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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].

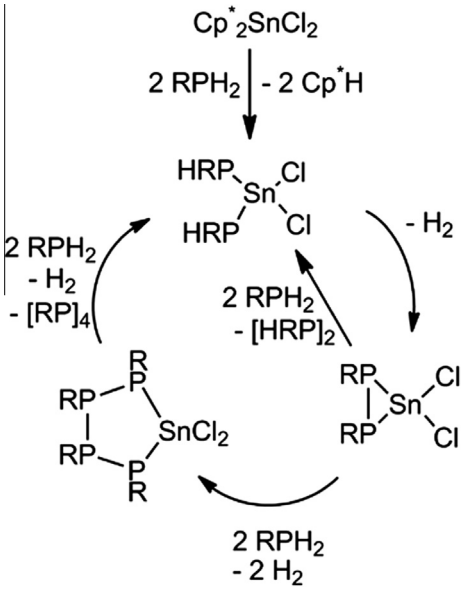
While the oxidation state of tin played a tremendous role in catalytic activity, ligand and substrate effects merited further study. Additionally, the facile P–H activation displayed by **1** suggested that further catalysis is possible, and hydrophosphination is a good initial target transformation 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*-$(PH_2)_2C_6H_4$.

compounds, $Cp^*_2SnR_2$ (R = Me, **2**; Ph, **3**) and Ph_2SnCl_2 (**4**), were used to dehydrocouple primary phosphines. The percent conversion of these reactions were compared to those achieved in reactions catalyzed by **1** under the same conditions (Table 3).

The more bulky but also more electron withdrawing phenyl ligands of compound **3** resulted in slightly lowered percent conversions to products as compared to those of catalyst **1** (73% and 80% conversion, respectively). The significantly less bulky methyl ligand in complex **2** is more electron donating, and the reaction with $PhPH_2$ resulted in significantly lowered product conversions than those of both **1** and **3**. In the dehydrocoupling of **2**, loss of Cp^* was observed in the ^1H NMR spectrum, which is also observed in reactions of **1** and **3** with phosphine. Methane loss could not be definitively observed due to multiple resonances region of methane in the ^1H NMR spectra. Thus, methane may have been obscured. Despite apparent protonation of ligands, clear spectroscopic evidence for a tin phosphido intermediate could not be accrued.

In dehydrocoupling reactions with **4**, it is apparent that the Cp^* ligand is essential for catalytic dehydrocoupling and leads to the conclusion that there are not only steric but electronic effects at play. In the original report, $^tBuPH_2$ was dehydrocoupled with **1** in 68% conversion, however when **4** is used as a catalyst, the catalytic activity is drastically reduced. While **4** has reduced steric hindrance around the metal center as compared to **1**, it is hypothesized that lower activity results from the ligand being less susceptible to protonation, which is a barrier to generating the active tin catalyst.

From these results, there are several inferences that can be made. First, the activity of the catalyst appears to be driven by the electronics of the ligand. The chloro ligand appears to be necessary for catalytic activity in Sn(IV) complexes as **2** and **3** are both less active than **1**. Compound **3** does exhibit greater catalytic activity than **2**, which is consistent with more electron-withdrawing phenyl substituents. Observation of C_5Me_5H during catalysis suggests that protonation of the Cp^* is a common if not necessary step to initiate phosphine dehydrocoupling, though the observation that Ph_2SnCl_2 is catalytically inactive shows that Cp^* is essential, even if it is lost. The greater observed catalytic activity for **1** as compared to **2** and **3** may be consistent with the stabilization of the tin(IV) center imparted by the more electronegative Cl ligands (hence the greater catalyst lifetime and turnovers).

