

Lewis-Acid-assisted Hydrogen Atom Transfer to Manganese(V)-Oxo Corrole through Valence Tautomerization

Curt J. Bougher^[a] and Mahdi M. Abu-Omar^{*[a, b]}

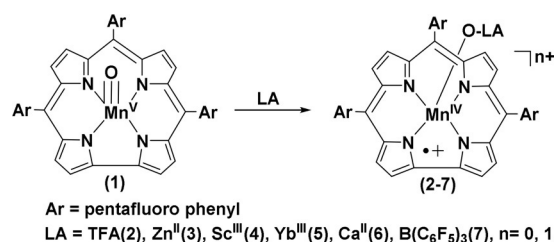
The kinetics of formation of the valence tautomers (tpfc)Mn^{IV}(O–LA)]ⁿ⁺ [where LA = Zn^{II}, Ca^{II}, Sc^{III}, Yb^{III}, B(C₆F₅)₃, and trifluoroacetic acid (TFA); tpfc = 5,10,15-tris(pentafluorophenyl) corrole] from (tpfc)Mn^V(O) were followed by UV/Vis spectroscopy, giving second-order rate constants ranging over five orders of magnitude from 10^{–2} for Ca to 10³ M^{–1} s^{–1} for Sc. Hydrogen atom transfer (HAT) rates from 2,4-di-*tert*-butyl phenol (2,4-DTBP) to the various Lewis acid valence tautomers of manganese oxo corrole complexes were evaluated and compared. For LA = TFA, Sc^{III}, or Yb^{III}, the rate constants of HAT were comparable to unactivated (tpfc)Mn^V(O). However, with LA = B(C₆F₅)₃, Zn^{II}, and Ca^{II}, 6-, 21-, and 31-fold rate enhancements were observed, respectively. Remarkably, [(tpfc)Mn^{IV}(OCA)]²⁺ gave the most enhancement despite its rate of formation being the slowest. Comparisons of HAT rate constants among the various Lewis acid tautomers revealed that both size and charge are important. This study underscores how valence may affect the reactivity of high-valent manganese-oxo compounds and sheds light on nature's choice of Ca in the activation of Mn-oxo in the oxygen-evolving complex.

High-valent metal-oxo compounds are important because of their biological significance,^[1] use as oxidation catalysts,^[2] and role in synthetic organic reactions.^[3] In many biological reactions, valence tautomers play an important role in tuning activity.^[4] Species known to exhibit this behavior include catalases,^[5] cytochrome P450,^[2a,6] and peroxidases.^[7] Cytochrome P450 enzymes are ubiquitous in plants, bacteria, insects, and mammals, with 57 so far identified in the human genome.^[6b,8] In substrate

oxidation with cytochrome P450, the active species has been shown to be compound I, the valence tautomer of iron(V) oxo.^[6c] Catalase has been shown to exhibit valence tautomerism with the addition of a stoichiometric amount of an oxidant in bovine liver catalase,^[5a] *Micrococcus lysodeikticus* catalase^[5b] and *Proteas mirabilis* catalase.^[5a,c] Likewise, manganese-mediated water oxidation involves a valence tautomer formed through the coordination of Ca²⁺ to the manganese-oxo ligand.^[9] These discoveries have led to an increased interest in valence tautomerism and the influence of Lewis acids on the reactivity of high-valent metal-oxo complexes.^[10]

Valence tautomerism has been seen in porphyrin,^[11] corrolazine,^[12] and corrole^[13] species. These complexes can be distinguished from other high-valent metal-oxo porphyrinoid compounds through the presence of a transition in the visible > 600 nm region, owing to the π -radical of the porphyrinoid ring. Goldberg and co-workers have shown interesting reactivity for these valence tautomers in corrolazines.^[14] They have illustrated differences in oxygen atom transfer (OAT) spanning three orders of magnitude, which is a 1000-fold rate enhancement.^[14b] Herein, we report the preparation of valence tautomers of manganese(V)-oxo corrole with various Lewis acids: Sc^{III}, Yb^{III}, Zn^{II}, Ca^{II}, B(C₆F₅)₃, and TFA. We have also investigated and quantified their ability to undergo hydrogen atom transfer (HAT) with 2,4-ditertiarybutyl phenol (2,4-DTBP).

