Inorganica Chimica Acta 378 (2011) 19-23

Contents lists available at SciVerse ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Efficient aerobic oxidation of hydrocarbons promoted by high-spin nonheme Fe(II) complexes without any reductant

Shinya Furukawa^a, Yutaka Hitomi^{b,*}, Tetsuya Shishido^a, Tsunehiro Tanaka^a

^a Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Kyoto Daigaku Katsura, Nishikyo-ku, Kyoto 606-8501, Japan ^b Department of Molecular Chemistry and Biochemistry, Doshisha University, Kyotanabe, Kyoto 610-0321, Japan

ARTICLE INFO

Article history: Received 3 March 2011 Received in revised form 28 July 2011 Accepted 2 August 2011 Available online 11 August 2011

Keywords: Aerobic oxidation Hydrocarbon oxidation High-spin Fe(II) complex Nonheme Fe complex

ABSTRACT

Fe(II)-tris(2-pyridylmethyl)amine complexes, Fe(II)-tpa, having different co-existing anions, [Fe(tpa) (MeCN)₂](ClO₄)₂ (**1**), [Fe(tpa)(MeCN)₂](CF₃SO₃)₂ (**2**) and [Fe(tpa)Cl₂] (**3**), were prepared. Effective magnetic moments (evaluated by the Evans method) revealed that while **1–3** in acetone and **3** in acetonitrile (MeCN) have a high-spin Fe(II) ion at 298 K, the Fe(II) ions of **1** and **2** are in the low-spin state in MeCN. The aerobic oxidation of **1–3** was monitored by UV–Vis spectral changes in acetone or MeCN under air at 298 K. Only the high-spin Fe(II)-tpa complexes were oxidized with rate constants of $k_{obs} = 0.1-1.3$ h⁻¹, while **1** and **2** were stable in MeCN. The aerobic oxidation of **1** or **2** in acetone was greatly accelerated in the presence of pure, peroxide-free cyclohexene (1000 equiv.) and yielded a large amount of oxidized products; 2-cyclohexe-1-ol (A) and 2-cyclohexene-1-one (K) (A + K: 23 940% yield based on Fe; A/K = 0.3), and cyclohexene oxide (810%). Besides cyclohexene, aerobic oxidation of norbornene, cyclooctene, ethylbenzene, and cumene proceeded in the presence of **1** in acetone at 348 K without any reductant. Essential factors in the reaction are high-spin Fe(II) ion and labile coordination sites, both of which are required to generate Fe(II)-superoxo species as active species for the H-atom abstraction of hydrocarbons.

1. Introduction

The catalytic oxidation of hydrocarbons such as alkanes, alkenes and aromatic compounds to oxygen-containing materials is one of the most important chemical transformations in industrial chemistry [1]. For economic and environmental reasons, the use of dioxygen as sole oxidant is highly desirable [2]. Since it reacts slowly with hydrocarbons owing to its triplet ground state, appropriate activation of dioxygen is required for efficient oxidation of hydrocarbons using dioxygen. In nature, such dioxygen activation is performed by iron- and/or copper-dependent enzymes such as cytochrome P450 [3], methane monooxygenase [4], tyrosinase [5], dopamine β -monooxygenases [6] and various types of mononuclear nonheme iron dioxygenases [7], where dioxygen is reductively activated via the Cu(I) or Fe(II) ion(s). It is noteworthy that a high-spin Fe(II) center activates dioxygen in heme and nonheme iron-dependent enzymes [8] and model complexes [9–11].

Previously, we reported that low spin Fe(III)-tpa catecholate complexes (tpa: tris(2-pyridylmethyl)amine, Fig. 1) have a lower dioxygen reactivity than the high-spin species, even though the former has a much higher Fe(II)-semiquinoate character [12]. This result motivated us to examine the spin-state dependency on the

* Corresponding author. Tel.: +81 077 465 7437.

dioxygen activation ability of simple Fe(II)-tpa complexes. Diebold and Hagen reported that the spin state of the Fe(II)-tpa complex is different depending on its counter anions [13]. Therefore, we prepared three Fe(II)-tpa complexes; $[Fe(tpa)(MeCN)_2](CIO_4)_2$ (1), $[Fe(tpa)(MeCN)_2](CF_3SO_3)_2$ (2) and $[Fe(tpa)Cl_2]$ (3), and examined their spin states and dioxygen activation ability. We also examined the aerobic oxidation of hydrocarbons in the presence of the Fe(II)tpa complexes.

