CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200903144

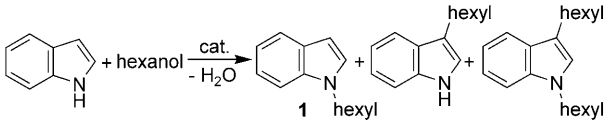
VIP

Selective Ruthenium-Catalyzed N-Alkylation of Indoles by Using Alcohols

Sebastian Bähn,[a] Sebastian Imm,[a] Kathleen Mevius,[a] Lorenz Neubert,[a] Annegret Tillack,[a] Jonathan M. J. Williams,*[b] and Matthias Beller*[a]

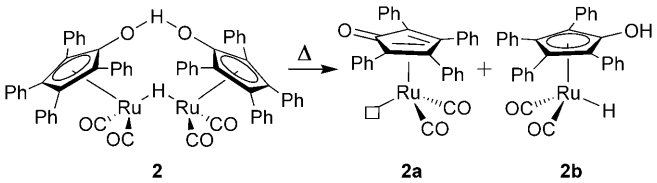
Indoles constitute important heterocyclic systems in nature. Based on the broad structural diversity and due to their biological activity, indoles have become an important component in several current pharmaceutical drugs.[1] Hence, the development of improved synthetic methodologies for the generation of the indole core, as well as functionalization reactions on the aromatic ring system continue to be of significant interest to organic chemists.[2] Among the numerous known bioactive indoles, various N-alkylated derivatives are known.[3] The classical approach for the introduction of these alkyl chains involves treatment of the indole with base and an alkyl halide.[4] A drawback of these reactions is the quantitative formation of waste salts. Clearly, this disadvantage can be overcome by using easily available alcohols as a more benign alkyl source. However, so far, the N-alkylation of indoles with alcohols has only been investigated in the presence of Raney nickel.[5] More recently, Grigg and co-workers[6] demonstrated that simple alcohols can be used for selective C-3-alkylation of indoles. This reaction is based on the so-called "borrowing hydrogen" methodology.[7] Thereby, an alcohol or amine is initially dehydrogenated, then undergoes a functionalization reaction, and finally is rehydrogenated. Applications of this elegant methodology have been developed by the groups of Yus,[8] Fujita,[9] Grigg,[10] Kempe,[11] and us.[12,13]

Based on our ongoing interest in the synthesis of novel indoles[14] and the activation of alcohols,[15] we became interested in the selective N-alkylation of this important class of natural products. At the start of our investigations we studied the reaction of indole with hexanol as a model system. In general, this alkylation might result in N-, C-, and dialkylated products (Scheme 1).



Scheme 1. Possible alkylations of indole by using hexanol.

An initial catalyst screening of the model reaction revealed that the Shvo catalyst[16,17] **2** (Scheme 2) provided the best activity and selectivity, whereas all other tested systems,



Scheme 2. Dissociation of the Shvo complex.

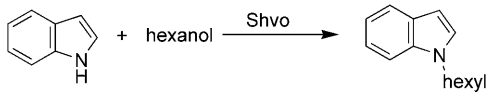
including [{Ru(*p*-cymene)Cl_2}$_2$]/dppf,[18] [Ru(PPh_3)$_3$(CO)H_2]/Xantphos,[19] [Ru_3(CO)$_{12}$]/CataCXiumPCy,[20] and [{Cp*IrI_2}$_2$],[21] gave unsatisfactory results (dppf = 1,1′-bis(diphenylphosphanyl)ferrocene, Xantphos = 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene, CataCXiumPCy = 2-(dicyclohexylphosphino)-1-phenyl-1*H*-pyrrole, Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl; yield: <15%, selectivity: <40%). Therefore, we optimized the reaction conditions employing **2** (Table 1). By using a small excess of hexanol and toluene as the solvent at 110°C in the presence of **2** (0.5 mol%) we obtained good conversion (85%) and yield (77%) of *N*-hexylindole (Table 1, entry 1). The conversion

