, with efforts to expand the utility of this catalyst class. Hydrophosphination is a ubiquitous metal-catalyzed route to P–C bonds,[30-37] and new catalysts that may relieve pressure on diminishing coinage metals often used in this reaction are of merit. Initial investigation of hydrophosphination catalyzed by **1** involved primary phosphine substrates.[18] The most pervasive phosphine substrate in this catalysis is Ph_2PH.[30-37] Thus, hydrophosphination reactions with this substrate were investigated to better compare tin catalysis with that of transition metals and gain insight into this new type of hydrophosphination catalyst.



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Results and discussion

Hydrophosphination catalysis

Catalytic hydrophosphination reactions of **1** with alkene substrates and Ph_2PH were sluggish under conditions by which alkenes were reacted with primary phosphines and **1**.[18] Moreover, the reactions were poorly selective for hydrophosphination products. In most reactions, dehydrocoupling of Ph_2PH to Ph_4P_2 and H_2 was the dominant process (Scheme 1). From our perspective, this is an unusual observation. Zirconium compounds affect catalytic hydrophosphination, and those reactions are much more favorable than dehydrocoupling, regardless of whether a primary or secondary phosphine substrate is used.[21, 26, 38, 39]

In the reactions catalyzed by **1**, some conversion to the anti-Markovnikov product was seen at longer reaction times. These products were observed when monitoring the reactions in closed, J-Young type NMR tubes. The observation of hydrogen in the ^{1}H NMR spectrum led to the hypothesis that competitive dehydrocoupling could be inhibited by an atmosphere of hydrogen during the reaction. Therefore, new conditions were devised.

For these reactions, NMR tubes were charged with alkene substrate, one equivalent of Ph_2PH, and 10 mole % of **1** in benzene-d_6 solution. After degassing, the system was backfilled with H_2 gas, and reactions were conducted at 65 °C. As hypothesized, reactions run under one atmosphere of H_2 were successful at catalytic hydrophosphination (Table 1).

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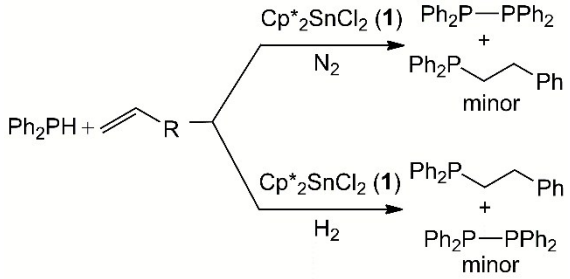


Scheme 1. Change in product distribution for hydrophosphination catalysis with **1**.

Table 1. Catalytic hydrophosphination reactions with Ph_2PH using 10 mol % of $Cp^*_2SnCl_2$ (**1**).

			products (%)[a]	
	substrate	conversion	hydrophosphination	$(Ph_2P)_2$
1	styrene	84	76	8
2	4-bromo-styrene	91	82	7
3	4-CF_3-styrene	93	82	5
4	4-methyl-styrene	90	85	5
5	phenyl acetylene	39	4	15
6	2-vinyl pyridine	100	78	22
7	acrylonitrile	100	86	14
8	vinyl ether	35	29	12
9	ethyl acrylate	81	68	13
10	1-hexene	10	0	10

Reactions were heated at 65 °C for 18 hours under an H_2 atmosphere. The conversion of products was measured by the relative integration of the respective resonances by $^{31}P\{^1H\}$ NMR spectroscopy.

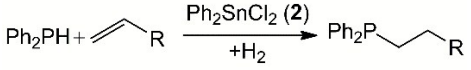
[a] Some unidentified phosphorus-containing products were also observed.