Some efforts were made to observe a Sn–P intermediate through $^{31}P\{^1H\}$ NMR spectroscopy of stoichiometric reactions. Phosphido reagents (PhPHLi and Ph_2PLi) were added to cold benzene solutions of **1**, and upon mixing, NMR spectra were collected. These reactions were allowed to further react at ambient temperature under monitoring by $^{31}P\{^1H\}$ NMR spectroscopy. These experiments did not result in the formation of any new intermediate that could be discerned by either $^{31}P\{^1H\}$ or $^{119}Sn\{^1H\}$ NMR spectroscopy. Instead, upon addition of PhPHLi, immediate formation of the products of dehydrocoupling (PhHP–PHPh, $[PPh]_4$, and $[PPh]_6$) as well as $PhPH_2$ were observed. These dehydrocoupling products are similar to stoichiometric reactions of tin compounds with phosphines in the presence of base [1,29–31]. The formation of $(PhPH)_2$ has been reported in similar reactions between lithiated phosphine and Sn(II) complexes and was an indicator that Sn(II) phosphinidiide cagwwwes formed [31]. When Ph_2PLi was reacted with **1**, only $Ph_2P–PPh_2$ was observed.

Main group hydrides have been implicated as important reactive intermediates in several main group catalytic reactions [1,17,45,46]. To attempt to observe hydrides or other catalyst species, $^{119}Sn\{^1H\}$ NMR spectra were obtained for phosphine dehydrocoupling reactions. Unfortunately, no signal from Sn-containing species could be detected. This situation may result from multiple tin species in the reaction mixture at relatively low concentrations and is consistent with the difficulty in observing new $^{31}P\{^1H\}$ NMR resonances.

2.2. Hydrophosphination of alkenes and alkynes

Facile P–H activation at tin suggested that other bond-forming reactions to phosphorus may be possible. Hydrophosphination is a natural choice because of its broad importance to a variety of fields [33–40,47]. The heightened reactivity of **1** with primary versus secondary phosphines governed the choice to explore this substrate. Initial experiments were designed using $PhPH_2$ with a series of unsaturated organic substrates and catalytic amounts of **1** to probe the viability of tin-catalyzed hydrophosphination.

Styrene, 1-hexene, 2,3-dimethylbutadiene, diphenylacetylene, and phenylacetylene were chosen as substrates of interest. Classic hydrophosphination substrates that are Michael acceptors were deliberately shunned in these studies to potentially identify insertion-based reactivity. In initial studies, these reactions were probed using 10 mol % catalyst loading in benzene-d_6 at 60 °C and with one equiv. of $PhPH_2$ for ca. 18 h after which ^1H, $^{31}P\{^1H\}$, and ^{13}C NMR spectra were collected. In the ^{13}C NMR spectrum, the absence of diagnostic sp^2 carbon resonances is noted, indicating the unsaturated substrate is fully reduced within the limits of detection. The presence of characteristic $^{31}P\{^1H\}$ NMR resonances demonstrated that the hydrophosphination of styrene and 2,3-dimethylbutadiene had occurred. Roughly half of diphenylacetylene was hydrophosphinated as well. 1-Hexene was inert under these preliminary reaction conditions, and further attempts to optimize this substrate were not pursued. The hydrophosphination reaction of phenylacetylene under these conditions afforded very low conversions to product and also suffered from low selectivity. Many unidentified resonances were observed in the $^{31}P\{^1H\}$ NMR spectrum. No additional efforts towards optimization were made.

In the hydrophosphination of styrene, a mixture of secondary and tertiary phosphine products ($PhCH_2CH_2PHPh$ and $(PhCH_2CH_2)_2PPh$,

Table 4
Product distribution of hydrophosphination reactions (relative %)[a].

Substrate	Mono- hydrophosphination	Bis-hydrophosphination	PhHP–PHPh	% conv. of substrate	Rxn time (h)
Styrene[b]	73 [48]	21 [48]	2	100	5
Styrene[c]	56	40	4	100	18
2,3-Dimethylbutadiene[b]	83 [48]	0	17	100	5
2,3-Dimethylbutadiene[c]	99	0	1	100	18
1-Hexene	0	0	100	0	18
Diphenylacetylene[b]	19 *E*, 37 *Z* [47]	0	44	25	18
Diphenylacetylene[c]	34 *E*, 45 *Z*	0	55	50	18
Diphenylacetylene[d]	24 *E*, 16 *Z*	0	29	30	18
Phenylacetylene[b]	14 *E*, 32 *Z* [49]	0	54	~10	18

[a] Reactions in benzene-d_6, heated at 60 °C. Relative percent yield determined through $^{31}P\{^1H\}$ NMR spectroscopy.
[b] ~2 equiv. $PhPH_2$.
[c] 1 equiv. $PhPH_2$.
[d] ~2 equiv. $PhPH_2$, reaction heated at 75 °C.