Recently, we showed that manganese-oxo corrole **1** is capable of undergoing valence tautomerization with a Brønsted acid (TFA) to form complex **2**.^[15] The valence tautomerization showed an increase in the rate of electron transfer (ET) but a decrease in OAT capability, and no change in HAT. Following this observation, we investigated Zn^{II}, Sc^{III}, Yb^{III}, Ca^{II}, and B(C₆F₅)₃ to form a variety of different valence tautomers (Scheme 1). Reaction of these Lewis acids with Mn^V(O) corrole complex **1** led to isosbestic conversion to [(tpfc)Mn^{IV}(O–LA)]ⁿ⁺ (**3–7**, where $n=0, 2, \text{ or } 3$). The valence tautomers gave different UV/Vis spectra, where the transition for the π -radical cor-



Scheme 1. Valence tautomerization of manganese(V)-oxo corrole induced by various Lewis acids.

[a] C. J. Bougher, Prof. Dr. M. M. Abu-Omar
Department of Chemistry, Purdue University
560 Oval Drive, West Lafayette, IN 47906 (USA)

[b] Prof. Dr. M. M. Abu-Omar
Current address:
Department of Chemistry and Biochemistry
Department of Chemical Engineering, University of California
Santa Barbara, CA 93106 (USA)
E-mail: abumar@chem.ucsb.edu

Supporting Information for this article can be found under <http://dx.doi.org/10.1002/open.201600117>.

© 2016 The Authors. Published by Wiley-VCH Verlag GmbH & Co. KGaA. This is an open access article under the terms of the Creative Commons Attribution-NonCommercial-NoDerivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.

role shifted depending on the Lewis acid (Figures S4–S9). The effect of the Lewis acid on the exact electronic structure of the resulting valence tautomers is beyond the scope of this report and merits an independent future investigation. The rates of formation of 2–7 also varied over a wide range, with second-order rate constants $k_1^{\text{LA}} = 10^{-2} - 10^3 \text{ M}^{-1} \text{ s}^{-1}$. Rates of reaction were monitored under pseudo-first-order conditions by following the disappearance of 1 at 345 nm, which, in all cases, produced clean isosbestic conversion, indicating no accumulation of an intermediate. The data (UV/Vis spectra and kinetic dependencies) for $\text{Zn}(\text{OTf})_2$ ($\text{OTf} = \text{trifluoromethanesulfonate}$) is presented in Figure 1. The final spectrum for each reaction is consistent with that of a π -radical corrole species.^[13] The second-order rate constants for the different Lewis acids are given in Table 1.

$\text{Sc}(\text{OTf})_3$ and TFA gave the fastest rates of tautomer formation of 3.4×10^3 and $2.3 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, respectively. $\text{Ca}(\text{OTf})_2$ gave the slowest rate of tautomerization at $k_1^{\text{Ca}} = 3.6 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ followed by $\text{Zn}(\text{OTf})_2$ at $k_1^{\text{Zn}} = 4.2 \text{ M}^{-1} \text{ s}^{-1}$. $\text{B}(\text{C}_6\text{F}_5)_3$ and $\text{Yb}(\text{OTf})_3$ fell in between the bookends with rate constants of $k_1^{\text{BAr}_3} = 650$ and $k_1^{\text{Yb}} = 1064 \text{ M}^{-1} \text{ s}^{-1}$, respectively. Differences in size

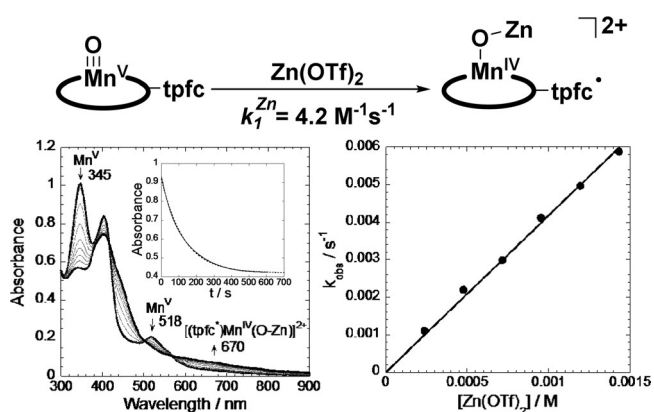


Figure 1. Reaction of $223 \mu\text{M}$ $\text{Zn}(\text{OTf})_2$ and $22.3 \mu\text{M}$ $(\text{tpfc})\text{Mn}^{\text{V}}(\text{O})$. a) Time-resolved UV/Vis spectral changes, measured every 60 s. Inset: changes in absorbance at 345 nm versus time for the disappearance of $(\text{tpfc})\text{Mn}^{\text{V}}(\text{O})$ (points are data and the dashed line best fit was obtained by using first-order rate law). b) Plot of the observed pseudo-first-order rate constants (k_{obs}) versus $[\text{Zn}(\text{OTf})_2]$. Slope = $k_1^{\text{Zn}} = 4.2 \pm 0.1 \text{ M}^{-1} \text{ s}^{-1}$.

