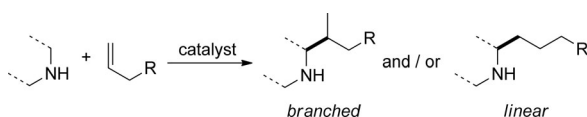


C–H Activation

# Phosphoramidate Tantalum Complexes for Room-Temperature C–H Functionalization: Hydroaminoalkylation Catalysis\*\*

Pierre Garcia, Ying Yin Lau, Mitchell R. Perry, and Laurel L. Schafer\*

Amines are critical functional groups that are incorporated into many biologically active compounds and functional materials of importance to the biomedical, agrochemical and fine-chemical industries.<sup>[1]</sup> An idealized synthetic approach for the preparation of this important class of compounds would take advantage of the direct and by-product free conversion of feedstock alkenes directly into unprotected amines with good regio- and stereoselectivity under mild reaction conditions. These goals could be realized with early transition metal catalyzed hydroaminoalkylation (Scheme 1), a C–H functionalization reaction  $\alpha$  to nitrogen



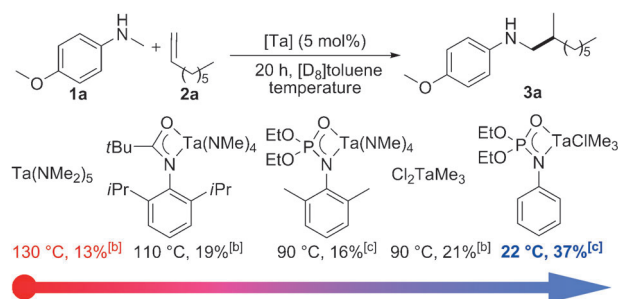
**Scheme 1.** Hydroaminoalkylation: a by-product-free C–H functionalization reaction using simple amine and alkene feedstocks.

that results in selective C–C bond formation.<sup>[2,3]</sup> However, to date, all promising Group 4 and 5 metal complexes for this transformation demand harsh reaction conditions.<sup>[4,5]</sup> The identification of a system that can be used with mild reaction conditions is desirable. Here we show that by using a sterically demanding, *N,O*-chelating, electron-withdrawing phosphoramidate as an easily installed auxiliary ligand, room-temperature alkene hydroaminoalkylation can be achieved for the first time.

Unlike late transition metal catalysts (Ir, Ru)<sup>[6,7]</sup> for this reaction, early transition metal catalysts (Ti,<sup>[4]</sup> Zr,<sup>[4a]</sup> Ta,<sup>[5]</sup> Nb,<sup>[5c–g]</sup>) do not require a removable directing group or activated alkene substrates. Hydroaminoalkylation results in unprotected amines ready for further functionalization. This transformation gives selectively substituted amines in a single and atom-economic catalytic reaction, using inexpensive early transition metals of low toxicity. Thus, hydroaminoalkylation is an excellent reaction to target for advances in green chemistry.

Ligand screening investigations by Herzon and Hartwig have shown that electron-withdrawing chloride ligands enhance reactivity, such that select substrate combinations yield products at 90 °C.<sup>[5b]</sup> Notably, the more challenging dialkylamine substrates required temperatures of 150 °C and thermally polymerizable styrene derivatives were not reported.<sup>[4b]</sup> Herein, we show that our phosphoramidate–ClTaMe<sub>3</sub> precatalyst is easily synthesized and can achieve room-temperature hydroaminoalkylation with a broad range of substrates. Importantly this complex shows functional group tolerance (OTBS, Cl, CF<sub>3</sub>, OMe, TMS) in both the amine and alkene substrates, it is effective with thermally sensitive styrene substrates, and even dialkylamines can be used at room temperature. While unactivated alkenes react regioselectively to give branched products in high yield, remarkably this low temperature reactivity permits a substrate-controlled shift in regioselectivity such that for the first time with Group 5 complexes, linear amine products can be obtained in good yield. Most importantly, this phosphoramidate Ta complex can be used under solvent-free conditions to promote the high yielding, room temperature, and atom-economic synthesis of substituted amines directly from alkenes.

