Dehydrogenation

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Frustrated Lewis Pair Catalyzed Dehydrogenative Oxidation of Indolines and Other Heterocycles

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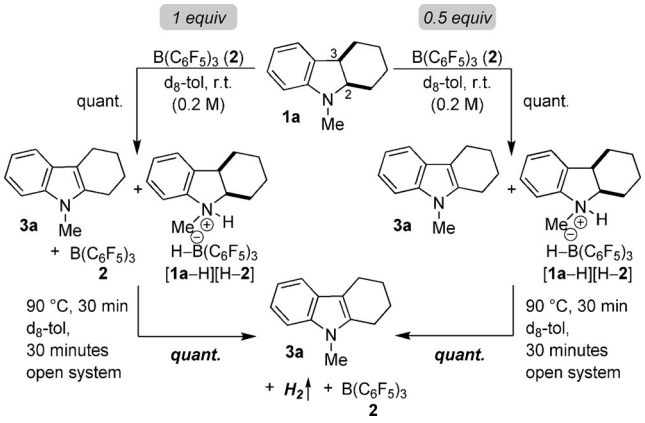
Dedicated to Professor Gerhard Erker on the occasion of his 70th birthday

Abstract: *An acceptorless dehydrogenation of heterocycles catalyzed by frustrated Lewis pairs (FLPs) was developed. Oxidation with concomitant liberation of molecular hydrogen proceeded in high to excellent yields for N-protected indolines as well as four other substrate classes. The mechanism of this unprecedented FLP-catalyzed reaction was investigated by mechanistic studies, characterization of reaction intermediates by NMR spectroscopy and X-ray crystal analysis, and by quantum-mechanical calculations. Hydrogen liberation from the ammonium hydridoborate intermediate is the rate-determining step of the oxidation. The addition of a weaker Lewis acid as a hydride shuttle increased the reaction rate by a factor of 2.28 through a second catalytic cycle.*

The oxidation of organic compounds is a key reaction in chemical synthesis. Immensely powerful and mild oxidation methods have been developed based on the use of transition metals,[1] hypervalent iodine reagents,[2] or organocatalysts.[3] In most cases, stoichiometric byproducts are generated, which need to be removed. Alternatively, the dehydrogenative oxidation of organic compounds can be achieved in the presence of transition metals and is globally applied for the synthesis of commodity chemicals.[4] However, such reactions usually require harsh conditions and sacrificial hydrogen acceptors.[5] The realization of acceptorless processes as desirable, environmentally benign transformations is highly challenging even for transition-metal complexes.[6] Metal-free acceptorless catalytic dehydrogenations are rare and have been reported for 1,4-cyclohexadienes[7] and ammonia–borane.[8] Boron-derived frustrated Lewis pairs (FLPs)[9] are recognized for their ability to activate hydrogen in the absence of any transition metal, and significant breakthroughs have been accomplished in the catalytic hydrogenation of organic molecules.[10] $C(sp^3)$–H bond activation through hydride abstraction by organoboranes has been observed as an undesired side reaction for selected amines[11] or was deliberately exploited for catalytic transfer hydrogenations using diisopropylamine[11a] or 1,4-cyclohexadienes[7] as dihydrogen surrogates. However, the catalytic oxidation of organic substrates with simultaneous release of molecular hydrogen by FLPs as a synthetic method has not been reported thus far.

We initiated our studies with stoichiometric and substoichiometric reactions of *N*-methyl hexahydrocarbazole (**1a**) with the strong Lewis acid $B(C_6F_5)_3$ (**2**). The reaction of 1 equiv of indoline **1a** with 1 equiv of borane **2** at room temperature rapidly furnished 50% of the indole **3a**, 50% of the ammonium hydridoborate, [**1a**–H][H–**2**], and 50% of the free borane **2** within < 5 min (Scheme 1, left).



Scheme 1. Stoichiometric (left) and substoichiometric (right) reactions of **1a** and **2**.