Inorganica Chimica Acta

2. Results and discussion

2.1. Characterizations of Fe(II)-tpa complexes

The effective magnetic moments of complexes **1–3** were measured in acetonitrile (MeCN) and acetone by the Evans NMR method [14]. The μ_{eff} values, listed in Table 1, indicate that **1** and **2** possess mainly a low spin Fe(II) ion in MeCN, whereas **3** is in the high-spin state in MeCN. The spin states of Fe(II)–tpa type complexes in MeCN have been widely investigated [13,15–17]. The present results in MeCN are well consistent with the reported data [13,15,16]. In contrast, all the Fe(II) ions of **1–3** were in the high-spin states in acetone. The complexes **1** and **2** are known to be in the low spin state in the solid state [13,15]. Therefore, the high spin state in acetone suggests the dissociation of coordinated π -accepting ligand MeCN. Then, we conducted ¹⁹F and ¹H NMR study to clarify the



E-mail address: yhitomi@mail.doshisha.ac.jp (Y. Hitomi).

^{0020-1693/\$ -} see front matter @ 2011 Elsevier B.V. All rights reserved. doi:10.1016/j.ica.2011.08.004



Fig. 1. Structure of the tpa ligand.

coordination environment of the Fe(II) complex in acetone (see Figs. S1 and S2 in Supplementary material). The chemical shift of the fluorine atom of triflate anion with paramagnetic Fe(II) complex widely varies based on the chemical environment; ca.+60 (bridging triflate), ca. -10 (terminal) and ca. -80 ppm (free triflate) [18,19]. The ¹⁹F NMR spectrum of **2** in acetone- d_6 exhibited a single broad peak at -41.4 ppm ($v_{1/2}$ = 1036 Hz), which suggest that the triflate anions weakly coordinated to Fe(II) and they are equivalent [16,20]. The observed line broadening indicates a fast exchange between coordinated and free triflate anions [16]. In addition, the ¹H NMR spectrum of $\mathbf{2}$ in acetone-d₆ shows that the all three pyridylmethyl moieties are equivalent, suggesting a fast exchange between a sixcoordinate and a five-coordinate conformation as proposed with the similar Fe(II) complexes by Britovsek et al. [16], which is shown in Scheme 1a. The electronic states of 1-3 in solution were also investigated by UV-Vis absorption spectroscopy (Table 1). Intense MLCT bands were observed for 1 and 2 in MeCN, but the MLCT bands for 1 and 2 in acetone were weaker in intensity. The MLCT bands of 3 were weak in intensity in both MeCN and acetone, similar to those observed for 1 and 2 in acetone. Thus, the intensity of the MLCT band was higher with low-spin Fe(II)-tpa complexes than with the high-spin. The similar correlation between intensity of the MLCT band and spin states of Fe(II) complexes has been reported by Britovsek et al. without rationale [16]. The correlation suggests that the low spin complex has the stronger interactions between $d\pi$ and pyridine π^* orbitals compared with the high-spin complexes.



Fig. 2. UV–Vis spectral changes of 3 in MeCN upon the reaction with O_2 . Inset: change in absorbance with time at 430 nm and fitted curve.

The preferential high spin state of 1 and 2 in acetone can be rationalized by coordination of the counter anions to the Fe(II) ion in acetone. On the other hand, the solvent-independent high spin state of 3 suggests that the two coordinated chloride ions of 3 are not exchanged by MeCN or acetone and result in the Fe(II) ion being in a high spin state [21].

2.2. Reaction with dioxygen

The reactions of **1–3** with dioxygen were examined by UV–Vis spectroscopy. In MeCN, only **3** showed a spectral change upon reaction with O₂ (Fig. 2), while **1** and **2** did not show any spectral changes for at least one day. The MLCT band of **3** disappeared in a first-order decay fashion with an isosbestic point at 413 nm over several hours. The observed first-order rate constant k_{obs} is comparable with the reported value (0.68 h⁻¹) by Thallaj et al.