Table 1. Rate constants for the various Lewis acid valence tautomers.			
Species ^[a]	Tautomer formation $k_1^{\text{LA}} [\text{M}^{-1} \text{ s}^{-1}]^{\text{[b]}}$	HAT $k_2^{\text{LA}} [\text{M}^{-1} \text{ s}^{-1}]$	Ionic radius [\AA] ^[c]
$(\text{tpfc})\text{Mn}^{\text{V}}(\text{O})$ (1)	na	45 ± 0.3	
$[(\text{tpfc})\text{Mn}^{\text{IV}}(\text{OH})]^+$ (2)	2300 ± 70	32.6 ± 0.5	
$[(\text{tpfc})\text{Mn}^{\text{IV}}(\text{O}-\text{Zn})]^{2+}$ (3)	4.2 ± 0.1	943 ± 26	0.74
$[(\text{tpfc})\text{Mn}^{\text{IV}}(\text{O}-\text{Sc})]^{3+}$ (4)	3400 ± 100	27.3 ± 0.7	0.75
$[(\text{tpfc})\text{Mn}^{\text{IV}}(\text{O}-\text{Yb})]^{3+}$ (5)	1064 ± 14	42 ± 2	0.87
$[(\text{tpfc})\text{Mn}^{\text{IV}}(\text{O}-\text{Ca})]^{2+}$ (6)	$(3.56 \pm 0.02) \times 10^{-2}$	1386 ± 5	1.00
$(\text{tpfc})\text{Mn}^{\text{IV}}(\text{O}-\text{B}(\text{C}_6\text{F}_5)_3)$ (7)	650 ± 10	271 ± 6	

[a] Species 2–7 were made from the reaction of 1 with the corresponding Lewis acid. [b] Rate of formation represents the rate of the reaction for 1 + Lewis acid, corresponding to the species being made. [c] Coordination number (CN) = 6.

(sterics) and charge (electronics) appear to contribute to the rates of valence tautomers formation. The ionic radius of Yb is larger than that of Sc, and this appears to influence the rate constant k_1^{LA} by a discernable amount (i.e. a factor of 3). However, the effect of size is not as significant as that of charge when comparing Zn^{2+} and Sc^{3+} (Table 1). Both are nearly identical in size (ionic radii), but the difference in charge/electronics translates to a 810-fold difference in rate constants, that is, nearly three orders of magnitude. On the other hand, Ca^{2+} is larger than Zn^{2+} and, indeed, their respective rate constants for tautomer formation span two orders of magnitude. This large difference could be attributed to a combination of size and electronics, given that calcium is a main-group element. Similarly, $\text{B}(\text{C}_6\text{F}_5)_3$ is not charged and bulky if the aromatic groups come into play; however, the strong B–O bond (electronics) in the valence tautomer potentially compensates for it, giving a rate constant that falls between Zn and Sc.

The valence tautomers $[(\text{tpfc})\text{Mn}^{\text{IV}}(\text{O}-\text{LA})]^{n+}$ (3–7) can be generated through the reaction of 1 equivalent of the Lewis acid with $(\text{tpfc})\text{Mn}^{\text{V}}(\text{O})$ (1) in CH_3CN . Subsequently, the resulting valence tautomer is reacted with 2,4-DTBP to give $(\text{tpfc})\text{Mn}^{\text{III}}$ and the coupled phenol dimer through HAT. Figure 2 illustrates this reaction alongside spectral changes and kinetic data for Zn. The EPR spectrum in parallel mode of the Mn corrole product is consistent with $\text{Mn}^{\text{III}} S = 2$ (Figure S3). Spectral changes for the HAT reactions showed isosbestic points, indicating no accumulation of an intermediate. The kinetics under pseudo-first-order conditions were first order in Mn and first order in 2,4-DTBP. Second-order rate constants for HAT k_2^{LA} were obtained from the slopes of k_{obs} versus $[\text{2,4-DTBP}]$ (Figure 2b for Zn; see the Supporting Information for other Lewis acids); details are given in Table 1.

