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A novel method for the reduction of alkenes using the system silane/oxo-rhenium complexes

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ABSTRACT

In this work, we report the first practical application of high-valent oxo-complexes for the reduction of alkenes to the corresponding alkanes. The catalytic system $Ph(Me)_2SiH/ReIO_2(PPh_3)_2$ (5 mol %) proved to be very efficient for the reduction of mono- and disubstituted alkenes under solvent-free conditions.

The reduction of alkenes is a fundamental reaction in organic synthesis. The most commonly used method for reducing C–C double bonds involves homogeneous or heterogeneous catalytic hydrogenation.[1] However, it requires the handling of the highly flammable hydrogen gas and pressurized conditions. As an alternative, catalytic hydrogen transfer methods that make use of solvents such as amines, alcohols and water as the hydrogen source have been widely employed for the reduction of alkenes.[2]

The reagent systems $NaBH_4/Pd/C$,[3] $NaBH_4/RuCl_3$,[4] $NaBH_4/Ru(PPh_3)_4H_2$[5] and $NaBH_4/InCl_3$[6] can also be used as reducing agents, but functional group compatibility of metal hydride reagents often becomes a problem.

Organosilanes are mild and environmentally benign reagents, which have applications in many kinds of reactions. However, they are known to be poor reducing agents, due to their low capacity to donate hydrogen atoms or hydrides. To overcome this limitation, a variety of modified silanes with weaker Si–H bonds and composite reducing systems based on a combination of a silane/transition-metal catalyst have been developed.[7]

Recently, Toste reported the first example of Si–H bond activation by a high-valent oxo-complex.[8] The novel catalytic system $silane/ReIO_2(PPh_3)_2$ proved to be very efficient for the hydrosilylation of aldehydes and ketones. We extended this result to the activation of Si–H bond and B–H bond by other oxo-rhenium complexes and oxo-molybdenum complexes. We also described the efficient hydrosilylation of aldehydes and ketones[9] and the reduction of several functional groups such as aromatic nitro compounds,[10] imines,[11] amides,[12] esters,[13] sulfoxides[14] and pyridine N-oxides[14a] with the catalytic system silane/oxo-complexes or borane/oxo-complexes. Royo and co-workers[15] reported the use of high-valent oxo-molybdenum and -rhenium complexes as catalysts for the hydrogenation of alkynes to the corresponding alkenes. However, these catalytic systems were inefficient for the reduction of alkenes.

It is known that the catalytic addition of silanes to alkenes usually gives alkylsilicon derivatives. Various complexes of transition metals have been used as effective catalysts for this reaction, including Rh, Ru and Ir.[16] Alkenes can also be reduced by silanes to the corresponding alkanes in the presence of Pd/C,[17] $PdCl_2$[17b] or $Pd(OAc)_2$.[18] The system silane/Pd/C proved to be efficient for the reduction of mono- and disubstituted alkenes, but the system $silane/PdCl_2$ or $silane/Pd(OAc)_2$ only reduces terminal double bonds.

During our previous work about the deoxygenation of aromatic nitro compounds with the catalytic system $PhMe_2SiH/ReIO_2(PPh_3)_2$ (5 mol %), we observed the reduction of the double bond in the substrates *m*-nitrostyrene and ethyl *p*-nitrocinnamate (see Eqs. 1 and 2).[10] These results suggested that the system silane/oxo-rhenium complexes could be appropriate for the reduction of alkenes. To the best of our knowledge, this is the first example of the reduction of a double bond catalyzed by high-valent oxo-complexes.

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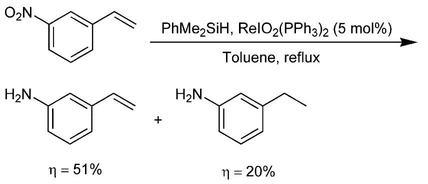
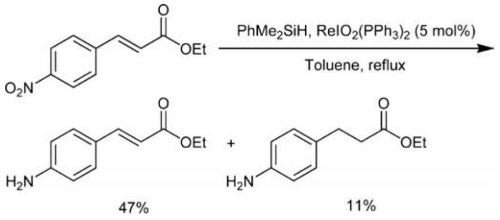


(1)



(2)

In this work, we investigated the reduction of alkenes with silanes catalyzed by high-valent oxo-rhenium complexes. Initially, we studied the reduction of the test substrate 4-chlorostyrene catalyzed by high-valent oxo-rhenium complexes $ReIO_2(PPh_3)_2$, $ReOCl_3(PPh_3)_2$, $ReOCl_3$(dppm), Re_2O_7 and MTO, with different silanes and using several solvents, in order to assess the best reaction conditions (Tables 1–3). The progress of the reactions was monitored by thin layer chromatography and by ^{1}H NMR.