Table 1

UV-Vis absorption properties, effective magnetic moments, rate constant of oxygen activation (k_{obs}) and catalytic activity of cyclohexene oxidation (TON) of Fe(II)-tpa complexes 1-3 in solution states.

Entry	Solvent	Complex	$\lambda_{\max}\left(\varepsilon^{a} ight)$	$\mu_{\mathrm{eff}}\left(\mu_{\mathrm{B}} ight)$	$k_{\rm obs}({\rm h}^{-1})$	TON ^b
1	acetonitrile	1	368 sh, 398 (6379), 506 (150)	0.740	0 ^c	8.7
2		2	368 sh, 398 (6608), 521 (141)	0.834	0 ^c	8.8
3		3	426 (1468)	5.29	0.529	1.3
4	acetone	1	362 (1268)	5.07	1.28	239
5		2	364 (1476)	5.33	0.118	253
6		3	470 (1331)	5.46	0.311	0.1

^a Units of M⁻¹ cm⁻¹.

^b TON was defined as mol of products (2-cyclohexene-1-ol and 2-cyclohexene-1-one)/mol of complex (5 µmol) after 24 h.

^c No spectral change was observed after 24 h. In the absence of the catalyst, only a small amount of product was evolved (15 µmol in acetone after 24 h).



Scheme 1. Reaction of dioxygen with the Fe(II) center via dissociative mechanism: (a) fast ligand exchange; (b) coordination of dioxygen; and (c) release of superoxide.

(a)

Yield based on Fe (%)

40000

30000

20000

10000

0

n

10

O● total



2.3. Aerobic oxidation of alkenes in the presence of the Fe(II) complexes

To examine the effect of the Fe(III)-superoxo species on the aerobic oxidation of alkenes, we first chose cyclohexene as a substrate with weak allylic C-H bonds; bond dissociation energy (BDE) = 81 kJ/mol [27]. The aerobic oxidation of cyclohexene was carried out in the presence of 1-3 (0.1 mol%) both in MeCN and acetone. Gas chromatography analysis of the products revealed that 1 and 2 are capable of promoting aerobic oxidation of cyclohexene in acetone but not in MeCN (Table 1). Thus, these results clearly indicate that the high-spin Fe(II)-tpa complex can be a good promoter in the aerobic oxidation of cyclohexene. Complex 1 gave allylic oxidation products of cyclohexene, 2-cyclohexen-1-ol and 2-cyclohexene-1-one, (y. 23940% based on Fe), and cyclohexene oxide (y. 810%) in acetone after 24 h. The alcohol/ketone (A/K) ratio was ca. 1.0 at the beginning and decreased to 0.3 as the reaction proceeded (Fig. 3). The decrease in A/K ratio from 1.0 indicates that the allylic oxidation occurs via a radical auto-oxidation process. followed by over-oxidation of the alcohol to ketone by radicals or other oxidants. Production of cyclohexene oxide, however, implies that metal-based oxidants are also formed during the oxidation reaction. Interestingly, 3 is virtually ineffective in initiating the aerobic oxidation of cyclohexene in both MeCN and acetone (Table 1). Thus, these results suggest that labile coordination sites on the high-spin Fe(II) center are a requisite for efficient aerobic oxidation of cyclohexene. In the presence of 1, oxidation of other alkenes and alkanes with weak or moderate C-H BDE (81-97 kJ/mol) were also examined, whose results are listed in Table 2. At 298 K, cumene (BDE: 83 kJ/mol) [28] was oxidized; however, hydrocarbons with C-H BDE of more than 85 kJ/mol such as cyclooctene (85 kJ/mol) [27], ethylbenzene (86 kJ/mol) [27] and norbornene (97 kJ/mol) [29] were intact under these conditions. The latter hydrocarbons were oxidized when the temperature was elevated to 348 K in 2butanone. The product yield in the oxidation of cumene was effectively enhanced with increase in temperature. These results clearly show that the C-H activation of hydrocarbon is the key step in the catalytic system.