Although the valence tautomer resulting from TFA gave a k_2^{TFA} value for HAT of $33 \text{ M}^{-1} \text{ s}^{-1}$, which is slightly slower than that observed for 1, the valence tautomer resulting from $\text{Zn}(\text{OTf})_2$ showed a 21-fold acceleration, with $k_2^{\text{Zn}} = 943 \text{ M}^{-1} \text{ s}^{-1}$.

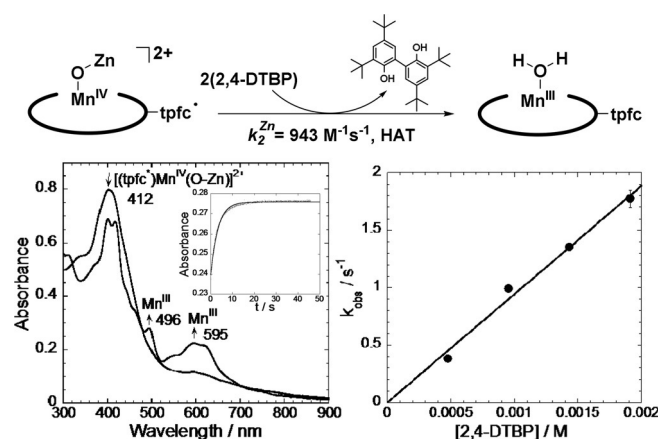


Figure 2. Plots corresponding to a HAT of $23.9 \mu\text{M}$ $[(\text{tpfc})\text{Mn}^{\text{IV}}(\text{O}-\text{Zn})]^{2+}$ with $956 \mu\text{M}$ 2,4-DTBP. a) Time-resolved UV/Vis spectra of the reaction at 25°C , measured every 19 s. Inset: Change in absorbance at 496 nm versus time, corresponding to the formation of $(\text{tpfc})\text{Mn}^{\text{III}}$ (point) and the best fit refers to the first-order rate law equation (dashed line). c) Plot of k_{obs} versus $[\text{2,4-DTBP}]$. Slope = $k_2^{\text{Zn}} = 943 \pm 26 \text{ M}^{-1} \text{ s}^{-1}$.

The biggest enhancement was observed for the Ca complex **6** ($k_2^{\text{Ca}} = 1386 \text{ M}^{-1} \text{ s}^{-1}$). It is interesting to note that the trend for HAT is essentially the reverse of that observed for the kinetics of tautomer formation. The Ca tautomer, being the slowest to form, was found to be most reactive towards HAT. Sc and Yb, similar to TFA, showed fast kinetics of formation, yet their HAT rate constants were quite comparable to the manganese(V)-oxo complex **1**. Factors that influence HAT are not evident from the available data so far; there is no trend that can be discerned with respect to electronics or sterics. The borane Lewis acid, $\text{B}(\text{C}_6\text{F}_5)_3$, falls in the middle again between the bookends, as it did for the kinetics of tautomer formation. These results highlight the importance of the Lewis acid in activating the oxo complex and that the rates of HAT are sensitive to the nature of the Lewis acid, spanning almost two orders of magnitude in reaction rate constants. Furthermore, it is worthy to note that calcium provided superior activity in activating/enhancing the redox activity of manganese(V)-oxo, as exemplified by this HAT reaction. Calcium is involved in the oxygen evolving complex (OEC) and could be playing a similar role in kinetically enhancing the redox activity of the manganese-oxo in the cubane cluster.

In conclusion, we have demonstrated that high-valent manganese(V)-oxo corrole complex **1** undergoes valence tautomerization with a variety of different Lewis acids. The rate at which these valence tautomers are formed varies over five orders of magnitude. Although sterics might play a part, electronic factors appear to be the primary influencer. Valence tautomers of Zn and Ca enhance the rate of HAT to the manganese(V)-oxo by 21 and 33 times that for complex **1**, respectively. The trend for HAT is inversely correlated to the tautomer formation rate constants. The superior kinetics of the Ca tautomer is consistent with nature's choice in using Ca in the OEC. The identity of the Lewis acid plays an important role in the redox kinetics of the manganese(V)-oxo compound.