The reduction of 4-chlorostyrene with different catalysts was carried out with $Ph(Me)_2SiH$ in the absence of solvent, at 45 °C under air atmosphere. Among the oxo-rhenium complexes tested, $ReIO_2(PPh_3)_2$ proved to be the most efficient (Table 1, entry 1), reducing the 4-chlorostyrene with 100% conversion after 20 h, using 5 mol % of this catalyst. At room temperature, similar reduction afforded the alkane in only 66% conversion (Table 1, entry 2). A decrease in the catalyst loading to 2.5 mol % resulted in a moderate conversion of the alkane (Table 1, entry 3). In the presence of $ReOCl_3(PPh_3)_2$, Re_2O_7 and MTO, the expected product was obtained in 41–50% conversions (Table 1, entries 4–6). In contrast, the oxo-rhenium complex $ReCl_3O$(dppm) was ineffective for this reduction, producing the alkane in very low conversion after 17 h (Table 1, entry 7). Finally, no reaction was observed in the absence of catalyst (Table 1, entry 8).

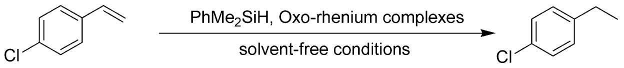
The reduction of 4-chlorostyrene was studied with the silanes dimethylphenylsilane, phenylsilane, triethylsilane, triphenylsilane and polymethylhydrosiloxane (PMHS) in the presence of 5 mol % of $ReIO_2(PPh_3)_2$ under air atmosphere. We observed that by using only 200 mol % of dimethylphenylsilane, the reaction was incomplete (Table 2, entry 1). However, the product was obtained in 100% conversion, starting the reaction with 200 mol % of silane and adding more 200 mol % after 2 h (Table 2, entry 2). In contrast, the reductions carried out with PMHS, triethylsilane, phenylsilane and triphenylsilane gave the product in moderate to low conversions (Table 2, entries 3–6).

This novel methodology was also explored in different solvents and under solvent-free conditions. Among the solvents tested, ether proved to be the best, affording the product in 100% conversion after 41 h at refluxing temperature (Table 3, entry 1). At room temperature, the corresponding alkane was obtained in only 35% conversion (Table 3, entry 2). Toluene, dichloromethane, ethanol or acetonitrile led to moderate or low conversions (Table 3, entries 3–6). However, the best result was obtained under solvent-free conditions affording the product in 100% conversion after 20 h (Table 3, entry 7). At room temperature, similar reduction gave the alkane in only 67% conversion (Table 3, entry 8).

In order to study the scope and the limitations of this novel methodology, we tested the catalytic system $Ph(Me)_2SiH/ReIO_2(PPh_3)_2$ (5 mol %) with several alkenes under solvent-free conditions at 45 °C.[19] Initially, we explored the reduction of styrene and a series of 4-substituted styrenes. The reduction of 4-bromostyrene

Table 1

Reduction of 4-chlorostyrene with dimethylphenylsilane catalyzed by high-valent oxo-rhenium complexes[a]



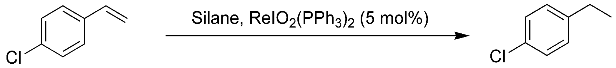
Entry	Catalyst	(mol %)	Temperature (°C)	Time (h)	Conversion[b] (%)
1	$ReIO_2(PPh_3)_2$	5	45	20	100
2	$ReIO_2(PPh_3)_2$	5	rt	20	66
3	$ReIO_2(PPh_3)_2$	2.5	45	24	45
4	$ReOCl_3(PPh_3)_2$	5	45	17	41
5	Re_2O_7	5	45	24	48
6	MTO	5	45	24	50
7	$ReOCl_3$(dppm)	5	45	17	3
8	Without catalyst	—	45	24	No reaction

[a] All reactions were carried out with 1.0 mmol of alkene and 400 mol % of silane.

[b] Conversion was determined by ^{1}H NMR.