[a] S. Bähn, S. Imm, K. Mevius, L. Neubert, Dr. A. Tillack, Prof. Dr. M. Beller
Leibniz-Institut für Katalyse an der Universität Rostock e.V.
Albert-Einstein-Str. 29a, 18059 Rostock (Germany)
Fax: (+49) 381-1281-51113
E-mail: matthias.beller@catalysis.de

[b] Prof. Dr. J. M. J. Williams
Department of Chemistry, University of Bath
Claverton Down, Bath, BA2 7AY (UK)
Fax: (+44) 1225-383-942
E-mail: j.m.j.williams@bath.ac.uk

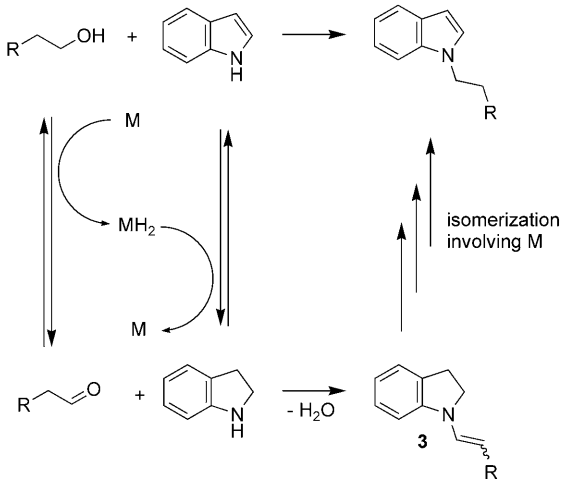
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200903144.

Table 1. N-Alkylation of indole with hexanol.[a]



Entry	Alcohol/ indole	Shvo [%]	PTSA [%]	Solvent	Conv.[b] [%]	Yield[b] [%]
1	1.2	0.5	–	toluene	85	77
2	1.2	0.5	2	toluene	99	45
3	1.1	0.2	0.1	toluene	99	69
4	1.1	0.2	0.025	toluene	99	85
5	1.1	0.2	0.001	toluene	95	81
6[c]	1.1	0.2	0.025	toluene	93	79
7	1.1	0.2	0.025	heptane	99	82
8	1.1	0.2	0.025	*t*-amyl alcohol	90	72

[a] Reaction conditions: indole (1 mmol), solvent (0.5 mL), 24 h. [b] Conversion and yield are determined by GC analysis with hexadecane as the internal standard; conversion and yield are based on the indole. [c] 18 h.



Scheme 3. Possible mechanism for the N-alkylation of indoles with alcohols.

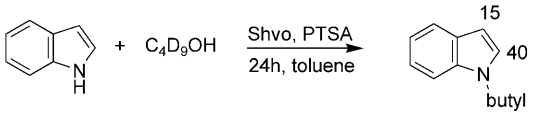
is increased further by adding *p*-toluenesulfonic acid (PTSA; Table 1, entries 2–5). However, by using 2 mol% of PTSA the selectivity of the reaction dropped considerably. To our delight, lowering the amount of PTSA to 0.025 mol% (Table 1, entry 4) in the presence of only 0.2 mol% catalyst still resulted in quantitative conversion and an excellent product yield of 85%. Further reduction of the amount of PTSA (Table 1, entry 5) as well as a reduction of the reaction time resulted in a decrease of the conversion. Variation of the solvent (Table 1, entries 7 and 8) revealed that heptane can be used too, whereas *tert*-amyl alcohol reduced the reactivity of the system.

In addition to the desired transformation, small amounts of C-3-alkylation and dialkylation of indole, as well as the formation of hexyl hexanoate are observed as side reactions (<5%).

Considering the previous work of Grigg and co-workers,[6] who performed their reactions in the presence of KOH (20 mol%), our selective N-alkylation is rather remarkable. The difference in pH seems to be the main reason for the altered regioselectivity. Apparently, the typical "borrowing hydrogen"[7] mechanism, in which hexanol is oxidized by the catalyst to give hexanal, which is attacked by indole, cannot be applied here. Indeed, direct reaction of hexanal with indole gave a mixture of N-, C-, and disubstituted indoles, but only a small amount of the N-substituted product.