It is important to note that competitive dehydrocoupling remained prevalent but was relegated to less than 15% conversion in most cases. For hydrophosphination catalysis with **1** using primary phosphine substrates, some competitive dehydrocoupling was observed, but for receptive unsaturated substrates, the dehydrocoupling products were minor.[18]

Trends from substrates are mixed. Styrene derivatives and Michael acceptors were the most effective substrates. Unactivated alkenes exhibited poor reactivity. For example, only 29% of ethyl vinyl ether was converted to hydrophosphination product over an 18 hour reaction time (Table 1, entry 8), and 1-hexene was not converted at all under the reaction conditions (Table 1, entry 10). Surprisingly, less than catalytic conversion to the vinyl phosphine product was observed with phenylacetylene as the unsaturated substrate (Table 1, entry 5). With some of the other limitations in this catalysis, alkynes were not further pursued until better understanding and more optimized catalysts could be found. The styrene substrates did not appear to reflect a strong electronic preference. While run in parallel, conversions were not systematically affected by either electron donating (Table 1, entry 4) and withdrawing (Table 1, entries 2,3) substituents in the *para* position. Hydrophosphination of styrene substrates, among others, has become more common with lanthanide catalysts, and the conditions (temperature, length of reaction) are comparable to recent work with those systems.[29, 40, 41]

Despite the observation of successful hydrophosphination catalysis, there are three unsavory features of **1** as a catalyst. The conversions to hydrophosphination products are modest at elevated temperatures, the reaction displays substantial competitive dehydrocoupling of phosphine substrate, and to achieve these optimal conversions, reactions need to be run under an atmosphere of hydrogen. Substantial improvements in hydrophosphination reactivity were achieved through catalyst modification for calcium compounds.[42-45] This precedent gives impetus to pursue further the development of these tin catalysts because Hill's original calcium catalyzed hydrophosphination of styrene proceeded with similar conversion under comparable conditions and reaction time.[42] That precedent further suggests that modification of the cyclopentadienyl ligand would be the route to promote more productive reactivity. In all catalysis runs, however, the formation of pentamethylcyclopentadiene was observed. Furthermore, reaction of **1** with two equivalents of Ph_2PH resulted in the formation of Ph_4P_2 and pentamethylcyclopentadiene, as observed by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy. A colorless precipitate also formed, which is attributed to tin decomposition products. This stoichiometric reaction is consistent with the catalytic reactions, where pentamethylcyclopentadiene is also observed. The net protonation of the Cp* ligand, suggests that this ligand may be unimportant in the catalysis. Thus, a new strategy was employed. A search for more convenient precursors and greater understanding of the reaction was undertaken.

Using the same conditions as those for reactions with **1**, Ph_2SnCl_2 (**2**) was tested for hydrophosphination activity (eqn 2 and Table 2). Catalysis with compound **2** is attractive because it is a commercially available stannane. Under these conditions, styrene derivatives and phenylacetylene were not converted to hydrophosphination products. Activated alkenes (Table 2, entries 1, 2 and 4) showed similar reactivity with **2** as with **1**. Despite the inertness of styrene substrates to this catalyst, better and more selective hydrophosphination of ethyl vinyl ether was observed in reactions with **2** (Table 2, entry 3).



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The oxidation state of tin appears to be important. Reactions using catalytic Cp^*_2Sn (**3**) failed to produce appreciable hydrophosphination of styrene, acrylonitrile, or 2-vinyl pyridine. The lack of hydrophosphination catalysis with **3** is consistent with prior reports in which **3** displays no catalytic dehydrocoupling behavior. Comparison of the reactivities of **1**, **2**, and **3** in the dehydrocoupling of Ph_2PH, revealed no conversion by **3** and confirmed the prior observation that **1** is substantially more active catalyst for dehydrocoupling than is **2** (Table 3).[18] Compound **3** does engage in some dehydrocoupling, but this is scarcely catalytic under the

reaction conditions. Thus, dehydrocoupling reactivity provides course predictor about the activity of these tin compounds with respect to hydrophosphination.

