Electronic Supplementary Information

Catalytic oxidation of alkanes by iron bispidine complexes and dioxygen: oxygen activation versus autoxidation.

Peter Comba,[a] Yong-Min Lee,[b] Wonwoo Nam[b] and Arkadius Waleska[a]*

[a] Universität Heidelberg, Anorganisch-Chemisches Institut, D-69120 Heidelberg, Germany

[b] Department of Bioinspired Science, Department of Chemistry and Nano Science, Center for Biomimetic Systems, Ewha Womans University, Seoul 120-750, Korea

The synthesis of the iron complexes *1* and *2* as triflate salts was reported previously.[1-3] UV/vis spectra were recorded on a Tidas II instrument (J&M Analytik, Essingen-Dauerwang, Germany), on an Agilent 8453 spectrometer (Santa Clara, USA) with a cooling unit by Unisoku (Osaka, Japan) or an SX18MV-R stopped flow instrument (Applied Photophysics, Leatherhead, England). EPR experiments were made with a Biospin ELEXSYS E500 spectrometer (Bruker, Karlsruhe, Germany). CV data were recorded on a CH Instruments 660 D Electrochemical Workstation (Austin, USA).

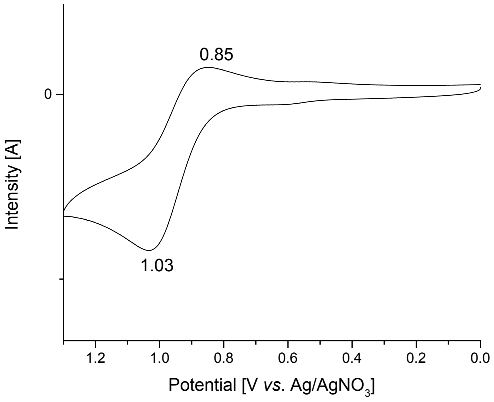

Fig. S1 CV of *1* with 0.10 M tetra-n-butylammonium perchlorate in MeCN at 25 °C at a scan rate of 200 mV/s, glassy carbon working electrode, Pt auxiliary electrode, Ag/AgNO$_3$ reference electrode (S. Wunderlich, PhD thesis, University of Heidelberg, 2010).

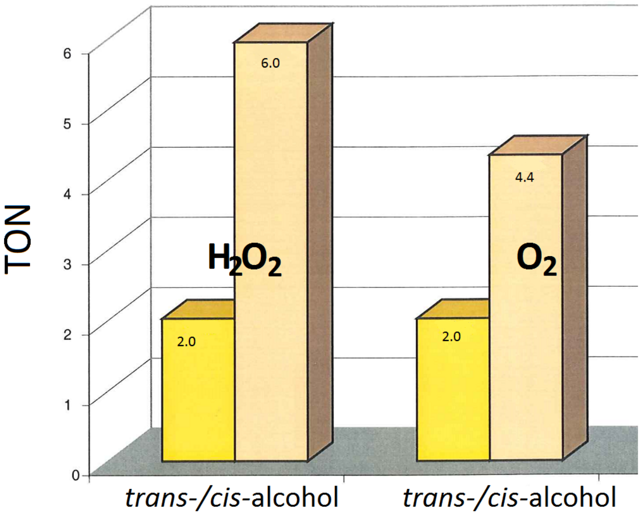

Fig. S2 Product ratios of *cis*- and *trans*-alcohol products of the oxygenation of DMCH, catalyzed by 0.70 mM of *1*, using 10 equiv. of H_2O_2 as the oxidant and 1000 equiv. of the substrate DMCH at 25 °C in MeCN (TON_{total} limited to 10, left), and 0.70 mM *1* with 1000 equiv. DMCH at 25 °C in MeCN under atmospheric conditions (right) (M. Merz, PhD thesis, University of Heidelberg, 2002); *trans*- and *cis*-alcohol refers to the configuration of the methyl groups of the main product, i.e. 1,2-dimethylcyclohexanol. 2,3-dimethylcyclohexanol and 2,3-dimethylcyclohexanone were detected as minor side products (not quantified).