2.4. Reaction mechanism

Next, we monitored UV-Vis absorption spectral changes of 1 in the presence of cyclohexene in acetone. The abundance fraction of Fe(II) species estimated by intensity of the MLCT band is plotted against reaction time in Fig. 4. The Fe(II) species disappeared within 5 s with a small induction period in the presence of cyclohexene, which is significantly faster than the oxidation rate of **1** in the





Fig. 3. Time course of (a) product yield based on Fe and (b) A/K ratios in the oxidation of cyclohexene with 1 (filled symbols) and 2 (open symbols) in acetone.

absence of cyclohexene (ca. 2 min). These results indicate that cyclohexene-derived radicals induce the oxidation of Fe(II) species. We propose that H-atom abstraction from cyclohexene by an Fe(III)-superoxo species is the key step in producing cyclohexene-derived radicals, which quickly oxidize Fe(II) species (Scheme 2). The radicals generated would propagate the radical chain oxidation of cyclohexene. Thus, the observed induction period corresponds to the initial dioxygen activation step. The fact that **3** was aerobically oxidized but did not initiate the aerobic oxidation of cyclohexene implies that Fe(III)-superoxo species immediately converts to Fe(III) and superoxide by nucleophilic attack of the chloride anion as discussed above. Superoxide has been reported to perform H-atom abstraction only from weak N-H [30] and O-H [31] bonds. The Fe(III)-superoxo species is also likely to generate a μ -peroxo dimer, followed by formation of a μ -oxo dimer as widely invoked in aerobic oxidation of heme and non-heme Fe(II) complexes [32-34]. The formation of stable µ-oxo dimer can finally lead to deactivation of the catalysis.

Que and his co-workers have been studying hydrocarbon oxidation catalyzed by the Fe(II)-tpa complex and its derivatives with H₂O₂ or *t*BuOOH as oxidant [21,35,36]. Recently, they reported that Fe(III)-hydroperoxo and -alkylperoxo species supported by the tpa ligand were transformed to Fe(IV)-oxo species in acetone [37]. Production of cyclohexene oxide supports the generation of Fe(IV)-oxo species in our system, although the aerobic oxidation mainly proceeds via radical chain oxidation, as shown by the A/K ratio.

The reactivity of metal-superoxo species involved in hydrocarbon oxidation reactions has attracted much attention recently in the field of bioinorganic chemistry, since Cu(II)-superoxide species

Table 2
Product yields in the aerobic oxidation of hydrocarbons in the presence of 1.

Substrate	Solvent	<i>T</i> (K)	Product	Yield (%) ^a	Sel. (%)
^b Norbornene	2-butanone	348	norbornene oxide	18 340	51 ^c
Cyclooctene	2-butanone	348	cyclooctene oxide	12 300	21
			1,2-cyclooctanediol	13 250	23
			cyclooctanone	14 830	26
Cyclohexene	acetone	298	cyclohexene oxide	810	2.9
			2-cyclohexene-1-ol	6070	22
			2-cyclohexene-1-one	17 870	64
Ethylbenzene	2-butanone	348	acetophenone	2000	54
			1-phenylethanol	1700	32
Cumene	2-butanone	348	acetophenone	2200	93
			cumylalcohol	100	4.0
	acetone	313	acetophenone	940	72
			cumylalcohol	360	28
	acetone	298	acetophenone	130	50
			cumylalcohol	130	50

 $^{a}\,$ Based on Fe (5 $\mu mol)$ after 24 h of reaction.

^b 2100 equiv. of norbornene used.

^c Several byproducts also detected.



Fig. 4. Change in fraction of Fe(II) species with time during oxidation of **1** in acetone in the presence (filled circle) or absence (open circle) of cyclohexene upon the reaction with O_2 . The fraction of Fe(II) species was calculated from the MLCT band intensity. Inset shows the initial phase.