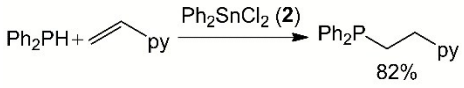
Table 2. Catalytic hydrophosphination reactions with Ph_2PH using 10 mol % of Ph_2SnCl_2 (**2**).

			products (%)	
	substrate	conversion [a]	hydrophosphination	$(Ph_2P)_2$
1	2-vinyl pyridine	92	71	3
2	acrylonitrile	60	60	0
3	vinyl ether	52	52	0
4	ethyl acrylate	98	93	5

Reactions were run at 65 °C for 18 hours under an H_2 atmosphere. The conversion of products was measured by the relative integration of the respective resonances by $^{31}P\{^1H\}$ NMR spectroscopy.

[a] Percent of Ph_2PH consumed as measured by $^{31}P\{^1H\}$ NMR spectroscopy.

Based on the dehydrocoupling reactivity, compound **2** should not need a hydrogen atmosphere for hydrophosphination. Indeed this is the case, and the hydrophosphination of 2-vinyl pyridine proceeds smoothly under the same conditions (vide supra) without a hydrogen atmosphere to give the hydrophosphination product in 82% yield (eqn 3).



3

Measurement of the kinetic isotope effect for the hydrophosphination of styrene using **1** gave KIE = 3.1(3). The value was obtained by an internal competition between an equivalent excess of Ph_2PH and Ph_2PD, and the ratio of products (1-diphenylphosphino-2-phenylethane and 1-diphenylphosphino-2-phenylethane-d_1) was measured to give the KIE value (eqn 4). This is a large value, which demonstrates substantial P–H/D cleavage in the turnover limiting step. The magnitude is similar to that seen for σ-bond metathesis reactions,[46] which may explain why the catalysis is only operant for the higher oxidation state tin compounds.

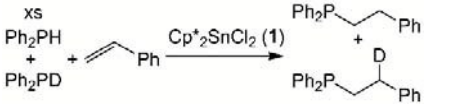


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Table 3. Comparison of dehydrocoupling activity of Ph_2PH using 10 mol % of compounds **1**, **2**, and **3**, respectively.

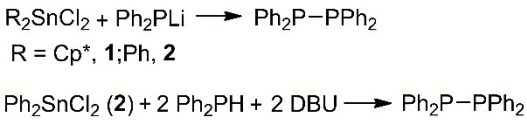
cmpd.	Ph_4P_2
$Cp^*_2SnCl_2$ (**1**)	13 [a]
Ph_2SnCl_2 (**2**)	0
Cp^*_2Sn (**3**)	2

Reactions were run at 65 °C for 18 hours. The conversion to Ph_4P_2 was calculated based on relative integration in $^{31}P\{^1H\}$ NMR spectra.

[a] Extended reaction times improve conversion to product, see reference 18.

Stoichiometric reactions

An effort was made to prepare and isolate tin derivatives that may be relevant to the catalysis. A potential candidate intermediate, $Ph_2Sn(PPh_2)_2$ has been reported.[47, 48] Efforts to prepare $Cp^*_2Sn(PPh_2)_2$ by metathesis of **1** with diphenylphosphide anion (Ph_2PLi) met with substantial formation of Ph_4P_2 (Scheme 2), consistent with prior reports of stoichiometric dehydrocoupling of phosphines mediated by tin reagents and BuLi.[20, 49] In our hands, efforts to prepare $Ph_2Sn(PPh_2)_2$ by salt metathesis resulted in significant formation of Ph_4P_2 and limited amounts of the desired product. Reaction of **2** with Ph_2PH and 1,8-diazabicycloundec-7-ene (DBU) also afforded Ph_4P_2. Interestingly, attempted preparation of Sn–P bonds has been observed to result in the formation of Sn–Sn products rather than those with P–P bonds.[48]



Scheme 2. Stoichiometric reactions of **1** and **2** targeted at $R_2Sn(PPh_2)_2$ products largely give Ph_4P_2.