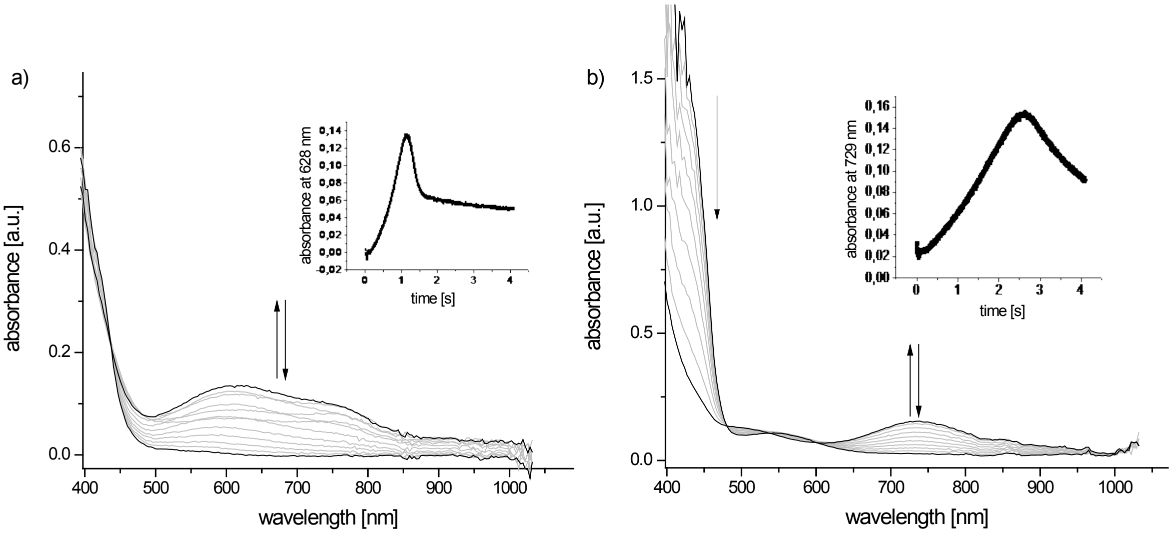

Fig. S3 UV-vis-NIR spectral changes observed in the reactions of 1.0 mM *1* (a) and 1.0 mM *2* (b) with 200 equiv. $DMCH^{aged}$ at 25 °C in MeCN (half saturated with dioxygen). Insets show the time profiles of the absorbance at 628 nm (a) and 729 nm (b).

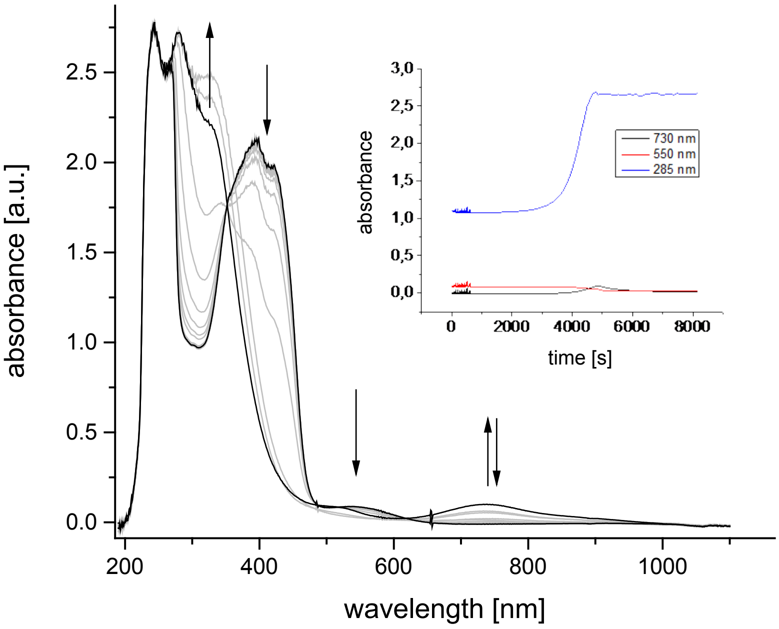

Fig. S4 UV-vis-NIR spectral changes observed in the reaction of 1.0 mM *1* with 200 equiv. DMCH at 20 °C in MeCN under ambient conditions. Inset shows the time profiles of the absorbance at 285 (blue), 550 (red) and 730 nm (black). Note that spectra are overranged and only depticted for visualization purposes of sigmoidal activation curves.