Table 2

Reduction of 4-chlorostyrene with different silanes catalyzed by $ReIO_2(PPh_3)_2$[a]

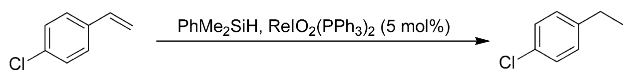


Entry	Silane	Silane (mol %)	Solvent	Temperature (°C)	Time (h)	Conversion[b] (%)
1	$PhMe_2SiH$	200	Neat	45	20	31
2	$PhMe_2SiH$	400	Neat	45	20	100
3	PMHS	400	Neat	45	27	52
4	Et_3SiH	400	Neat	45	10	37
5	$PhSiH_3$	200	Ether	Reflux	24	10
6	Ph_3SiH	400	Ether	Reflux	24	12

[a] All reactions were carried out with 1.0 mmol of alkene and 5 mol % of $ReIO_2(PPh_3)_2$.

[b] Conversion was determined by ^{1}H NMR.

Table 3
Reduction of 4-chlorostyrene in different solvents[a]



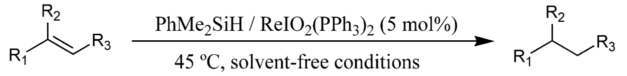
Entry	Solvent	Temperature (°C)	Time (h)	Conversion[b] (%)
1	Ether	Reflux	41	100
2	Ether	rt	42	35
3	Toluene	Reflux	22	40
4	CH_2Cl_2	Reflux	18	18
5	EtOH	Reflux	24	16
6	CH_3CN	Reflux	20	5
7	Neat	45	20	100
8	Neat	rt	20	67

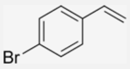
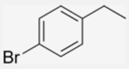
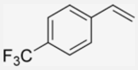
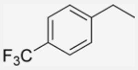
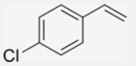
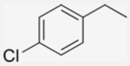
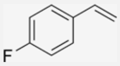
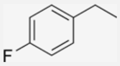
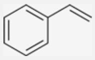
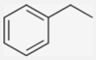
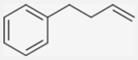
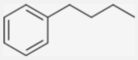
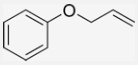
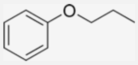
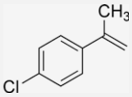
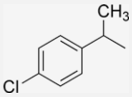
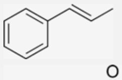
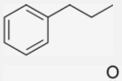
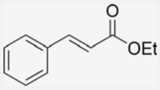
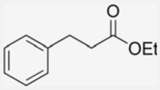
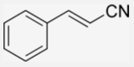
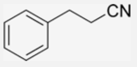
[a] All reactions were carried out with 1.0 mmol of alkene, 400 mol % of silane and 5 mol % of ReIO$_2$(PPh$_3$)$_2$.
[b] Conversion was determined by ^{1}H NMR.

and 4-(trifluoromethyl)styrene was very fast, affording the products in only 2 h with 100% yield (Table 4, entries 1 and 2). The 4-chloro and 4-fluorostyrenes were also completely reduced, but required 20 h (Table 4, entries 3 and 4). Of particular importance is the tolerance of halo substituents on the aromatic ring observed under our catalytic conditions. Finally, the reaction of styrene gave the ethylbenzene in 98% yield (Table 4, entry 5).

The reductions of the monosubstituted terminal olefins 3-butenylbenzene and (allyloxyl)benzene were also investigated under our catalytic conditions. The olefin 3-butenylbenzene was completely reduced, but the (allyloxyl)benzene afforded the propoxybenzene in only 50% yield (Table 4, entries 6 and 7).

Table 4
Reduction of alkenes with the system PhMe$_2$SiH/ReIO$_2$(PPh$_3$)$_2$[a]



Entry	Substrate	Product	Time (h)	Yield[b] (%)
1			2	100
2			2	100
3			20	100
4			20	100
5			26	98
6			20	100
7			20	50
8			16	81
9			45	88
10			24	80
11			45	22

[a] All the reactions were carried out with 2.0 mmol of alkene, 400 mol % of silane and 5 mol % of ReIO$_2$(PPh$_3$)$_2$.
[b] The yields were determined by NMR using toluene (2.0 mmol) as an internal standard.