Scheme 2. Proposed reaction paths in the initial phase of oxidation of 1 in the presence of cyclohexene.

have been postulated to initiate H-atom abstraction from substrates in the catalytic cycles of copper-dependent enzymes such as dopamine β -monooxygenase and peptidylglycine α -hydroxylating monooxygenase (PHM) [38-40], and the Fe(III)-superoxo species have been proposed as active species in a di-iron-dependent enzyme, myo-inositol oxygenase [41,42]. It has been reported by using model complexes that Cu(II)-superoxo species can perform H-atom abstraction from weak O-H and N-H bonds [43-45]. Recently, Itoh and co-workers synthesized a series of Cu(II) endon superoxo species which mimic a tetrahedral geometry in the X-ray structure of oxy-PHM reported by Amzel and co-workers [46,47], and demonstrated that this species also mimics the H-atom abstraction from aliphatic C–H bonds [47]. H-atom abstraction by Fe(III)-superoxo species had been reported rarely, but recently, Fukuzumi and Nam et al. reported that Fe(III)-superoxo species generated in the reaction of the mononuclear nonheme Fe(II) complex with dioxygen performs H-atom abstraction from cycloalkenes [48,49]. We believe that the same mechanism should be operative in the aerobic oxidation reaction promoted by **1** in acetone.

3. Conclusions

We found that aerobic oxidation of alkenes was efficiently promoted by the Fe(II)-tpa complex, when the Fe center was in the high-spin state. It is noteworthy that the aerobic oxidation proceeded without any reductants, since most of the aerobic oxidation systems catalyzed by heme or nonheme iron complexes require stoichiometric co-reductants such as aldehydes and Zn/AcOH [50]. We propose that an Fe(III)-superoxo species is a key intermediate in the efficient aerobic oxidation of alkenes. The essential factor in the reaction is the presence of labile coordination sites that provides stable coordination of dioxygen, giving Fe(III)-superoxo species active for the H-atom abstraction; the strong interaction of MeCN with the low-spin iron(II) center would prevent the formation of the Fe(III)-superoxo species, and chloride ion may shorten the life-time of the Fe(III)-superoxo species probably through nucleophilic attack. Thus, the ligand-exchange chemistry including dioxygen should be of important in the performance of the efficient aerobic oxidation¹. Consequently, high-spin Fe(II)-tpa complexes except for the chloride complex effectively initiated aerobic oxidation of hydrocarbons. We will further study the relationship between spin sate and dioxygen activation ability.

¹ We appreciate an anonymous referee for valuable and insightful comments on our manuscript.

4. Experimental

4.1. Materials

The tpa ligand was synthesized according to published procedures [12]. All other reagents and dehydrated solvents were purchased from commercial sources. All dehydrated solvents were deoxygenated by N₂ bubbling prior to use. Treatment of the tpa ligand with Fe(ClO₄)₂, Fe(OTf)₂ and FeCl₂ in MeCN gave the corresponding complexes **1–3** as crystalline solids in high yield.

 $[Fe(tpa)(MeCN)_2](ClO_4)_2$ (1): ESI-MS calcd. (found): m/z 193.6 (193.5) ($[Fe^{II}(tpa)(MeCN)]^{2+}$).

 $[Fe(tpa)(MeCN)_2](OTf)_2$ (2): ESI-MS calcd. (found): m/z 193.6 (193.5) $([Fe^{II}(tpa)(MeCN)]^{2*})$.

 $[Fe(tpa)Cl_2]$ (**3**): ESI-MS calcd. (found): m/z 381.1 (381.4) $([Fe^{II}(tpa)Cl)]^+)$.

4.2. Physical methods

Electrospray ionization mass spectrometry (ESI-MS) spectra were recorded on a PE SCIEX API 2000 mass spectrometer. ¹H and ¹⁹F NMR spectra were recorded on a JEOL ECX400P spectrometer; chemical shifts for ¹H and ¹⁹F NMR are referenced to tetramethylsilane and trifluoroacetic acid, respectively. UV–Vis spectra were recorded on a Hitachi UV-3000 spectrophotometer.

4.3. Aerobic oxidation of hydrocarbons

Oxygen was bubbled for 1 min into 5 ml of 1.0 mM Fe(II)-tpa complex solution containing 1000 equiv. of hydrocarbon as substrate, followed by vigorous stirring under 1 atm O_2 in a batch reactor tube equipped with an O_2 balloon. Organic products were analyzed by FID-GC (Shimadzu GC-14B) and GC-MS (Shimadzu GC-MS QP5050). Prior to use, substrates were dried over molecular sieves 4 Å and deoxygenated by N₂ bubbling. 2-Butanone was used instead of acetone for the reaction at 348 K to avoid boiling.