Lewis acids

The remarkable chemistry of Lewis acid and FLP systems raises the possibility that Lewis acidic tin may be catalyzing the reaction. The stoichiometric hydrophosphination of alkenes was reported recently by Erker.[50] Indeed, Stephan and co-workers demonstrated P–H bond activation to generate a stabilized phosphenium (i.e., hydride abstraction) using Lewis acids, chemistry which was leveraged into catalytic phosphine dehydrocoupling and hydrogenation.[51] Therefore, simple tin chloride compounds were screened. Reactions in which each tin(II) chloride and tin(IV) chloride were used as a catalyst (10 mol %) failed to give appreciable hydrophosphination of styrene when applying the same conditions used for the organometallic tin derivatives.

The possibility of Lewis acid-mediated hydrophosphination could not be ignored, and $B(C_6F_5)_3$, a more potent Lewis acid, was also tested. Treatment of an equimolar mix of styrene and Ph_2PH with $B(C_6F_5)_3$ in benzene-d_6 solution gave no detectable formation of the hydrophosphination product at 65 °C. However, reactions run at high temperatures gave hydrophosphination products. Thus, heating an equimolar mix of styrene and Ph_2PH with $B(C_6F_5)_3$ in benzene-d_6 solution to 100 °C resulted in about one turnover to give 1-diphenylphosphino-2-phenylethane after 12 hours (eqn 5), and further heating resulted in catalysis. While Lewis acid catalyzed hydrophosphination appears to be possible based on these results, it is inefficient under these conditions. It is likely that better Lewis acid catalysts can be identified to promote this transformation.

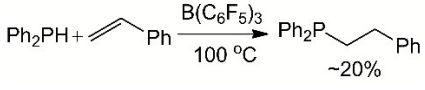


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Table 4. Catalytic hydrophosphination reactions with Ph_2PH using 10 mol % of $B(C_6F_5)_3$ and control reactions in the absence of borane.

			products (%)[a]	
	substrate	conversion	hydrophosphination	$(Ph_2P)_2$
1	4-bromo-styrene	31 (29)	24 (27)	7 (0)
2	4-CF_3-styrene	42 (36)	33 (34)	8 (0)
3	4-methyl-styrene	20 (23)	16 (23)	4 (0)
5	2-vinyl pyridine	84 (56)	77 (15)	2 (0)
6	acrylonitrile	67 (15)	58 (15)	5 (0)
7	vinyl ether	57 (8)	52 (8)	5 (0)
8	ethyl acrylate	82 (23)	72 (23)	3 (0)

Reactions were heated at 65 °C for 18 hours under an H_2 atmosphere. The conversion of products was measured by the relative integration of the respective resonances by $^{31}P\{^1H\}$ NMR spectroscopy.

[a] Values are for the catalytic runs, and values in parentheses are for control reactions in the absence of added borane.

Extension of that initial observation to the substrates screened throughout this study show that styrene derivatives are poorly hydrophospinated by this Lewis acid (Table 4, entries 1–3). Michael acceptors show moderate activity as substrates (Table 4, entries 5–8). These results are highly preliminary, but in this proof of concept series, Lewis acids appear to be potentially viable hydrophosphination catalysts.

Experimental Section

General considerations

All manipulations were performed with rigorous exclusion of air and water by means described in prior publications.[18] All NMR spectra were collected at 25 °C in benzene-d_6 on a Bruker Ascend 500 MHz NMR spectrometer and referenced internally to solvent residual resonances or to external phosphoric acid (85%).

Catalytic hydrophosphination reactions using R_2SnCl_2 (R = Cp*, 1; R = Ph, 2)

All reactions were conducted in J-Young type polytetrafluroethylene (PTFE)-valved NMR tubes. A mixture of one equiv. of unsaturated substrate, one equiv. of phosphine, and 10 mol % of **1** or **2** were then dissolved in 0.4 mL of benzene-d_6 (Table 4 and 5, respectively). The resulting solution was transferred to an NMR tube. The nitrogen atmosphere was removed from the J-Young PTFE-valved NMR tube via a freeze-pump-thaw cycle, and the tube was backfilled with a positive pressure of H_2 gas. The headspace was evacuated and backfilled again to ensure a pure H_2 atmosphere. Initial ^1H and ^{31}P NMR spectra were then collected. The solution was then heated to 65 °C, and NMR spectra collected periodically with a final spectrum at 18 hours reaction time. In all reactions, the yellow initial solution gradually lost its color upon heating and formation of a colorless precipitate was observed during the course of the reaction.