The borane-induced hydride abstraction from indoline **1a** evidently proceeds at room temperature, and a second equivalent of **1a** is required to scavenge the proton from the transiently generated 3*H*-indolium intermediate. Reactions with selectively isotope-labeled [2-D]-**1a** and [3-D]-**1a**

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confirmed C2 as the hydride donor site and C3 as the proton donor site in **1a** (see the Supporting Information). The ammonium salt [**1a**–H][H–**2**] is not susceptible to hydride abstraction, leaving 50% of free borane **2** unreacted. Accordingly, the reaction of **1a** with 0.5 equiv of $B(C_6F_5)_3$ generated equimolar amounts of the oxidation product **3a** and indolinium hydridoborate [**1a**–H][H–**2**] as a precursor for hydrogen release through proton–hydride recombination (Scheme 1, right). Indeed, subsequent heating of both reactions to 90°C for 30 min liberated molecular hydrogen and furnished indole **3a** in quantitative yield with simultaneous regeneration of borane **2**. The important intermediate [**1a**–H][H–**2**] was characterized by 1D and 2D NMR spectroscopy. The NOESY spectrum of the ammonium borate salt revealed an intermolecular NH···HB dihydrogen bond,[12] which has thus far only been reported for weaker Lewis acids[12] (see the Supporting Information for details). This interaction supports the relatively high acidity of the ammonium species so that a dihydrogen bond is formed to the weak hydride donor moiety.

We succeeded in the crystallization of the 6-chloro derivative [**1j**–H][H–**2**], which was obtained from the analogous reaction of 2 equiv **1j** with 1 equiv **2** in toluene. Although the crystal quality was rather mediocre, the molecular structure of [**1j**–H][H–**2**] could be unambiguously determined (Figure 1).[13] The analysis confirmed the structure of an ammonium hydridoborate salt featuring a short (B)H10···H1(N) distance of 1.73 Å, indicating a dihydrogen bond.[14] These experiments clearly support rapid borane-induced hydride abstraction from C2 to generate the transient 3*H*-indolium ion (**4**; see also Figure 2) followed by intermolecular proton transfer from H3 to the indoline nitrogen atom to form the stable ammonium borate [**1**–H][H–**2**]. The detection and identification of the stable ammonium borate [**1a**–H][H–**2**] by NMR spectroscopy together with the heating required for H_2 liberation strongly support the rate-determining nature of this step.

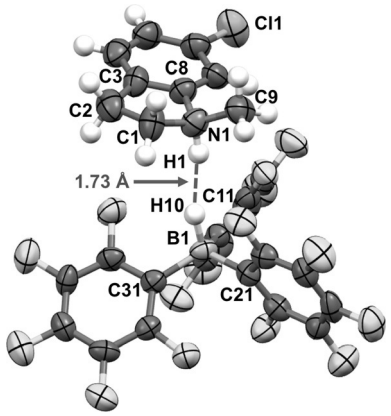
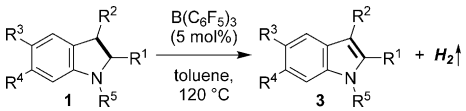


Figure 1. Molecular structure of [**1j**–H][H–**2**]. Selected bond lengths [Å] and angles [°]: N1–C1 1.506(8), N1–C8 1.486(8), N1–C9 1.497(7), C1–C2 1.555(8), C2–C3 1.507(9), B1–C11 1.636(9), B1–C21 1.608(9), B1–C31 1.653(10), B1–H10 1.21(5), N1–H1 0.93; (B)H10···H1(N) 1.73; C1-N1-C8 106.8(5), C1-N1-C9 113.0(5), C8-N1-C9 114.9(6), C11-B1-C21 110.8(6), C11-B1-C31 112.5(6), C21-B1-C31 116.1(6). Anisotropic displacement ellipsoids set at 50% probability.[13]

Next we expanded the scope of the acceptorless dehydrogenation to a catalytic version using 5 mol% of **2** and a series of N-protected indolines (Table 1).[15] Twenty-one indolines (**1a**–**u**) were subjected to the catalytic dehydrogenation, providing access to the corresponding indoles **3a**–**u**.

Table 1: FLP-catalyzed dehydrogenation of N-protected indolines.