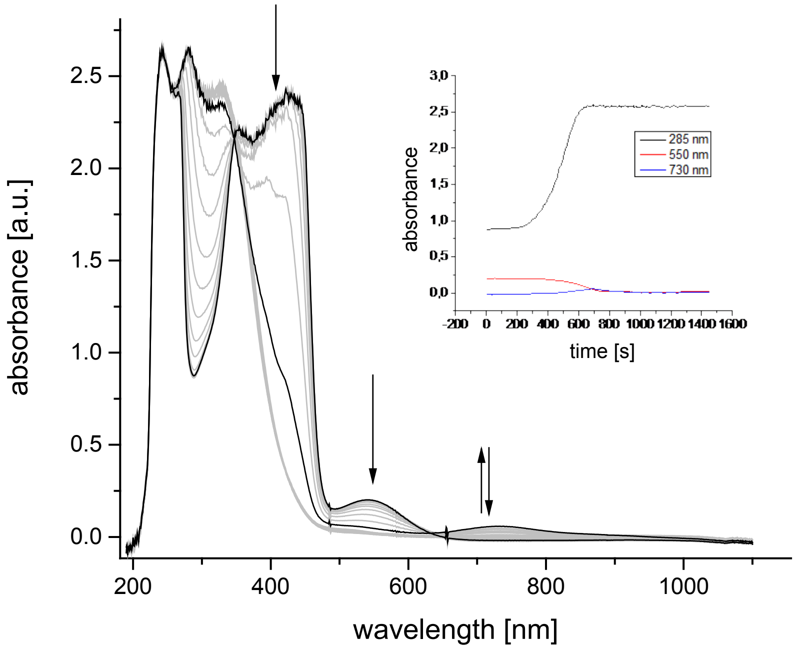

Fig. S5 UV-vis-NIR spectral changes observed in the reaction of 1.0 mM *2* with 200 equiv. cyclohexene at 0 °C in MeCN under oxygen atmosphere. Inset shows the time profiles of the absorbance at 285 (blue), 550 (red) and 730 nm (black). Note that spectra are overranged and only depticted for visualization purposes of sigmoidal activation curves.

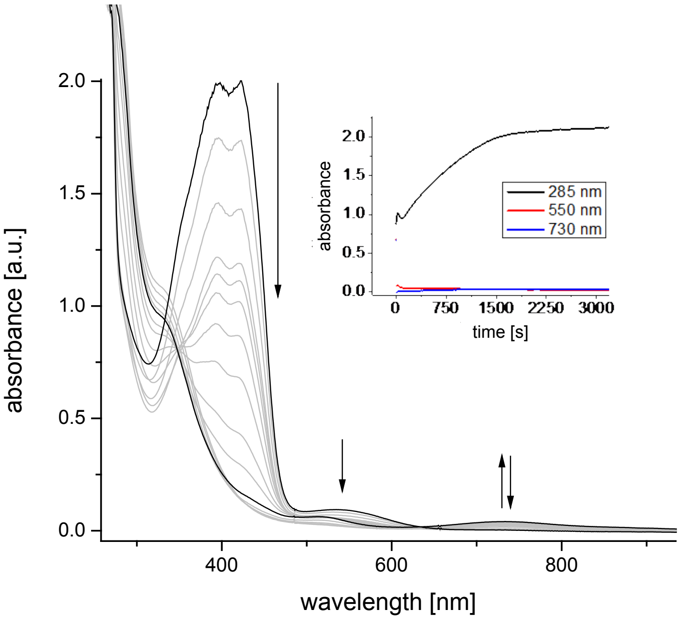

Fig. S6 UV-vis-NIR spectral changes observed in the reaction of 1.0 mM *2* with 200 equiv. cumene at 0 °C in MeCN under oxygen atmosphere. Inset shows the time profiles of the absorbance at 285 (blue), 550 (red) and 730 nm (black). Note that spectra are overranged and only depticted for visualization purposes of activation curves.