In an effort to identify catalyst systems that can realize C–H functionalization under mild reaction conditions, a benchmark hydroaminoalkylation reaction of 1-octene with *N*-methyl-*p*-methoxyaniline has been selected to compare various catalyst systems (Scheme 2). *N*-methyl-*p*-methoxyaniline is a commonly used substrate in hydroaminoalkylation catalyst development work,<sup>[4d,5a,c,f–j]</sup> as it has been shown to be favorably reactive while affording the opportunity for oxidative deprotection to access primary amine products.<sup>[5i]</sup> Notably, previous reports using Ta pre-



**Scheme 2.** Developing a precatalyst for room-temperature reactivity.<sup>[a]</sup> [a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.75 mmol), [D<sub>8</sub>]toluene (0.6 mL), [Ta] (0.025 mmol), 20 h. Conversion determined by <sup>1</sup>H NMR spectroscopy. [b] From isolated complex. [c] From in situ generated complexes.

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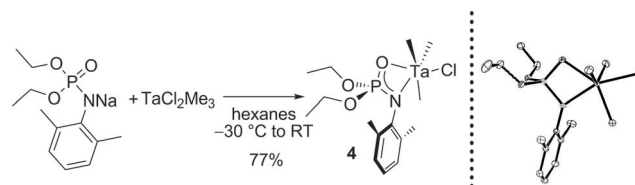
catalysts for hydroaminoalkylation of unactivated alkenes with *N*-methyl-*p*-methoxyaniline typically disclose reaction temperatures of 130–160 °C with a few exceptions reported at 90–110 °C.<sup>[5b,g,i,j]</sup>

We identified the minimum temperature required to achieve at least three turnovers within 20 h for several Ta<sup>V</sup> precatalysts. The commercially available Ta(NMe<sub>2</sub>)<sub>5</sub> requires a high reaction temperature of 130 °C to realize three catalyst turnovers within 20 h.<sup>[5a]</sup> Our reported *N,O*-chelating amidate precatalyst<sup>[5c]</sup> can realize this transformation at 110 °C. Previous investigations have shown that sufficient steric bulk is critical for promoting efficient reactivity in this class of precatalysts, while *N,O*-chelating ligands promote enhanced substrate scope.<sup>[5c,h]</sup> Thus our attention turned to other readily available *N,O*-chelating motifs that could be easily modified to support enhanced steric bulk. Phosphoramidates are attractive due to their increased electron-withdrawing properties,<sup>[8]</sup> tunable steric bulk at both phosphorus and nitrogen, and their facile modular syntheses.<sup>[9]</sup>

The mixed phosphoramidate–Ta(NMe<sub>2</sub>)<sub>4</sub> complex prepared in situ by protonolysis of Ta(NMe<sub>2</sub>)<sub>5</sub> with the proligand can catalyze the desired hydroaminoalkylation reaction at 90 °C. This result is comparable to the recently reported Cl<sub>2</sub>TaMe<sub>3</sub> precatalyst which also requires 90 °C for observable catalytic turnover within 20 h.<sup>[5j]</sup> Gratifyingly, the combination of the steric bulk of the phosphoramidate ligand with the generation of a highly electrophilic metal center through the incorporation of both electron-withdrawing chloride and phosphoramidate ligands resulted in seven turnovers within 20 h at only room temperature.

Reaction optimization is shown in Table 1. A closer look at the steric bulk provided by the ligand, through 2,6-substitution of the aniline moiety, showed that 2,6-dimethylaniline enabled improved conversion (52 %, entry 2). However, even bulkier groups at the 2,6-positions (entry 3) or on the alkoxy substituents of phosphorus (entry 4) were detrimental to catalyst performance. Notably, the use of an *N*-alkyl

substituted phosphoramidate was not tolerated (entry 5). An increase in catalyst loading to 10 mol % resulted in a more favorable conversion within 20 h (entry 6). Common solvents such as toluene, hexanes and THF (entries 6–8) can all be used at room temperature, with toluene being preferred. In order to compare in situ prepared precatalysts with isolated complexes, salt metathesis has been used to prepare the desired complex **4** as yellow crystalline needles (77 % yield, Scheme 3). X-ray crystallographic analysis of this complex



**Scheme 3.** Salt metathesis to give crystalline precatalyst **4**.

reveals a distorted trigonal bipyramidal geometry with the  $\kappa^2$ -*N,O*-chelated phosphoramidate ligand trans to the axial chloride ligand.<sup>[10]</sup> Comparison of the metric parameters for the phosphoramidate ligand in **4** with the starting **L<sup>2</sup>-H** (see Supporting Information) proligand shows elongation of the P=O double bond, accompanied by a slight shortening of P–O and P–N  $\sigma$  bonds, as well as a significant reduction of the OPN angle from 113.01° to 98.67°.<sup>[10]</sup> These observations are all consistent with an *N,O*-chelating bonding mode. Solution-phase characterization data gives <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectra consistent with one species in solution, suggesting either static  $\kappa^2$  chelation, as observed in the solid state, or a highly fluxional complex ( $\kappa^2$ – $\kappa^1$ ) on the NMR timescale. Most importantly, the use of this isolated precatalyst gives the highest yielding room-temperature transformation (Table 1, entry 9).