respectively) were formed, demonstrating that styrene is the limiting reagent. In the hydrophosphination of diphenylacetylene, some unknown products were also observed in the reaction mixtures in addition to a mixture of *E* and *Z* isomers of PhCH = CPhPHPh. Likewise, in the hydrophosphination reaction with 2,3-dimethylbutadiene, several unidentifiable products were formed. However, by increasing the equivalents of $PhPH_2$ to approximately two, significant improvements in selectivity was observed in these reactions. These reactions were monitored closely through $^{31}P\{^1H\}$ NMR spectroscopy where it was found that styrene and 2,3-dimethylbutadiene required only ~5 h to reach completion at 60 °C. In optimized reactions, the only byproduct of significant quantities are phosphine dehydrocoupling products (Table 4).

The preferential formation of the *Z* isomer was particularly interesting in the hydrophosphination of the acetylenes at 60 °C using either one equiv or excess amounts of $PhPH_2$. This isomer was the minor product in other reported catalytic examples of hydrophosphination [47]. A brief foray into the study of how these two isomers form led to the discovery that the temperature of the reaction has a large effect. In reactions at 75 °C, the *E* isomer predominates in the hydrophosphination of diphenylacetylene. Further study into the origin of regioselectivity, selectivity, and optimization of catalysis are under investigation. Nevertheless, these initial results are exciting. Alkaline earth elements are known and effective catalysts for hydrophosphination [8–12], but to the best of our knowledge, this is the first example of a p-block element as a catalyst for this reaction.

3. Conclusions

The goal of this work was to determine whether the activity of Sn(IV) catalysts towards phosphine dehydrocoupling could be enhanced through tuning the electronic and steric properties of the ligands. In addition, the expansion of the phosphine substrate scope was sought to afford additional insight into the mechanism. Finally, the activity of tin compounds towards P–H activation was applied to hydrophosphination.

Analysis of the products formed through the dehydrocoupling of bulky primary and secondary phosphines seems to support the catalytic cycle proposed by Wright and coworkers [25]. By exploring the phosphine substrate scope, it is apparent that increased steric bulk diminishes activity. This was observed in reactions with complex **1** and bulky primary phosphines as well as secondary phosphines. These results help to discount an α elimination-like mechanism and generally support the hypothesis of a mechanism that is more similar to a process involving σ-bond metathesis or 1,2-addition across a multiple bond. Further improvements in $PhPH_2$ dehydrocoupling were not achieved using other Sn(IV) catalyst precursors. Readily labile Cp^* ligands and electronegative ligands (Cl) appear to provide optimal catalytic activity.

Styrene, diene, and alkyne moieties were successfully hydrophosphinated with **1** and ~2 equiv. of $PhPH_2$. These reactions proceeded at mild temperatures and resulted in good selectivity for the monohydrophosphinated products using diphenylacetylene, styrene and 2,3-dimethylbutadiene, which justifies greater exploration the alkene and alkyne substrate scope as well as optimization of these initial results. In these preliminary studies some reaction conditions seemed to influence the *E* to *Z* ratios in alkyne hydrophosphination.

4. Experimental considerations

4.1. General considerations

All manipulations were performed under a dried nitrogen atmosphere with dry, oxygen-free solvents using an M. Braun glovebox or standard Schlenk techniques. Benzene-d_6 was degassed and dried over NaK alloy. Anhydrous THF-d_8 was used as received. ^1H, $^{31}P\{^1H\}$, and $^{119}Sn\{^1H\}$ NMR spectra were recorded on a Bruker Ascend 500 MHz NMR spectrometer. Reported ^1H NMR resonances are referenced to residual solvents (benzene-d_6 = δ 7.16 ppm, THF-d_8 = δ 1.72 or 3.58 ppm). All chemicals were either synthesized from literature methods or purchased from commercial suppliers and dried by conventional means. For pertinent NMR spectra, see Supporting information (see Tables 5 and 6).

Table 5
Catalytic dehydrocoupling of phosphines using Sn(IV) catalysts.