Table 5. Quantities of reagents (mg) for hydrophosphination catalysis with **1**.

substrate	PPh_2H	**1**	product [a]
styrene, 29.6	53.2	12.9	52
4-methyl styrene, 33.4	53.5	12.9	52
4-bromo styrene, 52.7	51.4	13.1	b
4-trifluromethyl styrene, 50.1	53.7	13.2	c
acrylonitrile, 28.8	74.5	18.4	53, 54
phenyl acetylene, 45.1	74.5	18.4	53
2-vinyl pyridine, 23.2	52.5	13.1	52
ethyl vinyl ether, 19.3	46.5	11.5	55
ethyl acrylate, 27.5	53.5	13.1	53

[a] Reference to spectroscopic characterization of the anticipated product of hydrophosphination catalysis.

[b] Selected data: $^{31}P\{^1H\}$ NMR: δ = –15.4; GCMS (EI): m/z = 369.4, 367.8

[c] Selected data: $^{31}P\{^1H\}$ NMR: δ = –15.8; GCMS (EI): m/z = 357.5

Table 6. Quantities of reagents (mg) for hydrophosphination catalysis with **2**.

substrate	PPh_2H	**2**
acrylonitrile, 27.1	95.2	17.2
2-vinyl pyridine, 28.2	52.0	9.2
ethyl vinyl ether, 24.8	58.5	10.5
ethyl acrylate, 35.1	63.4	11.5

Dehydrocoupling reactions

Reactions were conducted in PTFE-valved NMR tubes. One equivalent of diphenylphosphine and 10 mol % of pre-catalyst were dissolved in 0.4 mL of benzene-d_6 (Table 6). The resulting solution was added to the NMR tube. Initial ^1H and $^{31}P\{^1H\}$ NMR spectra were obtained. The NMR tube was then heated to 65 °C and data collected again periodically until 18 hours of reaction time was reached. Experiments were halted at this time because 18 hours was the typical length of a hydrophosphination run with these compounds.

Table 7. Reagents for the attempted catalytic dehydrocoupling of Ph_2PH (mg).

compound	amount	Ph_2PH
$Cp^*_2SnCl_2$ (**1**)	18.7	74.5
Ph_2SnCl_2 (**2**)	8.2	45.3
Cp^*_2Sn (**3**)	15.7	75.1

Reaction of $Cp^*_2SnCl_2$ with Ph_2PH

A scintillation vial equipped with a magnetic stir bar was charged with 30.1 mg (0.065 mmol) of $Cp^*_2SnCl_2$ and 5 mL of diethyl ether. Slowly 25.8 mg (0.139 mmol, 2.1 equiv) of neat Ph_2PH was added. The contents of the reaction were stirred at 23 °C for 18 h to give 90% conversion to Ph_4P_2 by ^{31}P NMR spectroscopy.

Reaction of $Cp^*_2SnCl_2$ with Ph_2PLi

A scintillation vial equipped with a magnetic stir bar was charged with 45.9 mg (0.247 mmol) of Ph_2PH. The reaction was given 5 mL of ether, cooled to –30 °C, and treated with 0.16 mL of a 1.6 M BuLi solution in hexanes. This was allowed to warm to 23 °C and stirred for 30 min. The reaction contents were cooled to -30 °C and slowly given 54.0 mg (0.117 mmol) of $Cp^*_2SnCl_2$. The contents of the reaction were stirred at 23 °C for 18 h to give quantitative conversion to Ph_4P_2 by ^{31}P NMR spectroscopy.

