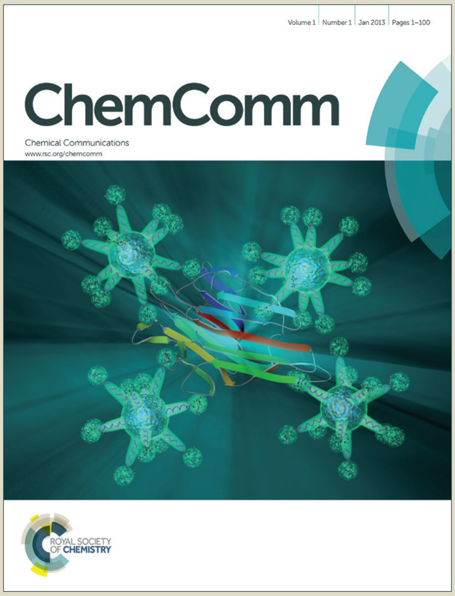
ChemComm

This article can be cited before page numbers have been issued, to do this please use: T. M. Laine, M. Kärkäs, R. liao, T. Åkermark, B. Lee, E. A. Karlsson, P. Siegbahn and B. Akermark, *Chem. Commun.*, 2014,



Dynamic Article Links ▶
View Article Online
DOI: 10.1039/C4CC08606F

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Efficient Photochemical Water Oxidation by a Dinuclear Molecular Ruthenium Complex

Tanja M. Laine,[a] Markus D. Kärkäs,*[a] Rong-Zhen Liao,*[a] Torbjörn Åkermark,[a] Bao-Lin Lee,[a] Erik A. Karlsson,[a] Per E. M. Siegbahn,[a] and Björn Åkermark*[a]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Herein is described the preparation of a dinuclear molecular Ru catalyst for H_2O oxidation. The prepared catalyst mediates the photochemical oxidation of H_2O with an efficiency comparable to state-of-the-art catalysts.

The development of sources of renewable energy is an increasingly acute problem for mankind. An attractive option would be to utilize solar energy but in order to use its full potential, means of storing it have to be developed. Solar driven splitting of H_2O into H_2 and O_2 provides an attractive way of achieving this. However, this process is very intricate because it involves multi-electron transfer, extensive bond breaking and bond formation. In the splitting of H_2O, the stumbling block is the oxidation of H_2O to generate molecular oxygen, electrons, and protons (Eq. 1). This is due to the fact that H_2O oxidation involves strongly oxidizing intermediates which leads to decomposition of the catalysts. There is thus an urgent need to develop more robust and efficient water oxidation catalysts (WOCs).[1]

$$2\,H_2O \rightarrow O_2 + 4\,H^+ + 4\,e^- \qquad (1)$$

During the past years a number of efficient Ru WOCs have been presented, both dinuclear[2] and mononuclear.[3] Much work has focused on mononuclear complexes because of the relative simplicity by which these complexes can be synthesized and mechanistically studied, thus aiding the development of improved WOCs. In addition to the widely developed Ru-based WOCs, earth-abundant metal WOCs based on Mn,[4] Co,[5] Fe[6] and Cu[7] have been reported.

The generation of ligands that can strongly bind and stabilize metal centers in high-valent oxidation states is of great interest. Thus far, the majority of the developed WOCs require a powerful sacrificial oxidant, such as Ce^{IV}, to drive H_2O oxidation. However, a sustainable H_2O splitting system needs a light-absorbing photosensitizer that can be regenerated and is stable at neutral pH. An appealing approach is to drive H_2O oxidation with $[Ru(bpy)_3]^{3+}$ type oxidants, which can be photogenerated from the well-studied $[Ru(bpy)_3]^{2+}$-type complexes.[8,9] This can be realized by lowering the redox potentials of the WOCs, by introducing anionic ligands into the ligand frameworks of the WOCs.[3f,g,10,11]