The catalytic system Ph(Me)$_2$SiH/ReIO$_2$(PPh$_3$)$_2$ (5 mol %) was also successfully applied to the reduction of disubstituted alkenes. From the reactions of 1-chloro-4-isopropenylbenzene and (1*E*)-1-propenylbenzene were obtained the 1-chloro-4-isopropylbenzene in 81% yield (Table 4, entry 8) and the propylbenzene in 88% yield (Table 4, entry 9), respectively.

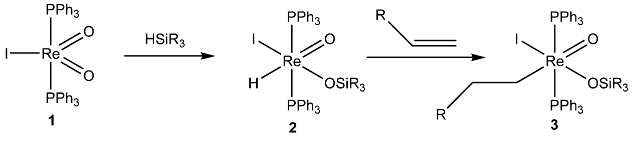
The alkenes ethyl (2*E*)-3-phenyl-2-propenoate and (2*E*)-3-phenyl-2-propenenitrile were also reduced under our catalytic conditions, giving the corresponding ethyl 3-phenylpropanoate and 3-phenylpropanenitrile in 80% and 22%, respectively (Table 4, entries 10 and 11). These results showed the chemoselective reduction of the double bonds in the presence of ester and cyano groups.

The results presented above clearly demonstrate the capacity of the Ph(Me)$_2$SiH/ReIO$_2$(PPh$_3$)$_2$ system to catalyze the hydrogenation of a variety of alkenes.

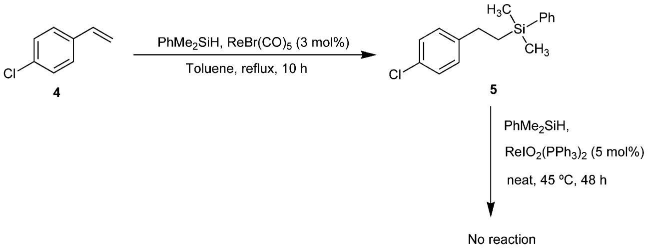
In contrast to the simplicity of the reaction, devising the corresponding mechanism is not a straightforward matter. In fact, the known reactivity of ReIO$_2$(PPh$_3$)$_2$ (**1**) has been probed both experimentally and computationally and seems to take place by the addition of the Si–H bond across the Re=O bond to form **2** (see Scheme 1)[8a,b,20] According to published work on oxo-hydride complexes like Tp*Re(O)H(OTf) and [Re(O)H$_2$(P3)] + (P3 = PhP{CH$_2$CH$_2$CH$_2$PCy$_2$}$_2$), the oxo-hydride complex **2** is quite likely to react with an olefin by insertion of the double bond in the Re–H bond forming the Re-alkyl complex **3** (see Scheme 1).[21] This intermediate could evolve by reverting to **1** and an alkylsilane, RCH$_2$CH$_2$SiR$_3$, which would then be reduced to the alkane. In many cases, alkene hydrosilylation is accompanied by alkene hydrogenation.[16e] We, therefore, decided to check whether our catalytic system was able to hydrogenate alkylsilanes to alkanes.

Thus, we prepared the alkylsilane derivative **5** reacting 4-chlorostyrene with dimethylphenylsilane in the presence of a catalytic amount of ReBr(CO)$_5$[16d] (see Scheme 2). The reduction of this compound was attempted with the catalytic system Ph(Me)$_2$SiH/ReIO$_2$(PPh$_3$)$_2$ (5 mol %) at 45 °C under solvent-free conditions. However, no reaction was observed. This result shows that alkylsilane **5** is not an intermediate in the hydrogenation of alkenes under our catalytic conditions.

Since Abu-Omar and co-workers[22] reported the formation of hydrogen by hydrolytic oxidation of silanes catalyzed by a cationic oxo-rhenium complex, raising the possibility that in our system



Scheme 1. Reaction of alkenes with the hydride (PPh$_3$)$_2$(O)IRe(H)OSiR$_3$.



Scheme 2. Synthesis of the alkylsilane **5**.

dihydrogen was being produced and immediately consumed in the hydrogenation of the alkene. However, the same author observed that $ReIO_2(PPh_3)_2$, $ReOCl_3(PPh_3)_2$ and MTO did not catalyze the production of hydrogen from silanes ruling out this possibility for our system.

It is clear that further studies are needed in order to gain a better understanding of the mechanism, mainly by identifying the fate of the R_3Si groups as well as by attempting to identify other Re containing intermediates or side products.