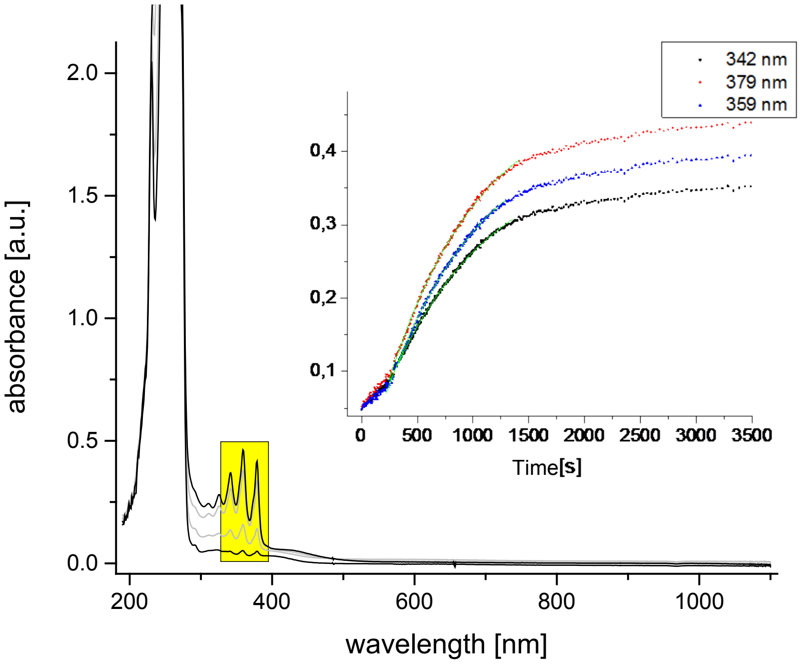

Fig. S7 UV-vis-NIR spectral changes observed in the reaction of 0.10 mM *1* with 100 equiv. 9,10-dihydroanthracene at 0 °C in dichloromethane under oxygen atmosphere (in yellow: characteristic anthracene bands). Inset shows the time profiles of the absorbance at 342 (black), 359 (red) and 379 nm (blue).