Acknowledgements

C.J.B. thanks Xikang Zhao for helpful suggestions and discussion. This research was supported by a grant from the U.S. National Science Foundation (CHE-1463900).

Keywords: hydrogen atom transfer • manganese • metal-oxo compounds • porphyrinoids • valence tautomers

- [1] a) M. J. Gunter, P. Turner, *Coord. Chem. Rev.* **1991**, *108*, 115–161; b) M. Sono, M. P. Roach, E. D. Coulter, J. H. Dawson, *Chem. Rev.* **1996**, *96*, 2841–2888.
[2] a) B. Meunier, S. P. de Visser, S. Shaik, *Chem. Rev.* **2004**, *104*, 3947–3980; b) Z. Gross, *J. Biol. Inorg. Chem.* **2001**, *6*, 733–738; c) J. L. McLain, J. Lee, J. T. Groves, *Biomimetic Oxidations Catalyzed by Transition Metal Complexes*, Imperial College Press, London, **2011**, pp. 91–169.
[3] I. G. Denisov, T. M. Makris, S. G. Sligar, I. Schlichting, *Chem. Rev.* **2005**, *105*, 2253–2278.
[4] M. Guo, H. Dong, J. Li, B. Cheng, Y.-q. Huang, Y.-q. Feng, A. Lei, *Nat. Commun.* **2012**, *3*, 1190.