With the straightforward synthesis of precatalyst **4** established, investigations of substrate scope showed that a variety of secondary amines are reactive with this catalyst system (Table 2). Electron-rich *N*-methyl anilines are preferred substrates, such that 4-methoxy- or 4-dimethylamino-*N*-methylanilines furnish the expected branched product **3a** and **3b** in high yields (entries 1 and 2). Consistent with this observation is the fact that *N*-methylaniline gives only 19 % yield under the same reaction conditions, yet the addition of electron-donating alkyl substituents improves reactivity such that *N*-methyl-*p*-toluidine gives **3c** in 46 % yield (entry 3), and the introduction of two methyl groups in the 3,4-positions of the phenyl ring enable the isolation of **3d** in 62 % yield (entry 4).<sup>[11]</sup> Halogen substituents are tolerated as shown with product **3e** (entry 5) to give amine building blocks ready for catalyzed coupling protocols.<sup>[5j]</sup> Even chelating catechol derivatives<sup>[12]</sup> can be used (entry 6) to give the expected compound **3f** in good yield (80 %), with extended reaction times. Using the same reaction conditions *N,N'*-dimethyl-1,4-phenylenediamine was monoalkylated to give **3g** (entry 7) and unreacted starting material.<sup>[13]</sup> Most importantly, in addition to arylamines, this precatalyst promotes room-temperature reactivity with known challenging dialkylamine

**Table 1:** Optimization of reaction conditions.<sup>[a]</sup>

Entry	L	x mol %	Solvent	Conv. [%]
1 <sup>[b]</sup>	L <sup>1</sup>	5	[D <sub>8</sub> ]toluene	37
2 <sup>[b]</sup>	L <sup>2</sup>	5	[D <sub>8</sub> ]toluene	52
3 <sup>[b]</sup>	L <sup>3</sup>	5	[D <sub>8</sub> ]toluene	28
4 <sup>[b]</sup>	L <sup>4</sup>	5	[D <sub>8</sub> ]toluene	24
5 <sup>[b]</sup>	L <sup>5</sup>	5	[D <sub>8</sub> ]toluene	0
6 <sup>[b]</sup>	L <sup>2</sup>	10	[D <sub>8</sub> ]toluene	76
7 <sup>[b]</sup>	L <sup>2</sup>	10	hexanes	62
8 <sup>[c]</sup>	L <sup>2</sup>	10	[D <sub>8</sub> ]THF	26
9 <sup>[c]</sup>	L <sup>2</sup>	10	[D <sub>8</sub> ]toluene	86

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.75 mmol), solvent (0.6 mL), [Ta] (x mol %), 20 h. Conversion determined by <sup>1</sup>H NMR spectroscopy. [b] In situ generated complex. [c] Isolated complex.

**Table 2:** Amine substrate scope.<sup>[a]</sup>

Entry	Amine	Product	Yield [%]
1			84
2			87
3			46
4			62 (44 h)
5			41
6			80 (64 h)
7			52
8			84 (50°C) 62 (168 h)
9			15

[a] Reactions conditions: **1a–i** (1 mmol), **2a** (1.5 mmol), toluene (1.2 g), **4** (0.1 mmol). Yield of isolated products.

substrates.<sup>[5b]</sup> Sterically comparable *N*-methylcyclohexylamine can be used in the hydroaminoalkylation of 1-octene to give **3h** in 62% yield. Here, prolonged reaction times are required at room temperature, but notably the reaction duration can be considerably shortened and the product yield can be significantly enhanced by warming to 50°C over 20 h (entry 8).<sup>[14]</sup> This precatalyst is very sensitive to steric bulk such that *tert*-butylmethylamine cannot be used for hydroaminoalkylation; however, dibutylamine can be selectively monoalkylated, albeit in low yield (**3i**, 15% yield, entry 9).