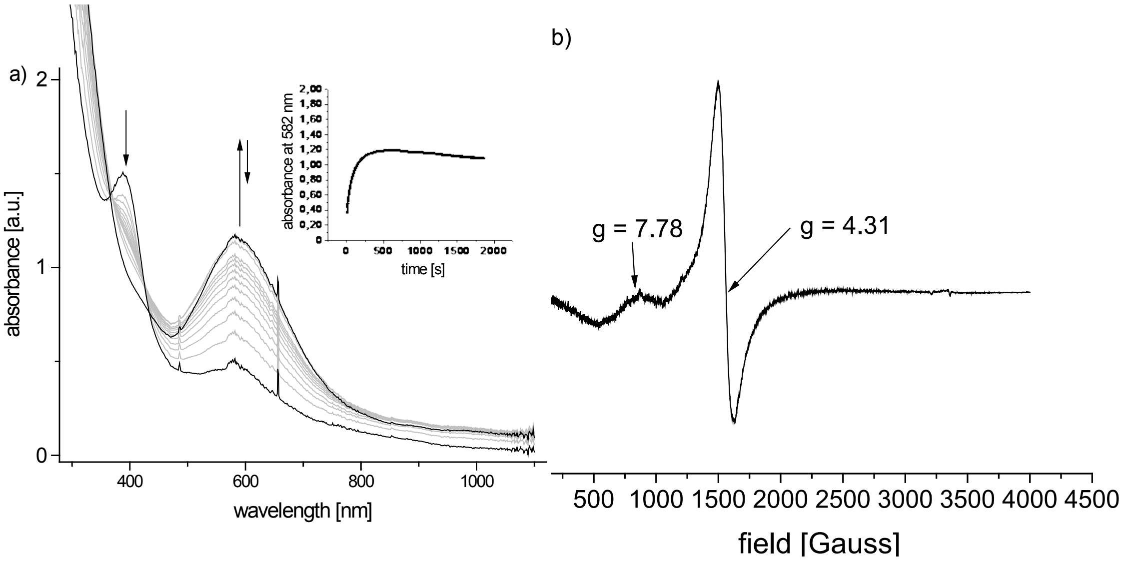

Fig. S8 (a) UV-vis-NIR spectral change observed in the reaction of 1.0 mM *1* with 200 equiv. DMCH^{aged} in O_2-saturated DCM at -80 °C. Inset shows the time profile of the absorbance at 582 nm. (b) EPR spectrum of the resulting solution obtained in the reaction of 1.0 mM *2* with 200 equiv. DMCH^{aged} in O_2-saturated DCM at -80 °C. EPR parameters: 9.4288 GHz, 5 K, 3.0×10^{-4} T modulation amplitude, 100 kHz modulation frequency.

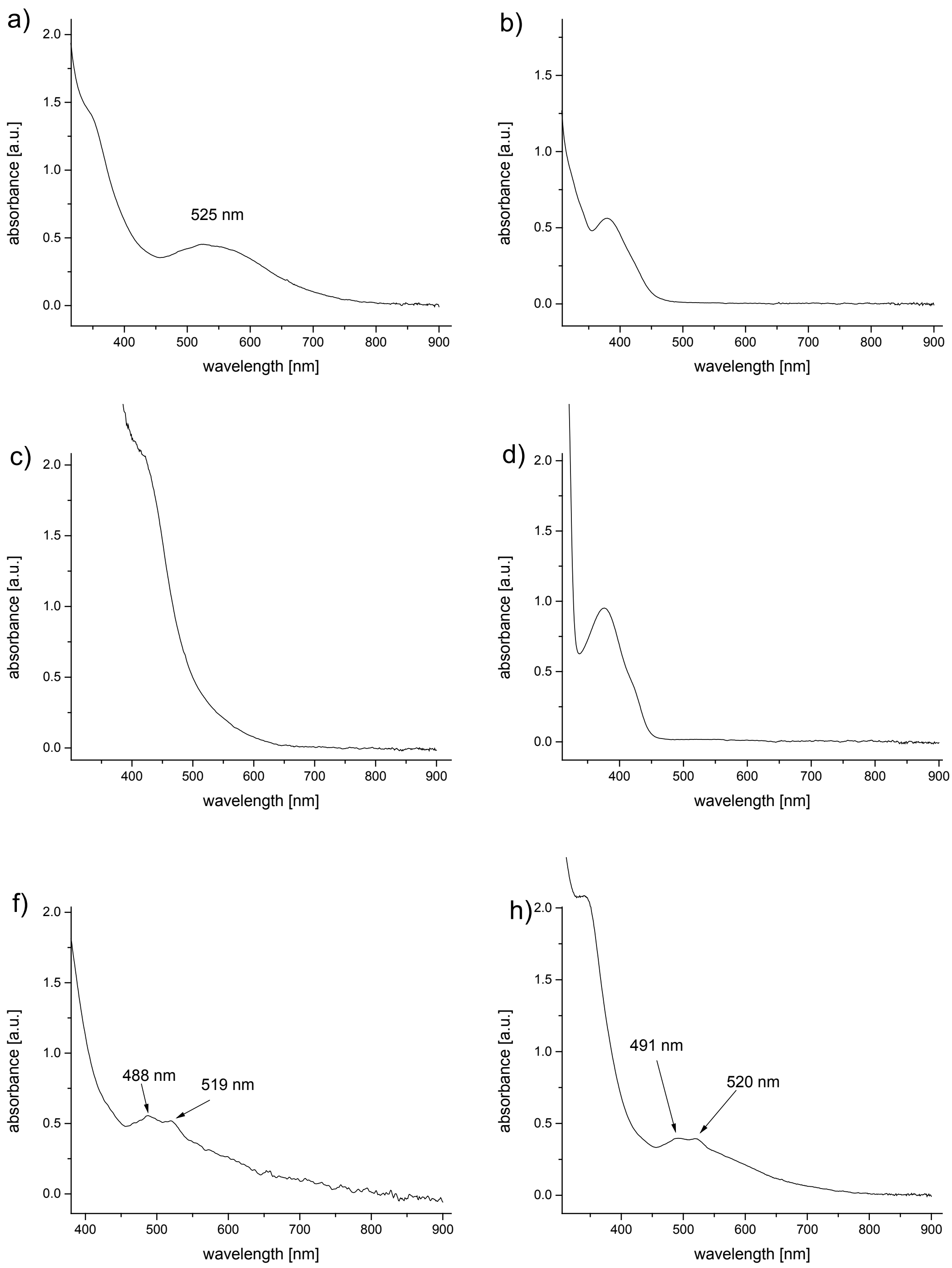

Fig. S9 UV-vis-NIR spectra of entries a – d and h in Table 1 of the main text.