We have recently reported on such a ligand (**1**), which contains phenol and imidazole donor groups.[12] However, reaction with $Ru(DMSO)_4Cl_2$ resulted in a dimeric Ru complex with a 1:1 ratio of Ru/ligand, instead of the anticipated dinuclear complex. Since this complex did indeed oxidize H_2O, using $[Ru(bpy)_3]^{3+}$ as oxidant, we decided to prepare a more open ligand that could potentially give a dinuclear complex. Ligand **2**, where the bridging phenol unit has been replaced by a pyrazole moiety provides such an open structure. As expected, coordination of two Ru centers yielded the dinuclear Ru complex **3** (Fig. 1 and Fig. 2). Herein, we show that the dinuclear Ru complex **3** catalyzes photochemical H_2O oxidation with high activity, reaching turnover numbers (TONs; defined as produced moles of O_2 per mole catalyst) of ~900, which is, to the best of our knowledge, among the highest obtained for a molecular catalyst in a single run. The observed high catalytic activity is ascribed to the ability of the designed ligand framework to stabilize the metal centers in high-valent redox states. This work thus highlights the importance of using negatively charged ligand scaffolds to carry out the oxidation of H_2O, which could be a general strategy for the design of future artificial WOCs with even higher catalytic efficiencies.

Ligand **2** was synthesized according to Scheme S1, starting from commercially available 3,5-dimethyl pyrazole **4**. The dinuclear $Ru_2^{II,III}$ complex **3** ($[(H_2L)Ru_2^{II,III}(pic)_6](PF_6)_2$) was obtained by refluxing the Ru precursor $[Ru(DMSO)_4Cl_2]$ and ligand **2** followed by the addition of picoline. The structure of the dinuclear Ru complex **3** was supported by several methods, such as ^1H NMR, high-resolution mass spectrometry (HRMS), elemental analysis and electron paramagnetic resonance (EPR). Initial ^1H NMR experiments of Ru complex **3** only resulted in broad signals due to the paramagnetic nature of the $Ru_2^{II,III}$ complex **3**. However, addition of a reductant, sodium dithionite ($Na_2S_2O_4$), resulted in distinct signals, which supported the proposed structure of the developed complex. HRMS measurements of the complex in positive mode resulted in a peak

---

[a] *Department of Organic Chemistry, Arrhenius Laboratory, Stockholm University, SE-106 91 Stockholm, Sweden. E-mail: markusk@organ.su.se, rongzhen@organ.su.se, bjorn.akermark@organ.su.se; Tel: +46 8 163223.*

† *Electronic Supplementary Information (ESI) available: Experimental details, NMR, electrochemistry, mass spectra and quantum chemical calculations details. See DOI: 10.1039/b000000x/*

View Article Online
DOI: 10.1039/C4CC08606F

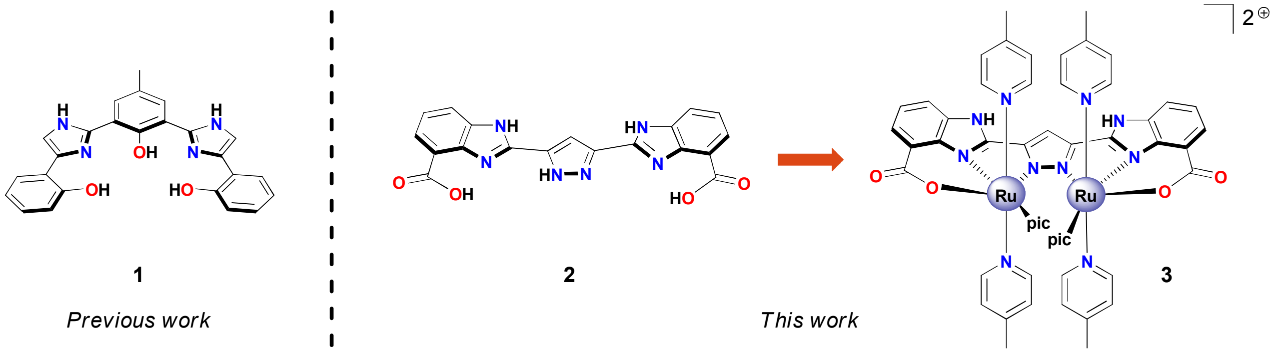
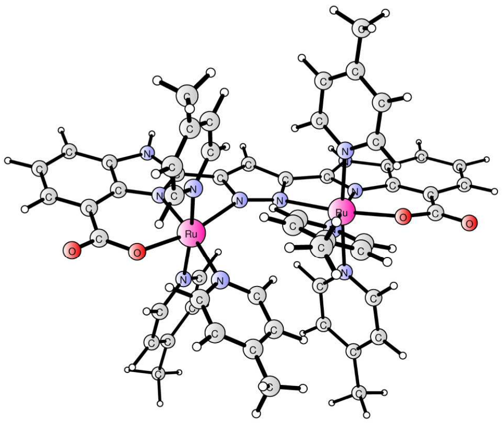