Various alkenes can successfully undergo room-temperature hydroaminoalkylation (Table 3). In addition to unactivated 1-octene, alkenes with protected alcohols at various positions (distal, **3j** and allyl, **3k**) are well tolerated (Table 3, entries 1 and 2), opening routes to further synthetic manipulation.<sup>[5b]</sup> Phenyl-substituted alkenes are well tolerated with **3l** isolated in 78% yield while **3m**, which is prepared using isomerizable allylbenzene, is reached in 70% yield (entries 3 and 4). When using bicyclic alkene substrates such as norbornene and norbornadiene, only the *exo*-diastereomer is prepared in both cases (**3n**, **3o**, entries 5 and 6).<sup>[15]</sup> In the case of norbornadiene the mono-substituted product is the major product isolated, although the overalkylated product can be detected.

**Table 3:** Alkene substrate scope.<sup>[a]</sup>

Entry	Amine	Product	Yield [%]
1			88
2			59
3			78
4			70
5			86
6			56
7			88 [68:1] <sup>[b]</sup> (50°C) 87 (168 h)
8			87 [14:1] <sup>[b]</sup> (50°C) 93 [26:1] <sup>[b]</sup> (168 h)
9			58 [10:1] <sup>[b]</sup> (50°C) 93 [10:1] <sup>[b]</sup> (168 h)
10			91 [1.6:1] <sup>[b]</sup> (50°C) 78 [1.8:1] <sup>[b]</sup> (168 h)
11			66 [1:7] <sup>[c]</sup>

[a] Reaction conditions: **1a** (1 mmol), **2b–l** (1.5 mmol), toluene (1.2 g), **4** (0.1 mmol). Yields of isolated products. [b] Major isomer presented, [branched/linear] ratio determined by GC of the crude material. Yields refer to combined regioisomers. [c] Major isomer presented, [branched/linear] ratio determined by GC of the inseparable purified isomers. Yield refers to combined regioisomers.

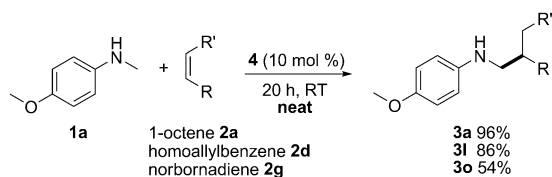
Room-temperature catalysis permits the exploration of temperature-sensitive substrates. To this end, styrenes were reacted with *p*-methoxy-*N*-methylaniline. In contrast to reports using Group 4 catalysts,<sup>[4e,g]</sup> in this case, electron-rich and electron-deficient styrenes are very well tolerated, although prolonged reaction times are required (entries 7–10, **3p–3s**). Here again, performing the reaction at 50°C shortens the required reaction time. When *p*-methoxystyrene is used at 50°C, a trace amount of the linear product can be detected by GC-MS analysis (**3p**, entry 7). While such linear products have been disclosed for Group 4 catalyzed hydroaminoalkylation,<sup>[4]</sup> this is the first example of Group 5 complexes giving both regioisomers with styrene substrates.

Interestingly, the *p*-substituent plays an important role in the branched:linear ratio. Indeed, the amount of linear adduct in **3p-s** increases when a stronger electron-withdrawing group is used, reaching 1.8:1 when a trifluoromethyl group is used (entry 10). It is noteworthy that in the case of the more electron-rich styrenes (entries 7 and 8), room-temperature reactions promote a more selective transformation with only the branched isomer being detected in the case of *p*-methoxystyrene.

As the observed amount of linear adduct in **3p-s** increases when a stronger electron-withdrawing group is used for styrene derivatives, the alkene is hypothesized to evolve transiently charged species. Here, as the substitution of the distal *para*-position with increasingly electron-withdrawing moieties is explored, the generation of such transiently charged species could be destabilized. Thus, modified substrate electronic effects may enable a competitive reaction pathway and varying amounts of linear products can be accessed (Table 3, entries 7–10).