Careful analysis of the side products revealed the possibility of another reaction mechanism. In addition to the N-alkylated product the formation of around 3% *N*-hexyl-2,3-dihydroindole is observed under the optimized conditions. Evidently, this product requires hydrogenation of the indole ring under the reaction conditions. As shown in Scheme 3, we propose an initial transfer hydrogenation from the alcohol to the indole to give the corresponding aldehyde and indoline. Subsequent condensation and final isomerization leads to the N-alkylated product. To the best of our knowledge, transfer hydrogenations of indoles to indolines have not been reported before. To support this novel mechanism we performed the reaction of indoline and hexanal under the optimized conditions (Table 1, entry 4). In fact, *N*-hexylindole is formed in 72% yield. When the experiment was repeated without catalyst, no product was formed, but the enamine **3** was obtained as the major product. This shows the necessity of the catalyst in the final isomerization step.

The groups of Bäckvall[22] and Casey[23] demonstrated that transfer-hydrogenation processes in the presence of **2** proceed through a monohydride mechanism. This implies that the deuterium removed from the electron-deficient α carbon of the butanol should be transferred to the electron deficient C-2-position of indole. The isomerization step should lead to an H:D ratio of 50/50 in the C-2-position. In agreement with our mechanistic proposal, the resulting *N*-butylindole contained 40% deuterium in the C-2-position (Scheme 4).[24] The discrepancy of 10%, as well as 15% deuterium incorporation at the C-3-position can be explained by H/D exchange reactions between water and the Shvo monomer **2b** (Scheme 2). In addition, hydrogen incorporation into the formerly completely deuterated butyl chain was observed. The increase in reactivity by the addition of PTSA can also be explained by the proposed mechanism. Here, we presume that protonation at the C-3-position of indole speeds up the indoline formation. Yet the question remains open as to whether the 2,3-double bond is hydrogenated directly or if subsequent formation of a 1,2-double bond occurs.

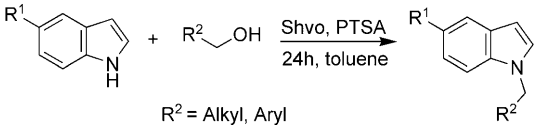


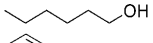
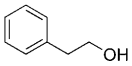
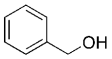
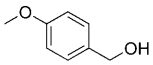
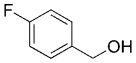
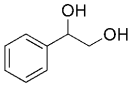
Scheme 4. Deuterium incorporation (%) during the alkylation reaction.

Next, we investigated the scope and limitation of our catalytic system. For this purpose, we studied the reaction of indole and 5-methoxyindole with different alcohols

(Table 2). We were pleased to find that indole was N-alkylated with different aliphatic alcohols selectively and in very good yields (Table 2, entries 1–5). Reaction of benzyl alcohol with indole resulted in a mixture of the N- and C-alkylated product. However, 5-methoxyindole is selectively N-alkylated with electron-rich, as well as electron-deficient benzylic alcohols (Table 2, entries 6–8). Clearly, by using benzylic alcohols, the enamine **3** (Scheme 3) cannot be formed. Thus, we assume that the alkylation proceeds via an iminium ion intermediate, which is more stabilized by the electron-rich 5-methoxyindole than by indole. To our delight, the N-alkylation of indole with phenyl-1,2-ethandiol also takes place with excellent selectivity (Table 2, entry 10). Thereby, the primary hydroxyl group of the diol is converted and the desired product is obtained in high yield. This reaction constitutes the first example of a selective N-alkylation of heterocycles with diols. In agreement with this finding, low reactivity was observed when secondary alcohols were employed.