In conclusion, we have developed, to the best of our knowledge, the first example of the practical, catalytic hydrogenation of alkenes to the corresponding alkanes by molecular high-valent oxo-rhenium (V) and (VII) complexes and a silane. This novel methodology was successfully applied to the reduction of mono- and disubstituted olefins, in contrast to the method using silanes catalyzed by $PdCl_2$ or $Pd(OAc)_2$, which only reduced monosubstituted terminal double bonds.[17b,18]

An important benefit of this method is that the reduction is done in the absence of hydrogen gas and high pressures. This novel method can be carried out in simple, readily available laboratory equipment, in contrast to catalytic hydrogenation, which demands handling of hydrogen gas and often requires rather expensive high-pressure equipment.

Other advantages of this methodology include high yields, good chemoselectivity, mild conditions, easy preparation of the catalyst[8a] and its stability towards air and moisture, allowing the reaction to be carried out under air atmosphere. We believe that this procedure will be a useful and attractive alternative to the existing methods for the reduction of alkenes.

Further mechanistic studies and other synthetic applications of this catalytic system, including asymmetric hydrogenation of alkenes are under investigation in our group.

Acknowledgements

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References and notes

1. (a) Church, T. L.; Andersson, P. G. *Coord. Chem. Rev.* **2008**, *252*, 513–531; (b) Roseblade, S. J.; Pfaltz, A. *Acc. Chem. Res.* **2007**, *40*, 1402–1411; (c) Cui, X.; Burgess, K. *Chem. Rev.* **2005**, *105*, 3272–3296; (d) Nakao, R.; Rhee, H.; Uozumi, Y. *Org. Lett.* **2005**, *7*, 163–165; (e) Jurvilliers, X.; Schneider, R.; Fort, Y.; Ghanbaja, J. *Appl. Organometal. Chem.* **2003**, *17*, 161–167; (f) Genet, J.-P. *Acc. Chem. Res.* **2003**, *36*, 908–918.
2. (a) Gaviglio, C.; Doctorovich, F. *J. Org. Chem.* **2008**, *73*, 5379–5384; (b) Sato, T.; Watanable, S.; Kiuchi, H.; Oi, S.; Inoue, Y. *Tetrahedron Lett.* **2006**, *47*, 7703–7705; (c) Moisan, L.; Hardouin, C.; Rousseau, B.; Doris, E. *Tetrahedron Lett.* **2002**, *43*, 2013–2015; (d) Sakaguchi, S.; Yamaga, T.; Ishii, Y. *J. Org. Chem.* **2001**, *66*, 4710–4712.
3. Tran, A.; Huynh, V.; Friz, E. M.; Whitney, S. K.; Cordes, D. B. *Tetrahedron Lett.* **2009**, *50*, 1817–1819.
4. Sharma, P. K.; Kumar, S.; Kumar, P.; Nielsen, P. *Tetrahedron Lett.* **2007**, *48*, 8704–8708.
5. Adair, G. R. A.; Kapoor, K. K.; Scolan, A. L. B.; Williams, J. M. J. *Tetrahedron Lett.* **2006**, *47*, 8943–8944.
6. (a) Ranu, B. C.; Samanta, S. *Tetrahedron* **2003**, *59*, 7901–7906; (b) Ranu, B. C.; Samanta, S. *J. Org. Chem.* **2003**, *68*, 7130–7132.
7. (a) Yang, J.; Brookhart, M. *Adv. Synth. Catal.* **2009**, *351*, 175–187; (b) Lee, O.-Y.; Law, K.-L.; Ho, C.-Y.; Yang, D. *J. Org. Chem.* **2008**, *73*, 8829–8837; (c) Rahaim, R. J.; Maleczka, R. E. *Org. Lett.* **2005**, *7*, 5087–5090; (d) Lipshutz, B. H.; Chrisman, W.; Noson, K. *J. Organomet. Chem.* **2001**, *624*, 367–371; (e) Ohta, T.; Kamiya, M.; Kusui, K.; Michibata, T.; Nobutomo, M.; Furukawa, I. *Tetrahedron Lett.* **1999**, *40*, 6963–6966.