In order to further test such substrate electronic effects, we explored the  $\beta$ -silicon effect.<sup>[16]</sup> A transient positive charge would then be preferentially stabilized at the terminal position, and in this case would provide access to linear amines. Indeed, when vinyltrimethylsilane was used (entry 11), linear product **3t** was found to be the main regioisomer with a branched:linear ratio of 1:7, in 66% overall yield. This selectivity is in sharp contrast to previous reports for Group 5 catalyzed hydroaminoalkylation including vinyltrimethylsilane, where the branched product is obtained virtually exclusively.<sup>[5a,g,17]</sup>

In addition to targeting mild reaction conditions for improving energy efficiency in catalytic transformations, the principles of green chemistry<sup>[18]</sup> promote the elimination of the use of solvent. Indeed, transition metal catalyzed C–H functionalization reactions have recently evolved to include solvent-free reaction protocols.<sup>[5a,19]</sup> In an effort to further challenge this new family of early transition metal *N,O*-chelated catalysts for use in sustainable approaches for selective amine synthesis, complex **4** was tested neat in three representative reactions (Scheme 4). The reactions were



**Scheme 4.** Solvent-free hydroaminoalkylation.

stirred for 20 h at room temperature to provide results that could be directly compared to those listed in Tables 2 and 3. In the case of compounds **3a** and **3l** the yields using the solvent-free conditions were superior to the more traditional catalytic reactions (Table 2, entry 1 and Table 3, entry 3, respectively), while reactivity with norbornadiene afforded product **3o** in comparable yield (Table 3, entry 6). These representative examples show that phosphoramidate complex **4** is suitable for use in solvent-free conditions.

In summary, the first room-temperature catalytic hydroaminoalkylation reactions have been realized through the development of a phosphoramidate–ClTaMe<sub>3</sub> precatalyst (**4**). This easily prepared complex enables the atom-economic synthesis of amines directly from simple amines and alkenes, including challenging substrates such as styrenes and dialkyl amines, and also tolerates the incorporation of functional groups suitable for further synthetic elaboration on both the amine and alkene substrates. Here we disclose the first Group 5 catalytic examples in which significant substrate electronic effects dramatically impact regioselectivity, including the first example of linear regioselectivity using a Ta hydroaminoalkylation precatalyst. Most importantly, this catalyst is amenable to application using solvent-free reaction conditions resulting in improved synthetic efficiency for a variety of substituted amine products. These preliminary results set a new benchmark for advancing sustainable approaches for amine synthesis. On-going work includes kinetic, mechanistic, and catalyst investigations to inform further development efforts. We are working to exploit this new, flexible ligand motif to access robust and efficient catalysts that can be used under solvent-free conditions to realize regio- and enantioselective transformations with a broad substrate scope.

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- [1] R. N. Salvatore, C. H. Yon, K. W. Jung, *Tetrahedron* **2001**, 57, 7785.
- [2] P. W. Roesky, *Angew. Chem.* **2009**, 121, 4988; *Angew. Chem. Int. Ed.* **2009**, 48, 4892.
- [3] a) M. G. Clerici, F. Maspero, *Synthesis* **1980**, 305; b) W. A. Nugent, D. W. Ovenall, S. J. Holmes, *Organometallics* **1983**, 2, 161.
- [4] Group 4 metals: a) J. A. Bexrud, P. Eisenberger, D. C. Leitch, P. R. Payne, L. L. Schafer, *J. Am. Chem. Soc.* **2009**, 131, 2116; b) R. Kubiak, I. Prochnow, S. Doye, *Angew. Chem.* **2009**, 121, 1173; *Angew. Chem. Int. Ed.* **2009**, 48, 1153; c) I. Prochnow, R. Kubiak, O. N. Frey, R. Beckhaus, S. Doye, *ChemCatChem* **2009**, 1, 162; d) R. Kubiak, I. Prochnow, S. Doye, *Angew. Chem.* **2010**, 122, 2683; *Angew. Chem. Int. Ed.* **2010**, 49, 2626; e) I. Prochnow, P. Zark, T. Müller, S. Doye, *Angew. Chem.* **2011**, 123, 6525; *Angew. Chem. Int. Ed.* **2011**, 50, 6401; f) D. Jaspers, W. Saak, S. Doye, *Synlett* **2012**, 2098; g) J. Dörfler, S. Doye, *Angew. Chem.* **2013**, 125, 1851; *Angew. Chem. Int. Ed.* **2013**, 52, 1806; h) T. Preuß, W. Saak, S. Doye, *Chem. Eur. J.* **2013**, 19, 3833.
- [5] Groups 5 metals: a) S. B. Herzon, J. F. Hartwig, *J. Am. Chem. Soc.* **2007**, 129, 6690; b) S. B. Herzon, J. F. Hartwig, *J. Am. Chem. Soc.* **2008**, 130, 14940; c) P. Eisenberger, R. O. Ayinla, J. M. P. Lauzon, L. L. Schafer, *Angew. Chem.* **2009**, 121, 8511; *Angew. Chem. Int. Ed.* **2009**, 48, 8361; d) G. Zi, F. Zhang, H. Song, *Chem. Commun.* **2010**, 46, 6296; e) F. Zhang, H. Song, G. Zi, *Dalton Trans.* **2011**, 40, 1547; f) A. L. Reznichenko, T. J. Emge, S. Audörsh, E. G. Klauber, K. C. Hultsch, B. Schmidt, *Organometallics* **2011**, 30, 921; g) A. L. Reznichenko, K. C. Hultsch, *J. Am. Chem. Soc.* **2012**, 134, 3300; h) P. R. Payne, P. Garcia, P. Eisenberger, J. C.-H. Yim, L. L. Schafer, *Org. Lett.* **2013**, 15, 2182; i) P. Garcia, P. R. Payne, E. Chong, R. L. Webster, B. J.