Fig. 1 Molecular structures of ligand **1**, ligand **2** and the dinuclear Ru complex **3** (where pic = 4-picoline).

with a characteristic isotope pattern at *m/z* 1146.2155, which could be assigned to $[\{(H_2L)Ru_2^{II,III}(pic)_6\}^{2+} - H^+]^+$ ($[\mathbf{3} - H^+]^+$). The calculated structure of Ru complex **3** is depicted in Fig. 2. The electrochemistry of Ru complex **3** was subsequently studied by means of cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in aqueous buffered solutions (phosphate buffer; 0.1 M, pH 7.2). From CV, a catalytic current corresponding to the electrochemical oxidation of H_2O was observed with an onset potential of ~1.20 V vs. NHE, as shown in Fig. S19. The DPV is depicted in Fig. S20 and revealed several redox peaks, which were assigned to the formal redox processes $Ru_2^{II,II} \rightarrow Ru_2^{II,III} \rightarrow Ru_2^{III,III} \rightarrow Ru_2^{III,IV} \rightarrow Ru_2^{IV,IV} \rightarrow Ru_2^{IV,V}$, where the latter state triggers O-O bond formation. The electrochemistry was subsequently studied at pH 1 (Figs. S21-S24). Also here, several redox events were observed, suggesting that the dinuclear Ru complex **3** is able to accommodate a wide variety of redox states. From the electrochemical measurements it is clear that the use of ligand **2** in Ru complex **3** results in lowering of the redox potentials and stabilizes the Ru centers in high-valent states, suggesting that H_2O oxidation can be driven by photogenerated $[Ru(bpy)_3]^{3+}$-type complexes.



3

$[(H_2L)Ru_2^{II,III}(pic)_6]^{2+}$

Fig. 2 Calculated structure of the dinuclear Ru complex **3** ($[(H_2L)Ru_2^{II,III}(pic)_6]^{2+}$).

The activity of complex **3** was initially evaluated for H_2O oxidation under neutral conditions, in an aqueous buffered solution (0.1 M, pH 7.2), using pregenerated $[Ru(bpy)_3]^{3+}$ as a mild one-electron chemical oxidant ($E_{1/2}$ Ru^{III}/Ru^{II} = 1.26 V vs. NHE). The evolved gaseous products were monitored and quantified by real-time mass spectrometry (MS). Indeed, when an aqueous solution containing complex **3** was added to the $[Ru(bpy)_3]^{3+}$ oxidant, O_2 evolution was immediately triggered and resulted in high TONs and initial turnover frequencies (TOFs; defined as produced moles of O_2 per mol catalyst per unit time) (Fig.S17 and Table 1). The source of the oxygen atoms in the evolved O_2 was also studied, using isotopically labeled H_2O ($H_2^{18}O$), whereby the different isotopes $^{18,18}O_2$, $^{16,18}O_2$ and $^{16,16}O_2$ were measured in real-time with MS (Fig. S17). The ratio of the different O_2 isotopes was in agreement with the calculated values, highlighting that H_2O is the sole source of the two oxygen atoms in the evolved O_2.

An important question was now if Ru complex **3** was able to mediate photochemical H_2O oxidation. The studied three-component catalytic system thus consisted of a $[Ru(bpy)_3]^{2+}$-type complex as the light-absorbing component, sodium persulfate ($Na_2S_2O_8$) as the sacrificial electron acceptor and Ru WOC **3**. In the Initial experiments, the stronger photosensitizer $[Ru(bpy)_2(deeb)]^{2+}$ ($E_{1/2}$ Ru^{III}/Ru^{II} = 1.40 V vs. NHE; deeb = diethyl (2,2'-bipyridine)-4,4'-dicarboxylate) was used in aqueous phosphate buffered solutions at pH 7.2 (Fig. 3).