Table 2. N-Alkylation of indole and 5-methoxyindole with different alcohols.[a]

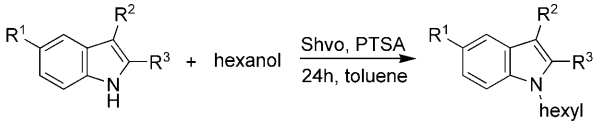


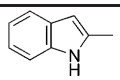
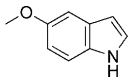
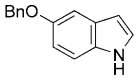
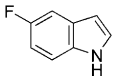
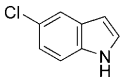
Entry	R^1	Alcohol	T [°C]	Shvo [%]	Conv.[b] [%]	Yield[b] [%]
1[c]	H		110	0.2	99	85 (82)
2[c]	H		110	0.5	97	84 (81)
3	H		110	0.2	89	77 (72)
4[d]	H		110	0.2	98	84
5	H		120	0.5	93	81 (74)
6	OMe		110	0.5	99	70 (19)
7	OMe		110	0.5	99	80 (53)
8	OMe		110	0.5	99	73 (62)
9[c]	OMe		110	0.5	99	93 (83)
10	H		120	0.5	98	94 (81)

[a] Reaction conditions: indole or 5-methoxyindole (1 mmol), alcohol (2 mmol), PTSA (0.025 mol%), toluene (0.5 mL), 24 h. [b] Conversion and yield are determined by GC analysis with hexadecane as the internal standard; conversion and yield are based on the indole. [c] Alcohol (1.1 mmol). [d] Alcohol (3 mmol).

Finally, different indoles were examined in reactions with hexanol (Table 3). Substitution at the 2-position of the indole ring is tolerated, but slightly increased temperature is required to obtain high activity and yield (Table 3, entry 1). Notably, substitution at the C-3-position is also tolerated but the reactivity was reduced slightly. This is in line with our proposed mechanism because the hydrogenation of a substituted double bond is more difficult. Indoles with electron-rich substituents (Table 3, entries 5 and 6) are easily alkylated, too. In contrast, indoles with electron-withdrawing substituents (Table 3, entries 7 and 8) showed reduced reactivity and required higher temperatures and catalyst loading. Nevertheless, N-alkylations are achieved in good yields and selectivities.

Table 3. N-Alkylation of different indoles with hexanol.[a]



Entry	Indole	T [°C]	Shvo [%]	Conv.[b] [%]	Yield[b] [%]
1[c]		120	0.5	89	82 (78)
2[c]		130	0.5	96	89
3		120	0.5	91	80 (79)
4		130	0.5	96	88
5		110	0.2	99	93 (92)
6		110	0.2	97	83 (81)
7		120	0.5	97	86 (76)
8		120	0.5	95	68 (62)

[a] Reaction conditions: indole (1 mmol), hexanol (1.1 mmol), PTSA (0.025 mol%), toluene (0.5 mL), 24 h. [b] Conversion and yield are determined by GC analysis with hexadecane as the internal standard; conversion and yield are based on the indole. [c] Alcohol (2 mmol).

In conclusion, we have developed the first homogeneously catalyzed N-alkylation of indoles with alcohols. In the presence of catalytic amounts of the Shvo catalyst and PTSA this atom-efficient reaction proceeds highly selectively and water is formed as the only byproduct. The protocol we have developed is benign and operationally simple: no additional hydrogen is required and the reaction can be carried out in commercially available pressure tubes. With respect to the mechanism an unusual in situ transfer hydrogenation of the indole takes place.

Experimental Section

General procedure for the selective N-alkylation of indoles: PTSA (0.00025 mmol from a *tert*-butyl methyl ether stock solution) was placed in an ACE pressure tube and the solvent was removed in an argon stream. Then indole (1 mmol) and Shvo catalyst (2.2 mg, 0.002 mmol, 0.2 mol%) were added and the pressure tube was purged. Under an argon atmosphere toluene (0.5 mL) and alcohol (1.1 mmol) were added. The pressure tube was fitted with a Teflon cap and stirred at 110 °C for 24 h. The solvent was removed in vacuo, and the crude product was purified by column chromatography.

Acknowledgements

This work has been supported by the BMBF (Bundesministerium für Bildung und Forschung) and the Deutsche Forschungsgemeinschaft (DFG BE 1931/16-1, Leibniz prize).