	R^1	R^2	R^3	R^4	R^5	t [h]	Yield [%][a]
3a	-$(CH_2)_4$-		H	H	Me	13.5	99 (93)
3b	Me	H	H	H	Me	0.75	99 (94)
3c	H	Me	H	H	Me	14.5	99 (97)
3d	Me	Me	H	H	Me	15.5	99 (94)
3e	H	H	H	H	Me	23.5	99 (94)
3f	Ph	H	H	H	Me	16.5	99 (99)[b]
3g	4-ClC_6H_4	H	H	H	Me	17	85 (89)[b]
3h	H	H	OMe	H	Me	20	82 (74)
3i	H	H	Br	H	Me	1.5	99 (82)
3j	Me	H	Cl	H	Me	1.5	99 (99)
3k	H	H	H	Cl	Me	23.5	99 (99)
3l	H	H	H	F	Me	23.5	99 (59)
3m	H	H	H	H	neopentyl	17	30
3n	Me	H	H	H	Bn	20.75	99 (86)
3o	Me	Me	H	H	Bn	18	99 (88)
3p	H	H	Br	H	Bn	15	99 (97)
3q	H	H	OMe	H	Bn	17.25	95 (93)
3r	Me	H	H	H	PMB	24	69 (51)
3s	Me	Me	H	H	PMB	30	51 (55)
3t	H	H	Br	H	PMB	14.75	99 (79)
3u	H	H	OMe	H	PMB	15.75	95 (94)

[a] Yields determined by ^{1}H NMR analysis with ferrocene as the internal standard. Reaction conditions: indoline (0.1 mmol), $B(C_6F_5)_3$ (5 μmol, 5 mol%), ferrocene (30 μmol), [D_8]toluene (0.2 M). Yields of isolated products are given in parentheses; these were obtained under the following conditions: indoline (0.7 mmol), $B(C_6F_5)_3$ (35 μmol, 5 mol%), toluene (0.2 M). [b] The yields of isolated **3f** and **3g** contain 4 and 11% of the respective indolines as impurities.

The reaction time was first confirmed by performing the reaction on 0.1 mmol scale. Most reactions provided quantitative yields of the corresponding indoles **3** after heating to 120°C for 1.5 to 23.5 h. Experiments on 0.7 mmol scale confirmed the excellent yields of the indoline oxidation on NMR scale (82–99%, **1a**–**l**). The slower formation of **3g** in comparison to **3f** (see also the Supporting Information) supports the importance of positive-charge stabilization in the hydride abstraction step.[16] The influence of steric bulk at the N atom was probed in the oxidation of neopentyl-substituted indoline **1m**. Indole **3m** was obtained in a low yield of 30% after 17 h, indicating that either hydride abstraction or proton transfer becomes unfavorable owing to steric congestion.

Furthermore, we expanded the scope of the dehydrogenative oxidation to indolines with removable N-protecting groups, for example, benzyl (Bn) and 4-methoxybenzyl (PMB) moieties (**1n**–**u**). The two PMB-protected indolines

1r and **1s** were converted into the corresponding indoles in diminished yields. Pleasingly, for all Bn- as well as for the two PMB-protected indolines **1t** and **1u**, the reaction proceeded in excellent yields. Generally, the reaction time and the yield of the dehydrogenative oxidation were only marginally influenced by the reaction scale.

We then investigated the mechanism of the dehydrogenative indoline oxidation by kinetic and quantum-mechanical experiments. DFT calculations at the PW6B95-D3//PBEh-3c + COSMO-RS level of theory[17] provided detailed mechanistic insight into the borane-catalyzed dehydrogenation of indoline **1a** (Figure 2). Owing to steric hindrance at the

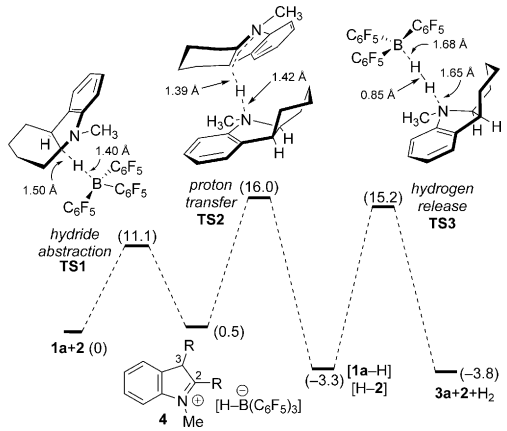
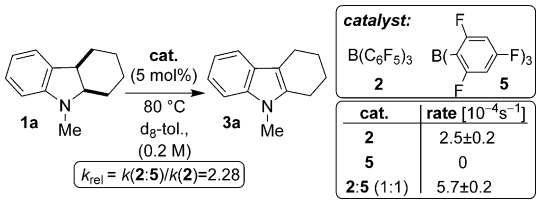


Figure 2. DFT-computed reaction free energies (in kcal mol^{-1}) for the $B(C_6F_6)_3$ (**2**) catalyzed dehydrogenation of indoline **1a**..