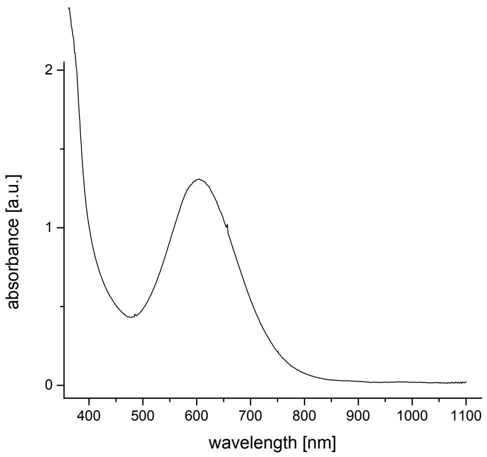

Fig. S10 UV-vis-NIR spectrum observed in the reaction of 1.0 mM *2* with 200 equiv. DMCH^{aged} in O_2-saturated DCM at -80 °C after the addition of 2 equiv. triflic acid.

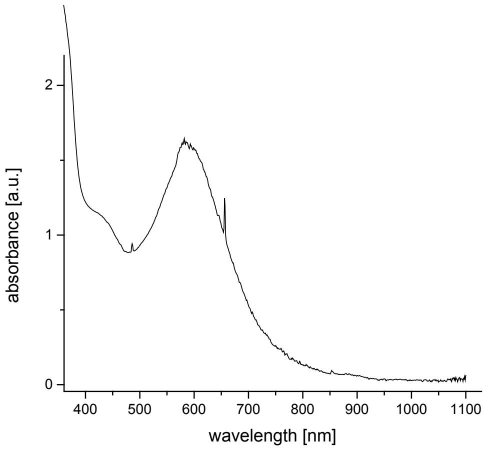

Fig. S11 UV-vis-NIR spectrum observed in the reaction of 1.0 mM *2* with 200 equiv. DMCH^{aged} in O_2-saturated DCM at -80 °C after the addition of 10 equiv. triethylamine.

Table S1 ESI-MS data of 1.0 mM *1* and 2 equiv. *tert*-butylhydroperoxide in MeCN at -40 °C (J. Bautz, PhD thesis, University of Heidelberg, 2006).

m/z (Intensity)	species	m/z (calculated
275.24 (61 %)	$[Fe^{III}(L)(OH)(MeCN)]^{2+}$	276.08
282.63 (83 %)	$[Fe^{III}(L)(OMe)(MeCN)]^{2+-}$	283.09
284.16 (100 %)	**$[Fe^{III}(L)O^{t}Bu)]^{2+}$**	283.60
643.14 (29 %)	$[Fe^{II}(L)(OTf)]^{+}$	643.08
659.91 (22 %)	$[Fe^{III}(L)(OH)(OTf)]^{+}$	660.08
674.01 (34 %)	$[Fe^{III}(L)(OMe)(OTf)]^{+}$	674.10
676.94 (47 %)	$[Fe^{IV}(L)(OH)_2(OTf)]^{+}$	677.08

References

1. P. Comba, M. Kerscher and W. Schiek, *Prog. Inorg. Chem.*, 2007, **55**, 613.

2. H. Börzel, P. Comba, K. S. Hagen, M. Merz, Y. D. Lampeka, A. Lienke, G. Linti, H. Pritzkow and L. V. Tsymbal, *Inorg. Chim. Acta*, 2002, **337**, 407-419.

3. P. Comba, B. Kanellakopulos, C. Katsichtis, A. Lienke, H. Pritzkow and F. Rominger, *J. Chem. Soc. Dalton Trans.*, 1998, 3997.