Keywords: alcohols · alkylation · homogeneous catalysis · hydrogen transfer · indoles · ruthenium

[1] a) R. J. Sundberg, *Indoles*, Academic Press, London, **1996**; b) R. J. Sundberg, *The Chemistry of Indoles*, Academic Press, New York, **1970**.

[2] For recent reviews about indoles, see: a) K. Krüger (née Alex), A. Tillack, M. Beller, *Adv. Synth. Catal.* **2008**, *350*, 2153–2167; b) G. R. Humphrey, J. T. Kuethe, *Chem. Rev.* **2006**, *106*, 2875–2911; c) S. Cacchi, G. Fabrizi, *Chem. Rev.* **2005**, *105*, 2873–2929.

[3] For examples, see: a) Clometacin (analgesic, anti-inflammatory): M. Negwer, H.-G. Scharnow in *Organic-Chemical Drugs and Their Synonyms, Vol. 3*, 9th ed., Wiley-VCH, Weinheim, **2007**, p. 1915; b) Indocate (antiserotonin, anti-alcoholic): M. Negwer, H.-G. Scharnow in *Organic-Chemical Drugs and Their Synonyms, Vol. 4*, 9th ed., Wiley-VCH, Weinheim, **2007**, p. 2631; c) Lindogrel (antithrombotic): M. Negwer, H.-G. Scharnow in *Organic-Chemical Drugs and Their Synonyms, Vol. 4*, 9th ed., Wiley-VCH, Weinheim, **2007**, p. 2632.

[4] a) G. Vavilina, A. Zicmanis, S. Drozdova, P. Mekss, M. Klavins, *Chem. Heterocycl. Compd.* **2008**, *44*, 530–541; b) A. Zicmanis, G. Vavilina, S. Drozdova, P. Mekss, M. Klavins, *CEJC* **2007**, *5*, 156–168; c) Y. R. Jorapur, J. M. Jeongb, D. Y. Chi, *Tetrahedron Lett.* **2006**, *47*, 2435–2438.

[5] a) F. De Angelis, M. Grasso, R. Nicoletti, *Synthesis* **1977**, 335–336; b) H. Plieninger, H. P. Kraemer, C. Roth, *Chem. Ber.* **1975**, *108*, 1776–1778.

[6] S. Whitney, R. Grigg, A. Derrick, A. Keep, *Org. Lett.* **2007**, *9*, 3299–3302.

[7] For reviews about "borrowing hydrogen" methodology, also known as hydrogen autotransfer, see: a) G. E. Dobereiner , R. H. Crabtree, *Chem. Rev.* **2010**, *110*, 681–703; b) G. Guillena, D. J. Ramón, M. Yus, *Chem. Rev.* DOI: 10.1021/cr9002159; c) T. D. Nixon, M. K. Whittlesey, J. M. J. Williams, *Dalton Trans.* **2009**, 753–762; d) G. W. Lamb, J. M. J. Williams, *Chim. Oggi* **2008**, *26*, 17–19; e) M. H. S. A. Hamid, P. A. Slatford, J. M. J. Williams, *Adv. Synth. Catal.* **2007**, *349*, 1555–1575; f) G. Guillena, D. J. Ramon, M. Yus, *Angew. Chem.* **2007**, *119*, 2410–2416; *Angew. Chem. Int. Ed.* **2007**, *46*, 2358–2364.

[8] a) R. Martínez, D. J. Ramon, M. Yus, *Org. Biomol. Chem.* **2009**, *7*, 2176–2181; b) R. Martínez, D. J. Ramon, M. Yus, *Tetrahedron* **2006**, *62*, 8982–8987; c) R. Martínez, D. J. Ramon, M. Yus, *Tetrahedron* **2006**, *62*, 8988–9001; d) R. Martínez, G. J. Brand, D. J. Ramon, M. Yus, *Tetrahedron Lett.* **2005**, *46*, 3683–3686.