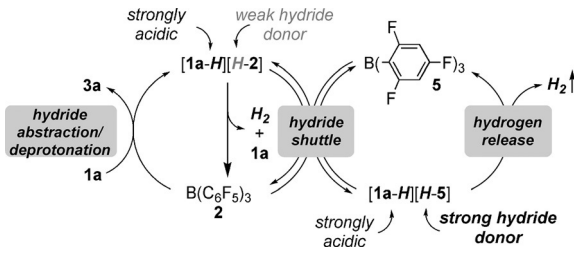
N center of indoline **1a**, Lewis basic indoline **1a** and $B(C_6F_6)_3$ (**2**) can only form an unstable frustrated Lewis pair (3.6 kcal mol^{-1} higher in free energy than separated **1a** and **2**; see the Supporting Information) rather than a tight acid–base complex through formation of a B–N donor bond. In solution, borane **2** can selectively abstract a hydride from the C2 position of **1a** to form the separated ion pair **4** over a low barrier of 11.1 kcal mol^{-1} (TS1). From this intermediate, two reactions are conceivable. The direct formation of indole **3a** and molecular H_2 from intermediate **4** was considered as kinetically incompetent[18] (not shown, see the Information Supporting) in comparison to a lower-barrier proton transfer (15.5 kcal mol^{-1}; TS2) to the N atom of a second indoline **1a**, which is in accord with the results of the isotope-labeling experiments (see the Supporting Information). The formation of this contact ion pair, [**1a**–H][H–**2**], and **3a** is exergonic by −3.3 kcal mol^{-1}, which enabled the NMR spectroscopic characterization of this species at room temperature, including the detection of the ion pairing by dihydrogen bonding. Upon heating to 90 °C, proton–hydride recombination may occur to release indoline **1a**, molecular H_2, and borane catalyst **2**, which is almost energy-neutral and involves a moderate barrier of 18.5 kcal mol^{-1} at room temperature. This reaction should be favored at higher temperatures owing to favorable entropy effects. The overall catalyzed dehydrogenation is thus exergonic by −3.8 kcal mol^{-1} with a barrier of 18.5 kcal mol^{-1}; proton–hydride recombination was determined to be the rate-limiting step, which is in acceptable agreement with the determined Eyring activation energy of 25.7 ± 6 kcal mol^{-1}. This proposed mechanism implies that the activation barrier of H_2 liberation may be reduced when the Brønsted acidity of the ammonium ion or the hydridic character of the hydridoborate is enhanced. The Lewis acidity of boranes in active FLPs has an immense impact on the reversibility of H_2 activation[9a,12b,19] and on the reaction rates.[12a,20] The Lewis acidity of partially fluorinated borane **5** is 15 % lower than that of **2**,[12a,21] which in turn may result in a lower energy barrier for the H_2 release from the corresponding ammonium borate owing to the increased hydride donor ability.[21a]

Disappointingly, borane **5** was entirely inactive in the dehydrogenative oxidation of **1a** as a consequence of the diminished Lewis acidity (Scheme 2). However, borane **5** may

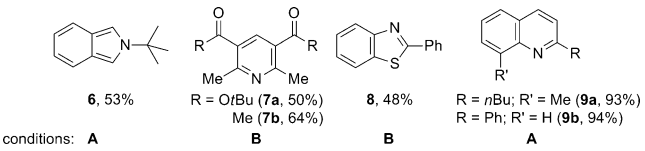


Scheme 2. Rate enhancement of the indoline dehydrogenation by the weak Lewis acid **5** acting as a hydride shuttle.