Acknowledgments

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 19028033, "Chemistry of Concerto Catalysis") from the Ministry of Education, Culture, Sports, Science and Technology, Japan. S.F. thanks the JSPS Research Fellowships for Young Scientists.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.08.004.

References

- G. Franz, R.A. Sheldon, Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH, Weinheim, 2005.
- [2] I. Hermans, E.S. Spier, U. Neuenschwander, N. Turra, A. Baiker, Top. Catal. 52 (2009) 1162–1174.

- [3] M. Sono, M.P. Roach, E.D. Coulter, J.H. Dawson, Chem. Rev. 96 (1996) 2841– 2887.
- [4] B.J. Wallar, J.D. Lipscomb, Chem. Rev. 96 (1996) 2625-2657.
- [5] E.I. Solomon, U.M. Sundaram, T.E. Machonkin, Chem. Rev. 96 (1996) 2563– 2605.
- [6] L.C. Stewart, J.P. Klinman, Annu. Rev. Biochem. 57 (1988) 551-592.
- [7] L. Que, R.Y.N. Ho, Chem. Rev. 96 (1996) 2607-2624.
- [8] A. De La Lande, D.R. Salahub, J. Maddaluno, A. Scemama, J. Pilme, O. Parisel, H. Gerard, M. Caffarel, J.-P. Piquemal, J. Comput. Chem. 32 (2010) 1178–1182.
- [9] A. Thibon, J. England, M. Martinho, V.G. Young, J.R. Frisch, R. Guillot, J.J. Girerd, E. Munck, L. Que, F. Banse, Angew. Chem., Int. Ed. 47 (2008) 7064–7067.
- [10] L. Benhamou, A. Machkour, O. Rotthaus, M. Lachkar, R. Welter, D. Mandon, Inorg. Chem. 48 (2009) 4777–4786.
- [11] M. Martinho, G. Blain, F. Banse, Dalton Trans 39 (2010) 1630-1634.
- [12] M. Higuchi, Y. Hitomi, H. Minami, T. Tanaka, T. Funabiki, Inorg. Chem. 44 (2005) 8810–8821.
- [13] A. Diebold, K.S. Hagen, Inorg. Chem. 37 (1998) 215-223.
- [14] D.F. Evans, J. Chem. Soc. (1959) 2003-2005.
- [15] Y. Zang, J. Kim, Y. Dong, E.C. Wilkinson, E.H. Appelman, L. Que, J. Am. Chem. Soc. 119 (1997) 4197–4205.
- G.J.P. Britovsek, J. England, A.J.P. White, Inorg. Chem. 44 (2005) 8125–8134.
 N.K. Thallaj, O. Rotthaus, L. Benhamou, N. Humbert, M. Elhabiri, M. Lachkar, R.
- Welter, A.-M. Albrecht-Gary, D. Mandon, Chem. Eur. J. 14 (2008) 6742–6753. [18] D.W. Blakesley, S.C. Payne, K.S. Hagen, Inorg. Chem. 39 (2000) 1979–1989.
- [19] H. Börzel, P. Comba, K.S. Hagen, Y.D. Lampeka, A. Lienke, G. Linti, M. Merz, H.
- Pritzkow, L.V. Tsymbal, Inorg. Chim. Acta 337 (2002) 407-419. [20] M.P. Jensen, S.J. Lange, M.P. Mehn, E.L. Que, L. Que, J. Am. Chem. Soc. 125
- (2003) 2113–2128. [21] T. Kojima, R.A. Leising, S.P. Yan, L. Que, J. Am. Chem. Soc. 115 (1993) 11328–
- 11335.
- [22] A. Wane, N.K. Thallaj, D. Mandon, Chem. Eur. J. 15 (2009) 10593-10602.
- [23] H. Jaafar, B. Vileno, A. Thibon, D. Mandon, Dalton Trans. 40 (2011) 92-106.