- Barron, A. C. Behrle, J. A. R. Smith, L. L. Schafer, *Tetrahedron* **2013**, 69, 5737; j) Z. Zhang, J. D. Hamel, L. L. Schafer, *Chem. Eur. J.* **2013**, 19, 8751.
- [6] Ruthenium: a) C.-H. Jun, D.-C. Hwang, S.-J. Na, *Chem. Commun.* **1998**, 1405; b) N. Chatani, T. Asaumi, S. Yorimitsu, T. Ikeda, F. Kakiuchi, S. Murai, *J. Am. Chem. Soc.* **2001**, 123, 10935; c) S. D. Bergman, T. E. Storr, H. Prokopcová, K. Aelvoet, G. Diels, L. Meerpoel, B. U. W. Maes, *Chem. Eur. J.* **2012**, 18, 10393. Iridium: d) S. Pan, K. Endo, T. Shibata, *Org. Lett.* **2011**, 13, 4692.
- [7] L. Shi, W. Xia, *Chem. Soc. Rev.* **2012**, 41, 7687.
- [8] The strength of the electron-withdrawing property was correlated from the  $pK_a$  of the conjugate acid. See: F. G. Bordwell, *Acc. Chem. Res.* **1988**, 21, 456.
- [9] Examples of single-step preparations of phosphoramidates: a) R. Serwa, I. Wilkening, G. Del Signore, M. Mühlberg, I. Claußnitzer, C. Weise, M. Gerrits, C. P. R. Hackenberger, *Angew. Chem.* **2009**, 121, 8382; *Angew. Chem. Int. Ed.* **2009**, 48, 8234; b) R. Haggam, J. Conrad, U. Beifuss, *Tetrahedron Lett.* **2009**, 50, 6627.
- [10] CCDC 932203 (**4**) and 932204 (**L<sup>2</sup>-H**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).
- [11] *o*-Substituted *N*-methyl anilines were not tolerated.
- [12] F. Marchetti, G. Pampaloni, S. Zacchini, *Eur. J. Inorg. Chem.* **2010**, 767.
- [13] No dialkylation product has been observed. When using 3 equivalents of alkene, a mixture of mono- and dialkylated product is obtained.
- [14] At temperatures higher than 50 °C, lower conversion is observed, indicating the thermal sensitivity of this catalyst system.
- [15] See the Supporting Information for further details.
- [16] See a) A. Karnezis, R. A. J. O'Hair, J. M. White, *Organometallics* **2009**, 28, 4276; b) X. Creary, E. D. Kochly, *J. Org. Chem.* **2009**, 74, 2134, and references therein.
- [17] No significant variations were observed when the reaction was run at higher or lower temperatures (4 °C and 50 °C).
- [18] P. Anastas, N. Eghbali, *Chem. Soc. Rev.* **2010**, 39, 301.
- [19] a) Z. Shi, C. He, *J. Org. Chem.* **2004**, 69, 3669; b) R. B. Bedford, C. J. Mitchell, R. L. Webster, *Chem. Commun.* **2010**, 46, 3095; c) S. Bensaid, H. Doucet, *ChemSusChem* **2012**, 5, 1559, and references therein.