However, replacing the strong photosensitizer $[Ru(bpy)_2(deeb)]^{2+}$ with the milder $[Ru(bpy)_3]^{2+}$ photosensitizer strongly decreased the TON (not shown), which can perhaps be explained by the low thermodynamic driving force ($E_{1/2}$ Ru^{III}/Ru^{II} for $[Ru(bpy)_3]$ = 1.26 V and $E_{1/2\ onset}$ = ~1.20 V vs. NHE). To ensure that the reaction between the photosensitizer and persulfate is not an important source of O_2 the even milder photosensitizer $[Ru(dmb)_3]^{2+}$ (dmb = 4,4'-dimethyl-2,2'-bipyridine), which generates a Ru^{III} complex with a redox potential of 1.10 V vs. NHE, was also used. As was anticipated, this potential is insufficient for H_2O oxidation and only traces of O_2 were generated (Fig. 3).

It was therefore decided to continue using the stronger $[Ru(bpy)_2(deeb)]^{2+}$ photosensitizer. Further experiments focused on studying the effect of pH on the catalytic O_2 evolution activity

View Article Online
DOI: 10.1039/C4CC08606F

since it was previously shown that the catalytic activity could be pH-dependent.[13] The photochemical experiments were therefore performed at different pH, under otherwise unchanged conditions (Fig. S18).

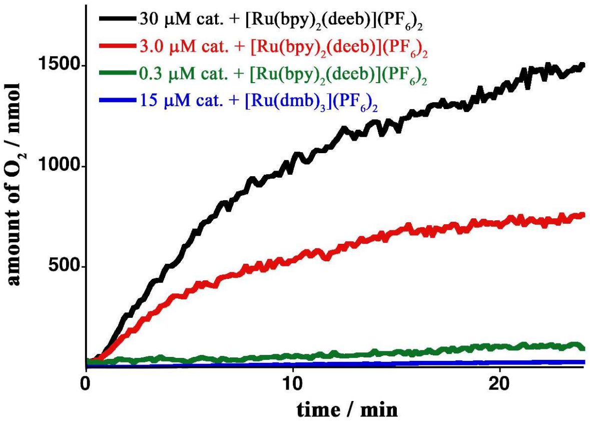


Fig. 3 Photochemical H_2O oxidation catalyzed by dinuclear Ru complex **3** at different catalyst concentrations. Reaction conditions: Reactions were performed in an aqueous phosphate buffer solution (0.1 M, pH 7.2, 0.50 mL) containing Ru complex **3**, $[Ru(bpy)_2(deeb)](PF_6)_2$ or $[Ru(dmb)_3](PF_6)_2$ as photosensitizer (0.60 mM) and $Na_2S_2O_8$ as sacrificial electron acceptor (23.5 mM).

Carrying out the catalytic experiments at higher pH would intuitively be expected to result in a higher catalytic activity due to the higher driving force for H_2O oxidation at this pH. However, this was not what was observed. At pH 8.2, almost no activity at all was observed, most likely due to decomposition of the oxidized photosensitizer. Driving H_2O oxidation at lower pH is hence associated with a lower driving force, however, it is believed that photosenssitizer decomposition is reduced under these conditions. At pH 5.5, the lower driving force thus reduced the amounts of generated O_2.

Table 1 Catalytic data for the dinuclear Ru complex **3** in chemical and photochemical H_2O oxidation.

Concentration [μM]	Chemical Oxidation[a] pH 7.2 TON (TOF[c])	Chemical Oxidation[a] pH 6.2 TON (TOF[c])	Photochemical Oxidation[b] pH 7.2 TON	Photochemical Oxidation[b] pH 6.2 TON
30	-	-	100	-
3.0	-	-	500	890
0.6	470 (1.3)	800 (0.5)	-	-
0.3	-	-	830	-

[a] Reaction conditions: An aqueous phosphate buffer solution (0.1 M, 0.50 mL) containing Ru complex **3** (0.60 μM) was added to the oxidant $[Ru(bpy_3)](PF_6)_3$ (3.0 mg, 3.0 μmol). [b] Reaction conditions: Reactions were performed in an aqueous phosphate buffer solution (0.1 M, pH 7.2, 0.50 mL) containing Ru complex **3** (the concentrations used are those that are indicated in the Table), $[Ru(bpy)_2(deeb)](PF_6)_2$ as photosensitizer (0.60 mM) and $Na_2S_2O_8$ as sacrificial electron acceptor (23.5 mM). [c] Turnover frequencies (TOFs) are given in s^{-1}.