[9] a) R. Yamaguchi, Z. Mingwen, S. Kawagoe, C. Asai, K.-i. Fujita, *Synthesis* **2009**, 1220–1223; b) R. Yamaguchi, S. Kawagoe, C. Asai, K.-i. Fujita, *Org. Lett.* **2008**, *10*, 181–184; c) K.-i. Fujita, Y. Enoki, R. Yamaguchi, *Tetrahedron* **2008**, *64*, 1943–1954.

[10] a) C. Löfberg, R. Grigg, M. A. Whittaker, A. Keep, A. Derrick, *J. Org. Chem.* **2006**, *71*, 8023–8027; b) C. Löfberg, R. Grigg, A. Keep, A. Derrick, V. Sridharan, C. Kilner, *Chem. Commun.* **2006**, 5000–5002; c) R. Grigg, T. R. B. Mitchell, S. Sutthivaiyakit, N. Tongpenyai, *J. Chem. Soc. Chem. Commun.* **1981**, 611–612.

[11] a) B. Blank, S. Michlik, R. Kempe, *Chem. Eur. J.* **2009**, *15*, 3790–3799; b) B. Blank, M. Madalska, R. Kempe, *Adv. Synth. Catal.* **2008**, *350*, 749–758.

[12] a) O. Saidi, A. J. Blacker, M. M. Farah, S. P. Marsden, J. M. J. Williams, *Angew. Chem.* **2009**, *121*, 7511–7514; *Angew. Chem. Int. Ed.* **2009**, *48*, 7375–7378; b) M. H. S. A. Hamid, C. L. Allen, G. W. Lamb, A. C. Maxwell, H. C. Maytum, A. J. A. Watson, J. M. J. Williams, *J. Am. Chem. Soc.* **2009**, *131*, 1766–1774; c) G. W. Lamb, A. J. A. Watson, K. E. Jolley, A. C. Maxwell, J. M. J. Williams, *Tetrahedron Lett.* **2009**, *50*, 3374–3377; d) S. J. Pridmore, P. A. Slatford, A. Daniel, M. K. Whittlesey, J. M. J. Williams, *Tetrahedron Lett.* **2007**, *48*, 5115–5120.

[13] a) D. Hollmann, S. Bähn, A. Tillack, R. Parton, R. Altink, M. Beller, *Tetrahedron Lett.* **2008**, *49*, 5742–5745; b) D. Hollmann, S. Bähn, A. Tillack, M. Beller, *Angew. Chem.* **2007**, *119*, 8440–8444; *Angew. Chem. Int. Ed.* **2007**, *46*, 8291–8294.

[14] a) N. Schwarz, A. Pews-Davtyan, K. Alex, A. Tillack, M. Beller, *Angew. Chem.* **2008**, *120*, 2337–2340; *Angew. Chem. Int. Ed.* **2008**, *47*, 2304–2307; b) N. Schwarz, A. Pews-Davtyan, D. Michalik, A. Tillack, K. Krüger, A. Torrens, J. L. Diaz, M. Beller, *Eur. J. Org. Chem.* **2008**, 5425–5435; c) K. Alex, N. Schwarz, V. Khedkar, I. A. Sayyed, A. Tillack, D. Michalik, J. Holenz, J. L. Diaz, M. Beller, *Org. Biomol. Chem.* **2008**, *6*, 1802–1807; d) I. A. Sayyed, K. Alex, A. Tillack, N. Schwarz, D. Michalik, M. Beller, *Eur. J. Org. Chem.* **2007**, 4525–4528; e) N. Schwarz, A. Pews-Davtyan, K. Alex, A. Tillack, M. Beller, *Synthesis* **2007**, 3722–3730; f) V. Khedkar, A. Tillack, M. Michalik, M. Beller, *Tetrahedron* **2005**, *61*, 7622–7631.

[15] a) S. Bähn, A. Tillack, S. Imm, K. Mevius, D. Michalik, D. Hollmann, L. Neubert, M. Beller, *ChemSusChem* **2009**, *2*, 551–557; b) A. Tillack, D. Hollmann, K. Mevius, D. Michalik, S. Bähn, M. Beller, *Eur. J. Org. Chem.* **2008**, 4745–4750; c) A. Tillack, D. Hollmann, D. Michalik, M. Beller, *Tetrahedron Lett.* **2006**, *47*, 8881–8885.