act as hydride shuttle as boranes can undergo hydride exchange[22] in equilibrium. Indeed, when a 1:1 ratio of catalytically active **2** and catalytically inactive **5** (5 mol % each) was used for the dehydrogenation of **1a**, a substantial rate enhancement of $k_{rel} = 2.28$ was observed (Scheme 2). This boost in reactivity can be rationalized by the hydride exchange equilibrium between [H–**2**] and **5**. The hydride is preferably located at the stronger Lewis acid **2** but small quantities of the stronger hydride donor [H–**5**] may still be accessible (Scheme 3). This leads to the transient formation of the ion pair [**1a**–H][H–**5**],[23] which is now capable to liberate H_2 more readily than the comparatively weaker hydride donor [H–**2**] (right cycle). Furthermore, free borane **2** liberated in the equilibrium (left cycle) is again reactive in hydride abstraction from **1a**. In summary, the substantial rate increase by a factor of 2.28 is due to direct hydrogen release from the initially formed hydridoborate salt [**1a**–H][H–**2**] as well as to **5** acting as a hydride shuttle.



Scheme 3. Proposed function of borane **5** in the rate enhancement of the dehydrogenation through a hydride shuttle mechanism.



Scheme 4. Oxidation of other heterocyclic compound classes. Conditions A: 0.2 M, $B(C_6F_5)_3$ (10 mol%), mesitylene, 165 °C; conditions B: 0.2 M, $B(C_6F_5)_3$ (5 mol%), toluene, 120 °C.

Having established a method for indoline oxidation, we investigated the viability of this approach for other compound classes (Scheme 4). All tested substrates were susceptible to FLP-catalyzed acceptorless dehydrogenation. The pyridine derivatives **7a** and **7b** as well as thiazole **8** were obtained from the corresponding 1,4-dihydropyridines and thiazoline in 48–64% yield. For the oxidation of an isoindoline and two 1,2-dihydroquinolines, elevated temperatures were required to obtain *N-tert*-butyl-isoindole (**6**) in 53% yield and the 2-substituted quinolines **9a** and **9b** in 93% and 94% yield.

In summary, we have developed an FLP-catalyzed acceptorless dehydrogenation of N-protected indolines that provides the corresponding products in excellent yields. This approach also proved successful for the oxidation of isoindolines, 1,4-dihydropyridines, thiazoles, and 1,2-dihydroquinolines. The dehydrogenation proceeds by borane-induced hydride abstraction from the C2 atom of the indoline. The generated 3*H*-indolium intermediate is rapidly deprotonated by a second indoline, generating an ammonium hydridoborate. This intermediate was unambiguously characterized by NMR spectroscopy and X-ray structure analysis. The release of H_2 through proton–hydride recombination is the rate-determining step. This step was accelerated by the addition of catalytic amounts of the weak Lewis acid **5**, which acts as a hydride shuttle and transiently generates a stronger hydride donor. This interplay between stronger and weaker Lewis acids might inspire the development of innovative FLP-catalyzed reactions.

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Angew. Chem. **2016**, *128*, 12407–12411