8. (a) Kennedy-Smith, J. J.; Nolin, K. A.; Gunterman, H. P.; Toste, F. D. *J. Am. Chem. Soc.* **2003**, *125*, 4056–4057; (b) Nolin, K. A.; Krumper, J. R.; Puth, M. D.; Bergman, R. G.; Toste, F. D. *J. Am. Chem. Soc.* **2007**, *129*, 14684–14696.
9. (a) Fernandes, A. C.; Fernandes, R.; Romão, C. C.; Royo, B. *Chem. Commun.* **2005**, 213–214; (b) Costa, P. J.; Romão, C. C.; Fernandes, A. C.; Royo, B.; Reis, P. M.; Calhorda, M. J. *Chem. Eur. J.* **2007**, *13*, 3934–3941.
10. Noronha, R. G.; Romão, C. C.; Fernandes, A. C. *J. Org. Chem.* **2009**, *74*, 6960–6964.
11. Fernandes, A. C.; Romão, C. C. *Tetrahedron Lett.* **2005**, *46*, 8881–8883.
12. Fernandes, A. C.; Romão, C. C. *J. Mol. Catal A: Chem.* **2007**, *272*, 60–63.
13. Fernandes, A. C.; Romão, C. C. *J. Mol. Catal A: Chem.* **2006**, *253*, 96–98.
14. (a) Fernandes, A. C.; Romão, C. C. *Tetrahedron* **2006**, *62*, 9650–9654; (b) Fernandes, A. C.; Romão, C. C. *Tetrahedron Lett.* **2007**, *48*, 9176–9179; (c) Sousa, S. C. A.; Fernandes, A. C. *Tetrahedron Lett.* **2009**, *50*, 6872–6876; (d) Fernandes, A. C.; Fernandes, J. A.; Almeida Paz, F. A.; Romão, C. C. *Dalton Trans.* **2008**, 6686–6688.
15. Reis, P. M.; Costa, P. J.; Romão, C. C.; Fernandes, J. A.; Calhorda, M. J.; Royo, B. *Dalton Trans.* **2008**, 1727–1733.
16. (a) Ge, S.; Meetsma, A.; Hessen, B. *Organometallics* **2008**, *27*, 3131–3135; (b) Konkol, M.; Kondracka, M.; Voth, P.; Voth, P.; Spaniol, T. P.; Okuda, J. *Organometallics* **2008**, *27*, 3774–3784; (c) Buch, F.; Brettar, J.; Harder, S. *Angew. Chem., Int. Ed.* **2006**, *45*, 2741–2745; (d) Zhao, W.-G.; Hua, R. *Eur. J. Org. Chem.* **2006**, 5495–5498; (e) Marciniec, B. *Coord. Chem. Rev.* **2005**, *249*, 2374–2390; (f) Horino, Y.; Livinghouse, T. *Organometallics* **2004**, *23*, 12–14; (g) Glaser, P. B.; Tilley, T. D. *J. Am. Chem Soc.* **2003**, *125*, 13640–13641.
17. (a) Mandal, P. K.; McMurray, J. S. *J. Org. Chem.* **2007**, *72*, 6599–6601; (b) Mirza-Aghayan, M.; Boukherroub, R.; Bolourtchian, M. *Appl. Organomet. Chem.* **2006**, *20*, 214–219.
18. Mirza-Aghayan, M.; Boukherroub, R.; Bolourtchian, M.; Hossein, M. *Tetrahedron Lett.* **2003**, *44*, 4579–4580.
19. In a typical experiment, to a mixture of alkene (2.0 mmol) and catalyst (5 mol %) was added dimethylphenylsilane (200 mol %). The reaction mixture was stirred at 45 °C under air atmosphere. After 2 h was added more silane (200 mol %). The progress of the reactions was monitored by ^1H NMR. The NMR yields were determined using toluene (2.0 mmol) as an internal standard.
20. Chung, L. W.; Lee, H. G.; Lin, Z. Y.; Wu, Y. D. *J. Org. Chem.* **2006**, *71*, 6000–6009.
21. (a) Matano, Y.; Brown, S. N.; Northcutt, T. O.; Mayer, J. M. *Organometallics* **1998**, *17*, 2939–2941; (b) Matano, Y.; Northcutt, T. O.; Brugman, J.; Bennett, B. K.; Lovell, S.; Mayer, J. M. *Organometallics* **2000**, *19*, 2781–2790; (c) Kim, Y.; Rende, D. E.; Gallucci, J. C.; Wojcicki, A. *J. Organomet. Chem.* **2003**, *682*, 85–101.
22. Ison, E. A.; Corbin, R. A.; Abu-Omar, M. M. *J. Am. Chem. Soc.* **2005**, *127*, 11938–11939.