Catalyst (mg, mmol)	Substrate (mg, mmol)
1, (6.2 mg, 0.013 mmol)	$PhPH_2$ (14 mg, 0.12 mmol)
1, (8.2 mg, 0.018 mmol)	Ph_2PH (37 mg, 0.20 mmol)
1, (7.2 mg, 0.016 mmol)	$dmpPH_2$ (47 mg, 0.13 mmol)
1, (4.2 mg, 0.009 mmol)	Cy_2PH (20 mg, 0.021 mmol)
1, (5.4 mg, 0.012 mml)	Mes_2PH (34 mg, 0.13 mmol)
2, (4.2 mg, 0.010 mmol)	$PhPH_2$ (14 mg, 0.12 mmol)
3, (4.1 mg, 0.008 mmol)	$PhPH_2$ (12 mg, 0.11 mmol)
4, (10 mg, 0.031 mmol)	$^tBuPH_2$ (50 mg, 0.55 mmol)

Table 6
Catalytic hydrophosphination of unsaturated organic substrates.

Catalyst	Substrate	$PhPH_2$
1 (4.5 mg, 0.009 mmol)	diphenylacetylene (20 mg, 0.11 mmol)	20 mg, 0.18 mmol
1 (12 mg, 0.026 mmol)	2,3-dimethylbutadiene (28 mg, 0.34 mmol)	56 mg, 0.51 mmol
1 (5.4 mg, 0.012 mmol)	styrene (16 mg, 0.16 mmol)	28 mg, 0.25 mmol
1 (11 mg, 0.023 mmol)	1-hexene (23 mg, 0.27 mmol)	63 mg, 0.57 mmol
1 (4.7 mg, 0.01 mmol)	phenylacetylene (15 mg, 0.15 mmol)	25 mg, 0.23 mmol

4.2. Catalytic phosphine dehydrocoupling reactions

All reactions were conducted using a J-Young type polytetrafluoroethylene (PTFE)-valved NMR tube in benzene-d_6 or THF-d_8. After the addition of reagents, an initial NMR spectrum was obtained. The solution was frozen and the headspace was evacuated. This was repeated at regular intervals during the course of the reaction to remove H_2. After thawing, the NMR tube was heated at 60 °C. The yellow reaction mixture gradually turned clear and resulted in the formation of colorless precipitates. All NMR spectra were collected at 25 °C.

4.3. Synthesis of $Cp^*_2SnMe_2$ (**2**)

A solution of $Cp^*_2SnCl_2$ (100 mg, 0.22 mmol) in hexanes (2 mL) was charged in a scintillation vial and cooled to ca −30 °C. Methyl lithium (0.3 mL of a 1.6 M solution in hexanes) was subsequently added to this solution, resulting in a color change from yellow to clear and the formation of a white precipitate. This reaction was allowed to stir at room temperature for 1 h. Afterwards, the mixture was filtered through a plug of glass fiber paper. The residual solvent was removed under vacuum yielding a fine white powder (91 mg, 0.22 mmol) in quantitative yield. The formation of this product was confirmed through comparison of ^1H and $^{13}C\{^1H\}$ NMR spectra with literature assignments [50].

4.4. Synthesis of $Cp^*_2SnPh_2$ (**4**)

A solution of Ph_2SnCl_2 (0.38 g, 0.0011 mol) in hexane was cooled to −30 °C. Freshly prepared Cp^*Li (0.31 g, 0.0022 mol)

suspended in 1 mL of hexane was added dropwise to the stirring solution. The reaction was allowed to proceed for 1 h at room temperature. Afterwards, the mixture was filtered through a plug of glass fiber paper. The residual solvent was removed under vacuum yielding a clear oil (0.164 g, 30 % yield) which solidified upon standing.. ^{1}H NMR: (C_6D_6): 1.73 (s, 30 H), 7.08 (m, 6 H), 7.47 (m, 4 H).

4.5. Catalytic hydrophosphination reactions

All reactions were conducted using a J-Young type polytetrafluoroethylene (PTFE)-valved NMR tube in benzene-d_6. Substrate and phosphine were mixed together prior to the addition of catalyst as a solid. After the addition of reagents to the NMR tube, the reaction mixture was heated to 60 °C for ca 18 h. NMR spectra were obtained at 25 °C.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2014.07.002.

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