[1] T. Punniyamurthy, S. Velusamy, J. Iqbal, *Chem. Rev.* **2005**, *105*, 2329–2363.
[2] A. Yoshimura, V. V. Zhdankin, *Chem. Rev.* **2016**, *116*, 3328–3435.
[3] O. A. Wong, Y. Shi, *Chem. Rev.* **2008**, *108*, 3958–3987.
[4] K. Weissermel, H.-J. Arpe, *Industrial organic chemistry*, Wiley, Hoboken, **2008**.
[5] a) G. E. Dobereiner, R. H. Crabtree, *Chem. Rev.* **2010**, *110*, 681–703; b) J. Choi, A. H. R. MacArthur, M. Brookhart, A. S. Goldman, *Chem. Rev.* **2011**, *111*, 1761–1779.
[6] a) M. W. Haenel, S. Oevers, K. Angermund, W. C. Kaska, H. J. Fan, M. B. Hall, *Angew. Chem. Int. Ed.* **2001**, *40*, 3596–3600; *Angew. Chem.* **2001**, *113*, 3708–3712; b) A. Paul, C. B. Musgrave, *Angew. Chem. Int. Ed.* **2007**, *46*, 8153–8156; *Angew. Chem.* **2007**, *119*, 8301–8304; c) R. Yamaguchi, C. Ikeda, Y. Takahashi, K.-i. Fujita, *J. Am. Chem. Soc.* **2009**, *131*, 8410–8412; d) P. M. Zimmerman, A. Paul, Z. Y. Zhang, C. B. Musgrave, *Angew. Chem. Int. Ed.* **2009**, *48*, 2201–2205; *Angew. Chem.* **2009**, *121*, 2235–2239; e) H. A. Ho, K. Manna, A. D. Sadow, *Angew. Chem. Int. Ed.* **2012**, *51*, 8607–8610; *Angew. Chem.* **2012**, *124*, 8735–8738; f) E. Alberico, P. Sponholz, C. Cordes, M. Nielsen, H. J. Drexler, W. Baumann, H. Junge, M. Beller, *Angew. Chem. Int. Ed.* **2013**, *52*, 14162–14166; *Angew. Chem.* **2013**, *125*, 14412–14416; g) J. J. Wu, D. Talwar, S. Johnston, M. Yan, J. L. Xiao, *Angew. Chem. Int. Ed.* **2013**, *52*, 6983–6987; *Angew. Chem.* **2013**, *125*, 7121–7125.
[7] a) I. Chatterjee, M. Oestreich, *Angew. Chem. Int. Ed.* **2015**, *54*, 1965–1968; *Angew. Chem.* **2015**, *127*, 1988–1991; b) I. Chatterjee, Z. W. Qu, S. Grimme, M. Oestreich, *Angew. Chem. Int. Ed.* **2015**, *54*, 12158–12162; *Angew. Chem.* **2015**, *127*, 12326–12330.
[8] a) F. H. Stephens, R. T. Baker, M. H. Matus, D. J. Grant, D. A. Dixon, *Angew. Chem. Int. Ed.* **2007**, *46*, 746–749; *Angew. Chem.* **2007**, *119*, 760–763; b) D. W. Himmelberger, C. W. Yoon, M. E. Bluhm, P. J. Carroll, L. G. Sneddon, *J. Am. Chem. Soc.* **2009**, *131*, 14101–14110; c) C. Appelt, J. C. Slootweg, K. Lammertsma, W. Uhl, *Angew. Chem. Int. Ed.* **2013**, *52*, 4256–4259; *Angew. Chem.* **2013**, *125*, 4350–4353; d) H. A. Kalviri, F. Gartner, G. Ye, I. Korobkov, R. T. Baker, *Chem. Sci.* **2015**, *6*, 618–624; e) Z. P. Lu, L. Schweighauser, H. Hausmann, H. A. Wegner, *Angew. Chem. Int. Ed.* **2015**, *54*, 15556–15559; *Angew. Chem.* **2015**, *127*, 15777–15780.
[9] a) G. C. Welch, R. R. S. Juan, J. D. Masuda, D. W. Stephan, *Science* **2006**, *314*, 1124–1126; b) G. C. Welch, D. W. Stephan, *J. Am. Chem. Soc.* **2007**, *129*, 1880–1881; c) D. W. Stephan, *J. Am. Chem. Soc.* **2015**, *137*, 10018–10032; d) D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* **2015**, *54*, 6400–6441; *Angew. Chem.* **2015**, *127*, 6498–6541.
[10] a) D. W. Stephan, *Org. Biomol. Chem.* **2012**, *10*, 5740–5746; b) J. Paradies, *Synlett* **2013**, 777–780; c) J. Paradies, *Angew. Chem. Int. Ed.* **2014**, *53*, 3552–3557; *Angew. Chem.* **2014**, *126*, 3624–3629; d) T. Mahdi, D. W. Stephan, *J. Am. Chem. Soc.* **2014**, *136*, 15809–15812; e) D. J. Scott, M. J. Fuchter, A. E. Ashley, *J. Am. Chem. Soc.* **2014**, *136*, 15813–15816.
[11] a) J. M. Farrell, Z. M. Heiden, D. W. Stephan, *Organometallics* **2011**, *30*, 4497–4500; b) N. Millot, C. C. Santini, B. Fenet, J. M. Basset, *Eur. J. Inorg. Chem.* **2002**, 3328–3335.
[12] a) S. Tussing, L. Greb, S. Tamke, B. Schirmer, C. Muhle-Goll, B. Luy, J. Paradies, *Chem. Eur. J.* **2015**, *21*, 8056–8059; b) L. Greb, C. G. Daniliuc, K. Bergander, J. Paradies, *Angew. Chem. Int. Ed.* **2013**, *52*, 5876–5879; *Angew. Chem.* **2013**, *125*, 5989–5992.
[13] a) Bruker (2002). SMART (Version 5.63), SAINT (Version 6.02). Bruker AXS Inc., Madison, Wisconsin, USA; b) G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112–122; c) for further information, see the Supporting Information. CCDC 1489310 ([**1j**–H][H–**2**]) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.
[14] R. Custelcean, J. E. Jackson, *Chem. Rev.* **2001**, *101*, 1963–1980.
[15] The turnover numbers for catalyst loadings of 3 mol% and 2 mol% are 29.7 and 27.4, respectively.
[16] The oxidation also does not proceed with Cbz-protected indoline owing to a lack of positive-charge stabilization.