It could subsequently be shown that pH 6.2 resulted in the best activity (Fig. S18). Performing the photochemical experiments at pH 6.2 resulted in increased catalytic activity to reach an impressive TON of ~900 when using $[Ru(bpy)_2(deeb)]^{2+}$ as photosensitizer (Fig. S18 and Table 1). It is believed that at pH 6.2, photosensitizer decomposition is reduced while still maintaining a relatively high driving force for carrying out H_2O oxidation. These two beneficial effects thus give rise to the catalytic efficiency observed at pH 6.2. Collectively, this shows that complex **3** is an unusually efficient donor of electrons to the oxidized photosensitizer, thus resulting in high catalytic efficiency, and highlights the ability of the custom-synthesized ligand **2** to facilitate access to the required high-valent redox states.

Conclusions

To conclude, a novel dinuclear Ru complex based on ligand **2** has been synthesized. The ligand scaffold was designed to stabilize the Ru centers at high oxidation states, which is of importance in H_2O oxidation catalysis. This approach was successful and resulted in an active WOC that could promote both chemical and photochemical H_2O oxidation with mild one-electron $[Ru(bpy)_3]^{3+}$-type oxidants. In the photochemical system, the developed Ru complex 3 showed to be an efficient WOC and gave TONs comparable to state-of-the-art WOCs. Insight into the catalytic features associated with complex **3** revealed that the designed ligand architecture has an important role by stabilizing the metal centers in a variety of different redox states, which is of fundamental importance during the multi-electron oxidation of H_2O. This highlights that the engineering of WOCs comprised of anionic ligand scaffolds could be a general strategy for future construction of more efficient WOCs.

Financial support from the Knut and Alice Wallenberg Foundation, the Swedish Research Council, the Carl Trygger Foundation and the Swedish Energy Agency is gratefully acknowledged.

Notes and references

1 (*a*) M. D. Kärkäs, O. Verho, E. V. Johnston and B. Åkermark, *Chem. Rev.*, 2014, DOI: 10.1021/cr400572f; (*b*) N. S. Lewis and D. G. Nocera, *Proc. Nat. Acad. Sci. U. S. A.*, 2006, **103**, 15729-15735; (*c*) M. D. Kärkäs, E. V. Johnston, O. Verho and B. Åkermark, *Acc. Chem. Res.*, 2014, **47**, 100-111.

2 (*a*) H.-W. Tseng, R. Zong, J. T. Muckerman and R. Thummel, *Inorg. Chem.*, 2008, **47**, 11763-11773; (*b*) X. Sala, I. Romero, M. Rodríguez, L. Escriche and A. Llobet, *Angew. Chem. Int. Ed.*, 2009, **48**, 2842-2852; (*c*) Y. Xu, T. Åkermark, V. Gyollai, D. Zou, L. Eriksson, L. Duan, B. Åkermark and L. Sun, *Inorg. Chem.*, 2009, **48**, 2717-2719; (*d*) Y. Xu, A. Fischer, L. Duan, L. Tong, E. Gabrielsson, B. Åkermark and L. Sun, *Angew. Chem. Int. Ed.*, 2010, **49**, 8934-8937.

3 (*a*) J. J. Concepcion, J. W. Jurss, J. L. Templeton and T. J. Meyer, *J. Am. Chem. Soc.*, 2008, **130**, 16462-16463; (*b*) X. Sala, M. Z. Ertem, L. Vigara, T. K. Todorova, W. Chen, R. C. Rocha, F. Aquilante, C. J. Cramer, L. Gagliardi and A. Llobet, *Angew. Chem. Int. Ed.*, 2010, **49**, 7745-7747; (*c*) D. J. Wasylenko, C. Ganesamoorthy, M. A. Henderson and C. P. Berlinguette, *Inorg. Chem.*, 2011, **50**, 3662-3672; (*d*) L. Duan, F. Bozoglian, S. Mandal, B. Stewart, T. Privalov, A. Llobet and L. Sun, *Nature Chem.*, 2012, **4**, 418-423; (*e*) N. Kaveevivitchai, R. Zong, H.-W. Tseng, R. Chitta and R. P. Thummel,

View Article Online
DOI: 10.1039/C4CC08606F

Inorg. Chem., 2012, **51**, 2930-2939; (*f*) M. D. Kärkäs, T. Åkermark, E. V. Johnston, S. R. Karim, T. M. Laine, B.-L. Lee, T. Åkermark, T. Privalov and B. Åkermark, *Angew. Chem. Int. Ed*., 2012, **51**, 11589-11593; (*g*) M. D. Kärkäs, T. Åkermark, H. Chen, J. Sun and B. Åkermark, *Angew. Chem. Int. Ed*., 2013, **52**, 4189-4193.