- [24] A.J. Simaan, S. Dopner, F. Banse, S. Bourcier, G. Bouchoux, A. Boussac, P.
- Hildebrandt, J.J. Girerd, Eur. J. Inorg. Chem. (2000) 1627–1633. [25] D. Lefevre-Groboillot, J.L. Boucher, D. Mansuy, D.J. Stuehr, FEBS J. 273 (2006) 180–191.
- [26] K. Shikama, Cell. Mol. Life Sci. 41 (1985) 701–706.
- [27] Y.-R. Luo, Handbook of Bond Dissociation Energies in Organic Compounds, CRC Press, Boca Raton, 2003.
- [28] Y. Feng, T.B. Gunnoe, T.V. Grimes, T.R. Cundari, Organometallics 25 (2006) 5456–5465.
- [29] P.M. Nunes, S.G. Estacio, G.T. Lopes, F. Agapito, R.C. Santos, B.J.C. Cabral, R.M.B. dos Santos, J.A.M. Simoes, J. Phys. Chem. A 113 (2009) 6524–6530.
- [30] P. Bernhard, F.C. Anson, Inorg. Chem. 27 (1988) 4574–4577.
- [31] A.A. Frimer, V. Marks, P. Gilinskysharon, G. Aljadeff, H.E. Gottlieb, J. Org. Chem. 60 (1995) 4510-4520.
- [32] J.P. Collman, Acc. Chem. Res. 10 (1977) 265-272.
- [33] A.L. Balch, Y.W. Chan, R.J. Cheng, Am. Chem. Soc. 106 (1984) 7779-7785.
- [34] D.M. Kurtz, Chem. Rev. 90 (1990) 585-606.
- [35] K. Chen, L. Que, J. Am. Chem. Soc. 123 (2001) 6327-6337.
- [36] K. Chen, M. Costas, J.H. Kim, A.K. Tipton, L. Que, J. Am. Chem. Soc. 124 (2002) 3026-3035.
- [37] A.M.I. Payeras, R.Y.N. Ho, M. Fujita, L. Que, Chem. Eur. J. 10 (2004) 4944–4953.
- [38] P. Chen, E.I. Solomon, Proc. Natl. Acad. Sci. 101 (2004) 13105–13110.
- [39] S. Itoh, Curr. Opin. Chem. Biol. 10 (2006) 115–122.
- [40] J.P. Klinman, J. Biol. Chem. 281 (2006) 3013–3016.
- [41] G. Xing, Y.H. Diao, L.M. Hoffart, E.W. Barr, K.S. Prabhu, R.J. Arner, C.C. Reddy, C. Krebs, J.M. Bollinger, Proc. Natl. Acad. Sci. 103 (2006) 6130–6135.
- [42] H. Hirao, K. Morokuma, I. Am. Chem. Soc. 131 (2009) 17206-17214
- [43] D. Maiti, H.C. Fry, J.S. Woertink, M.A. Vance, E.I. Solomon, K.D. Karlin, J. Am. Chem. Soc. 129 (2007) 264–265.
- [44] T. Fujii, S. Yamaguchi, S. Hirota, H. Masuda, Dalton Trans. (2008) 164-170.
- [45] D. Maiti, D.H. Lee, K. Gaoutchenova, C. Wurtele, M.C. Holthausen, A.A.N. Sarjeant, J. Sundermeyer, S. Schindler, K.D. Karlin, Angew. Chem., Int. Ed. 47 (2008) 82–85.
- [46] S.T. Prigge, B.A. Eipper, R.E. Mains, L.M. Amzel, Science 304 (2004) 864-867.
- [47] A. Kunishita, M. Kubo, H. Sugimoto, T. Ogura, K. Sato, T. Takui, S. Itoh, J. Am. Chem. Soc. 131 (2009) 2788–2789.
- [48] S. Hong, Y.M. Lee, W. Shin, S. Fukuzumi, W. Nam, J. Am. Chem. Soc. 131 (2009) 13910–13911.
- [49] Y.M. Lee, S. Hong, Y. Morimoto, W. Shin, S. Fukuzumi, W. Nam, J. Am. Chem. Soc. 132 (2010) 10668–10670.
- [50] T. Punniyamurthy, S. Velusamy, J. Iqbal, Chem. Rev. 105 (2005) 2329-2363.