[17] a) TURBOMOLE V7.0 2015, a development of the University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989–2007, TURBOMOLE GmbH, since 2007; available from http://www.turbomole.com; b) S. Grimme, J. G. Brandenburg, C. Bannwarth, A. Hansen, *J. Chem. Phys.* **2015**, *143*, 054107; c) A. Klamt, G. Schüürmann, *J. Chem. Soc. Perkin Trans. 2* **1993**, 799; d) K. Eichkorn, F. Weigend, O. Treutler, R. Ahlrichs, *Theor. Chem. Acc.* **1997**, *97*, 119; e) P. Deglmann, K. May, F. Furche, R. Ahlrichs, *Chem. Phys. Lett.* **2004**, *384*, 103; f) S. Grimme, *Chem. Eur. J.* **2012**, *18*, 9955; g) F. Eckert, A. Klamt in COSMOtherm, Version C3.0, Release 14.01, COSMOlogic GmbH & Co. KG, Leverkusen, Germany, **2013**; h) F. Eckert, A. Klamt, *AIChE J.* **2002**, *48*, 369; i) J. Tao, J. P. Perdew, V. N. Staroverov, G. E. Scuseria, *Phys. Rev. Lett.* **2003**, *91*, 146401; j) Y. Zhao, D. G. Truhlar, *J. Phys. Chem. A* **2005**, *109*, 5656; k) A. Schaefer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* **1994**, *100*, 5829; l) F. Weigend, M. Häser, H. Patzelt, R. Ahlrichs, *Chem. Phys. Lett.* **1998**, *294*, 143–152; m) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.

[18] The reaction between the 3*H*-indolium and borate to furnish indole **11** and H_2 is exergonic by -4.3 kcal mol^{-1} with a moderate barrier of 18.1 kcal mol^{-1}.

[19] a) M. Ullrich, A. J. Lough, D. W. Stephan, *J. Am. Chem. Soc.* **2009**, *131*, 52–53; b) L. Greb, S. Tamke, J. Paradies, *Chem. Commun.* **2014**, *50*, 2318–2320; c) L. Greb, S. Tussing, B. Schirmer, P. Ona-Burgos, K. Kaupmees, M. Lokov, I. Leito, S. Grimme, J. Paradies, *Chem. Sci.* **2013**, *4*, 2788–2796.

[20] L. Greb, P. Ona-Burgos, B. Schirmer, S. Grimme, D. W. Stephan, J. Paradies, *Angew. Chem. Int. Ed.* **2012**, *51*, 10164–10168; *Angew. Chem.* **2012**, *124*, 10311–10315.

[21] a) S. Tussing, K. Kaupmees, J. Paradies, *Chem. Eur. J.* **2016**, *22*, 7422–7426; b) S. Keess, A. Simonneau, M. Oestreich, *Organometallics* **2015**, *34*, 790–799.

[22] a) Z. M. Heiden, A. P. Lathem, *Organometallics* **2015**, *34*, 1818–1827; b) R. E. Williams, *J. Inorg. Nucl. Chem.* **1961**, *20*, 198–204; c) W. S. Koski, *Adv. Chem. Ser.* **1961**, *32*, 78–87.

[23] E. R. Clark, M. J. Ingleson, *Angew. Chem. Int. Ed.* **2014**, *53*, 11306–11309; *Angew. Chem.* **2014**, *126*, 11488–11491.

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