[16] For reviews on the Shvo catalyst, see: a) J. S. M. Samec, J. E. Bäckvall, *e-EROS Encycl. Reagents Org. Synth.* **2009**, *7*, 5557–5564; b) A. Comas-Vives, G. Ujaque, A. Lledós, *J. Mol. Struct. THEOCHEM* **2009**, *903*, 123–132; c) R. Karvembu, R. Prabhakaran, N. Natarajan, *Coord. Chem. Rev.* **2005**, *249*, 911–918; d) R. Prabhakaran, *Synlett* **2004**, 2048–2049.

[17] a) M. J. Mays, M. J. Morris, P. R. Raithby, Y. Shvo, D. Czarkie, *Organometallics* **1989**, *8*, 1162–1167; b) Y. Shvo, D. Czarkie, Y. Rahamim, *J. Am. Chem. Soc.* **1986**, *108*, 7400–7402; c) Y. Shvo, R. M. Laine, *J. Chem. Soc. Chem. Commun.* **1980**, 753–754.

[18] a) M. H. S. A. Hamid, J. M. J. Williams, *Chem. Commun.* **2007**, 725–727; b) M. H. S. A. Hamid, J. M. J. Williams, *Tetrahedron Lett.* **2007**, *48*, 8263–8265.

[19] a) S. J. Pridmore, P. A. Slatford, J. M. J. Williams, *Tetrahedron Lett.* **2007**, *48*, 5111–5114; b) S. J. Pridmore, P. A. Slatford, A. Daniel, M. K. Whittlesey, J. M. J. Williams, *Tetrahedron Lett.* **2007**, *48*, 5115–5120.

[20] D. Hollmann, A. Tillack, D. Michalik, R. Jackstell, M. Beller, *Chem. Asian J.* **2007**, *2*, 403–410.

[21] A. J. Blacker, M. M. Farah, M. I. Hall, S. P. Marsden, O. Saidi, J. M. J. Williams, *Org. Lett.* **2009**, *11*, 2039–2042.

[22] a) J. S. M. Samec, A. H. Ell, J. B. Åberg, T. Privalov, L. Eriksson, J.-E. Bäckvall, *J. Am. Chem. Soc.* **2006**, *128*, 14293–14305; b) J. S. M. Samec, J.-E. Bäckvall, P. G. Andersson, P. Brandt, *Chem. Soc. Rev.* **2006**, *35*, 237–248; c) J. B. Åberg, J. S. M. Samec, J.-E. Bäckvall, *Chem. Commun.* **2006**, 2771–2773; d) J. S. M. Samec, L. Mony, J.-E. Bäckvall, *Can. J. Chem.* **2005**, *83*, 909–916; e) J. S. M. Samec, A. H. Ell, J.-E. Bäckvall, *Chem. Commun.* **2004**, 2748–2749.

[23] a) C. P. Casey, S. E. Beetner, J. B. Johnson, *J. Am. Chem. Soc.* **2008**, *130*, 2285–2295; b) C. P. Casey, T. B. Clark, I. A. Guzei, *J. Am. Chem. Soc.* **2007**, *129*, 11821–11827; c) C. P. Casey, G. A. Bikzhanova, I. A. Guzei, *J. Am. Chem. Soc.* **2006**, *128*, 2286–2293; d) C. P. Casey, G. A. Bikzhanova, Q. Cui, I. A. Guzei, *J. Am. Chem. Soc.* **2005**, *127*, 14062–14071; e) C. P. Casey, J. B. Johnson, *J. Am. Chem. Soc.* **2005**, *127*, 1883–1894; f) C. P. Casey, J. B. Johnson, S. W. Singer, Q. Cui, *J. Am. Chem. Soc.* **2005**, *127*, 3100–3109.

[24] For ^{1}H NMR spectra see the Supporting Information.

Received: November 16, 2009
Published online: March 5, 2010