- [5] a) A. Ivancich, H. M. Jouve, B. Sartor, J. Gaillard, *Biochemistry* **1997**, *36*, 9356–9364; b) M. J. Benecky, J. E. Frew, N. Scowen, P. Jones, B. M. Hoffman, *Biochemistry* **1993**, *32*, 11929–11933; c) H. M. Jouve, P. Andreoletti, P. Gouet, J. Hajdu, J. Gagnon, *Biochimie* **1997**, *79*, 667–671.
[6] a) P. R. Ortiz de Montellano, *Chem. Rev.* **2010**, *110*, 932–948; b) T. Omura, *Biochem. Biophys. Res. Commun.* **1999**, *266*, 690–698; c) J. Rittle, M. T. Green, *Science* **2010**, *330*, 933–937.
[7] a) H. B. Dunford, J. S. Stillman, *Coord. Chem. Rev.* **1976**, *19*, 187–251; b) S. L. Edwards, X. Nguyen Huu, R. C. Hamlin, J. Kraut, *Biochemistry* **1987**, *26*, 1503–1511; c) W. R. Patterson, T. L. Poulos, D. B. Goodin, *Biochemistry* **1995**, *34*, 4342–4345; d) C. M. Hosten, A. M. Sullivan, V. Palaniappan, M. M. Fitzgerald, J. Terner, *J. Biol. Chem.* **1994**, *269*, 13966–13978; e) A. Khindaria, S. D. Aust, *Biochemistry* **1996**, *35*, 13107–13111; f) D. A. Proshlyakov, I. R. Paeng, K.-J. Paeng, T. Kitagawa, *Biospectroscopy* **1996**, *2*, 317–329; g) H.-P. Hersleth, U. Ryde, P. Rydberg, C. H. Görbitz, K. K. Andersson, *J. Inorg. Biochem.* **2006**, *100*, 460–476; h) R. K. Behan, M. T. Green, *J. Inorg. Biochem.* **2006**, *100*, 448–459; i) B. Chance, L. Powers, Y. Ching, T. Poulos, G. R. Schonbaum, I. Yamazaki, K. G. Paul, *Archives of Biochemistry and Biophysics* **1984**, *235*, 596–611; j) J. E. Penner-Hahn, K. Smith Eble, T. J. McMurry, M. Renner, A. L. Balch, J. T. Groves, J. H. Dawson, K. O. Hodgson, *J. Am. Chem. Soc.* **1986**, *108*, 7819–7825.
[8] *Cytochrome P450: Structure, Mechanism, and Biochemistry*, 4th ed., Springer, Berlin, Heidelberg, **2015**.
[9] a) J. P. McEvoy, G. W. Brudvig, *Chem. Rev.* **2006**, *106*, 4455–4483; b) P. E. M. Siegbahn, *Acc. Chem. Res.* **2009**, *42*, 1871–1880; c) Y. Umena, K. Kawakami, J.-R. Shen, N. Kamiya, *Nature* **2011**, *473*, 55–60.
[10] a) E. Y. Tsui, J. S. Kanady, T. Agapie, *Inorg. Chem.* **2013**, *52*, 13833–13848; b) S. Mukherjee, J. A. Stull, J. Yano, T. C. Stamatas, K. Pringouri, T. A. Stich, K. A. Abboud, R. D. Britt, V. K. Yachandra, G. Christou, *Proc. Natl. Acad. Sci. USA* **2012**, *109*, 2257–2262; c) L. Dong, Y. Wang, Y. Lv, Z. Chen, F. Mei, H. Xiong, G. Yin, *Inorg. Chem.* **2013**, *52*, 5418–5427; d) W. W. Y. Lam, S.-M. Yiu, J. M. N. Lee, S. K. Y. Yau, H.-K. Kwong, T.-C. Lau, D. Liu, Z. Lin, *J. Am. Chem. Soc.* **2006**, *128*, 2851–2858; e) Y. J. Park, J. W. Ziller, A. S. Borovik, *J. Am. Chem. Soc.* **2011**, *133*, 9258–9261; f) H. Yoon, Y.-M. Lee, X. Wu, K.-B. Cho, R. Sarangi, W. Nam, S. Fukuzumi, *J. Am. Chem. Soc.* **2013**, *135*, 9186–9194; g) J. Chen, Y.-M. Lee, K. M. Davis, X. Wu, M. S. Seo, K.-B. Cho, H. Yoon, Y. J. Park, S. Fukuzumi, Y. N. Pushkar, W. Nam, *J. Am. Chem. Soc.* **2013**, *135*, 6388–6391.
[11] a) C. M. Barzilay, S. A. Sibilina, T. G. Spiro, Z. Gross, *Chem. Eur. J.* **1995**, *1*, 222–231; b) N. Ehlinger, W. R. Scheidt, *Inorg. Chem.* **1999**, *38*, 1316–1321.
[12] H. M. Neu, T. Yang, R. A. Baglia, T. H. Yosca, M. T. Green, M. G. Quesne, S. P. de Visser, D. P. Goldberg, *J. Am. Chem. Soc.* **2014**, *136*, 13845–13852.
[13] a) L. Simkhovich, A. Mohammed, I. Goldberg, Z. Gross, *Chem. Eur. J.* **2001**, *7*, 1041–1055; b) A. E. Meier-Callahan, A. J. Di Bilio, L. Simkhovich, A. Mohammed, I. Goldberg, H. B. Gray, Z. Gross, *Inorg. Chem.* **2001**, *40*, 6788–6793.
[14] a) P. Leeladee, R. A. Baglia, K. A. Prokop, R. Latifi, S. P. de Visser, D. P. Goldberg, *J. Am. Chem. Soc.* **2012**, *134*, 10397–10400; b) J. P. T. Zaragoza, R. A. Baglia, M. A. Siegler, D. P. Goldberg, *J. Am. Chem. Soc.* **2015**, *137*, 6531–6540; c) R. A. Baglia, K. A. Prokop-Prigge, H. M. Neu, M. A. Siegler, D. P. Goldberg, *J. Am. Chem. Soc.* **2015**, *137*, 10874–10877; d) R. A. Baglia, M. Dürr, I. Ivanović-Burmazović, D. P. Goldberg, *Inorg. Chem.* **2014**, *53*, 5893–5895.
[15] C. J. Bougher, S. Liu, S. D. Hicks, M. M. Abu-Omar, *J. Am. Chem. Soc.* **2015**, *137*, 14481.
[16] a) Z. Gross, N. Galili, L. Simkhovich, I. Saltsman, M. Botoshansky, D. Bläser, R. Boese, I. Goldberg, *Org. Lett.* **1999**, *1*, 599–602; b) Z. Gross, G. Golubkov, L. Simkhovich, *Angew. Chem. Int. Ed.* **2000**, *39*, 4045–4047; *Angew. Chem.* **2000**, *112*, 4211–4213; c) M. J. Zdilla, M. M. Abu-Omar, *J. Am. Chem. Soc.* **2006**, *128*, 16971–16979; d) H.-Y. Liu, T.-S. Lai, L.-L. Yeung, C. K. Chang, *Org. Lett.* **2003**, *5*, 617–620.
[17] S. Kundu, E. Miceli, E. R. Farquhar, K. Ray, *Dalton Trans.* **2014**, *43*, 4264–4267.

Received: September 27, 2016

Published online on October 28, 2016