4 (a) J. Limburg, J. S. Vrettos, L. M. Liable-Sands, A. L. Rheingold, R. H. Crabtree and G. W. Brudvig, *Science,* 1999, **283**, 1524-1527; (b) A. K. Poulsen, A. Rompel and C. J. McKenzie, *Angew. Chem. Int. Ed*., 2005, **44**, 6916-6920; (c) E. A. Karlsson, B.-L. Lee, T. Åkermark, E. V. Johnston, M. D. Kärkäs, J. Sun, Ö. Hansson, J.-E. Bäckvall and B. Åkermark, *Angew. Chem. Int. Ed*., 2011, **50**, 11715-11718; (d) E. A. Karlsson, B.-L. Lee, R.-Z. Liao, T. Åkermark, M. D. Kärkäs, V. Saavedra Becerril, P. E. M. Siegbahn, X. Zou, M. Abrahamsson and B. Åkermark, *ChemPlusChem,* 2014, **79**, 936-950; (e) W. A. A. Arafa, M. D. Kärkäs, B.-L. Lee, T. Åkermark, R.-Z. Liao, H.-M. Berends, J. Messinger, P. E. M. Siegbahn and B. Åkermark, *Phys. Chem. Chem. Phys.,* 2014, **16**, 11950-11964.

5 (*a*) Q. Yin, J. M. Tan, C. Besson, Yurii V. Geletii, D. G. Musaev, A. E. Kuznetsov, Z. Luo, K. I. Hardcastle and C. L. Hill, *Science,* 2010, **328**, 342-345; (*b*) H. Lei, A. Han, F. Li, M. Zhang, Y. Han, P. Du, W. Lai and R. Cao, *Phys. Chem. Chem. Phys*., 2014, **16**, 1883-1893.

6 (*a*) W. C. Ellis, N. D. McDaniel, S. Bernhard and T. J. Collins, *J. Am. Chem. Soc*., 2010, **132**, 10990-10991; (*b*) J. Lloret Fillol, Z. Codolà, I. Garcia-Bosch, L. Gómez, J. J. Pla and M. Costas, *Nature Chem*., 2011, **3**, 807-813.

7 (*a*) S. M. Barnett, K. I. Goldberg and J. M. Mayer, *Nature Chem*., 2012, **4**, 498-502; (*b*) Z. Chen and T. J. Meyer, *Angew. Chem. Int. Ed*., 2013, **52**, 700-703.

8 A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser and A. von Zelewsky, *Coord. Chem. Rev*., 1988, **84**, 85-277.

9 J. M. R. Narayanam and C. R. J. Stephenson, *Chem. Soc. Rev*., 2011, **40**, 102-113.

10 B.-L. Lee, M. D. Kärkäs, E. V. Johnston, A. K. Inge, L.-H. Tran, Y. Xu, Ö. Hansson, X. Zou and B. Åkermark, *Eur. J. Inorg. Chem*., 2010, 5462-5470.

11 T. Norrby, A. Börje, B. Åkermark, L. Hammarström, J. Alsins, K. Lashgari, R. Norrestam, J. Mårtensson and G. Stenhagen, *Inorg. Chem*., 1997, **36**, 5850-5858.

12 M. D. Kärkäs, E. V. Johnston, E. A. Karlsson, B.-L. Lee, T. Åkermark, M. Shariatgorji, L.Ilag, Ö. Hansson, J.-E. Bäckvall and B. Åkermark, *Chem. Eur. J*., 2011, **17**, 7953-7959.

13 (*a*) Y. Xu, L. Duan, L. Tong, B. Åkermark and L. Sun, *Chem. Commun*., 2010, **46**, 6506-6508; (*b*) T. Takashima, K. Hashimoto and R. Nakamura, *J. Am. Chem.Soc*., 2012, **134**, 1519-1527.