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Reaction of Ph_2SnCl_2 with Ph_2PLi

A scintillation vial was given 47.8 mg (0.257 mmol) of Ph_2PH, a magnetic stir bar, and 5 mL of diethyl ether. The contents were cooled to -30˚C and given 0.16 mL of a commercial 1.6 M BuLi solution in hexanes. This was allowed to warm to 23˚C and stirred for 30 min. The reaction contents were cooled to –30 °C followed by slow addition of 44.0 mg (0.127 mmol) of Ph_2SnCl_2. The contents of the reaction were stirred at 23 °C for 18 h to give 46% conversion to Ph_4P_2 by ^{31}P NMR spectroscopy.

Reaction of Ph_2SnCl_2 with Ph_2PH and DBU

A flask was charged with 46.6 mg (0.136 mmol) of Ph_2SnCl_2, 5 mL of dichloromethane, and 53.4 mg (0.350 mmol, 2.57 equiv.) of DBU. Dropwise, 54.3 mg (0.292 mmol) of Ph_2PH were added. The contents were refluxed for 22 h. The volatiles were removed under reduced pressure to yield a complicated mixture of products including Ph_4P_2 by ^{31}P NMR spectroscopy. A second run at ambient temperature provided similar results.

Catalytic hydrophosphination of styrene using $B(C_6F_5)_3$

A J-Young NMR tube was charged with 2.9 mg (0.0057 mmol) of $B(C_6F_5)_3$, 7.9 mg (0.076 mmol) of styrene, and 0.50 mL of benzene-d_6. Finally, 15.8 mg (.085 mmol) of Ph_2PH was added. The reaction was heated at 65 °C or 100 °C and monitored by ^{31}P NMR spectroscopy. For styrene, No dehydrocoupling products were observed and after at least 6 hours, measurable quantities of $Ph_2PCH_2CH_2Ph$ were observed. Reactions with all other substrates (Table 4) were conducted similarly. In those reactions, only runs at 100 °C were made.

Kinetic isotope effect measurement

A J-Young NMR tube was charged with $Cp^*_2SnCl_2$ (2.8 mg, 0.0061 mmol), styrene (8.1 mg, 0.078 mmol), and 0.50 mL of benzene-d_6. A mixture of 17.5 mg of Ph_2PH and 17.8 mg of Ph_2PD was then added. The contents were heated to 65 °C for 18 h, and the relative integration of the methylene resonances was compared.

Conclusions

The catalytic hydrophosphination of alkenes with Ph_2PH using tin catalysts has been explored. The previously reported catalyst for this reaction, **1**, suffers from substantial competitive phosphine dehydrocoupling, but this undesired reactivity can be suppressed by running reactions under a hydrogen atmosphere. Compound **2** is also a hydrophosphination catalyst. While **2** does not exhibit as broad of a substrate scope as **1**, indications are that **2** does not require a hydrogen atmosphere because dehydrocoupling reactivity under these conditions by **2** is non-existent. Tin(IV) appears to be essential for this reactivity because **3** did not afford hydrophosphination products under the conditions tested. A large kinetic isotope effect value measured in an internal competition experiment suggests that the P–H bond activation may proceed via a σ-bond metathesis step. Furthermore, the catalysis does not appear to be driven by the potential Lewis acidity of these tin compounds, yet Lewis acid catalysis is a potentially viable route to hydrophosphination. Overall, there is a clear potential for growth and improvement with these tin-catalyzed reactions.

Though not the focus of this work, evidence for Lewis acid catalyzed hydrophosphination has been discovered. This catalysis is poorly efficient as compared to the tin catalysis reported herein as well as hydroamination catalysis using $B(C_6F_5)_3$.[56] This preliminary discovery suggests that Lewis acid or FLP catalysis may be an area of growth in hydrophosphination, and like these tin compounds, may be a route to alleviate pressure on coinage metals in this kind of catalysis.

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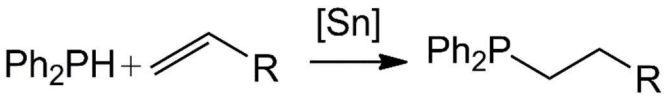

Tin-Catalyzed Hydrophosphination of Alkenes

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