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Facile C–C bond cleavage of β-diketones by tin(IV) porphyrin complex

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ABSTRACT

Reactions of *trans*-dihydroxo(*meso*-tetraphenylporphyrinato)tin(IV) [Sn(TPP)$(OH)_2$] with β-diketones such as acetylacetone (**1**), dibenzoylmethane (**2**), 1-phenylbutane-1,3-dione (**3**), or 4,4-dimethyl-1-phenylpentane-1,3-dione (**4**) were studied. All reactions afforded dicarboxylato tin(IV) porphyrin complexes [Sn(TPP)$(O_2CR)_2$] (R = Me, Ph, *t*-Bu) and ketonic compounds due to the C–C bond cleavage of β-diketones. The products were characterized by ^{1}H NMR spectroscopy and ESI mass spectrometry, and further proved by X-ray crystallographic analysis of Sn(TPP)$(O_2CCH_3)_2$. Possible reaction mechanisms involving four-centered intermediate species are discussed, in which the C–C and O–H bonds are cleaved along with the simultaneous formation of (Sn)O–C and H–C bonds.

The study on the C–C bond cleavage is one of the prime areas of research in chemistry for a long time due to its significant use in the degradation of environmentally hazardous and xenobiotic compounds as well as in the synthesis of biologically active organic compounds. Acetylacetone (2,4-pentanedione), one of widely used industrial chemicals, shows central neurotoxicity and toxic side effects on the immune system of mammals.[1] *Acinatobacter johnsonii acetylacetone dioxygenase* (Dke1) is a representative example to catalyze the oxidative degradation of acetylacetone and related β-carbonyl compounds capable of undergoing enolization to a *cis-β-keto-enol* structure.[2] Two enzymes are also known to be capable of degrading acetylacetone via hydrolytically cleaving the central C–C bond of the β-diketone moiety.[3] The C–C bond cleavage phenomenon of β-diketones in aqueous alkali solution is also evident to give carboxylic acids and ketones, and reveals the involvement of ketonic form of β-diketones rather than enolic form.[4] The facilitation of the reaction proceeds through the nucleophilic attack of hydroxide anion on the ketonic carbon to induce C–C bond cleavage adjacent to ketonic group. The cleavage of β-diketones was expected in the formation of $Y_2(\mu_2\text{-}O_2CCH_3)_2(acac)_4(H_2O)_2$[5] and $Cu(py)_4(O_2CCF_3)_2$,[6] where the carboxylato ligands may come from the degradation of the corresponding β-diketones. It was recently reported that the C–C bond cleavage of 1,3-diketones affords the 1,2-diketones by use of $FeCl_3$ as the catalyst and *tert*-butyl nitrite as the oxidant without the use of solvent.[7]

On the other hand, tin(IV) porphyrins readily form stable six-coordinate complexes with the two *trans* axial ligands of oxyanions due to the oxophilic nature of the high-valent tin(IV) center.[8] Tin(IV) porphyrin complexes have been readily synthesized by the acidolysis of the hydroxo ligands coordinated to tin(IV) porphyrins with a variety of carboxylic acids or alcohols because hydroxo-tin(IV) porphyrins preferentially recognize carboxylic acids or alcohols.[9] These previous results prompted us to explore the use of the hydroxo ligands in tin(IV) porphyrin complexes as a base in organic synthesis. We here report facile C–C bond cleavage of β-diketones generating carboxylates and ketones by *trans*-dihydroxo(*meso*-tetraphenylporphyrinato)tin(IV), [Sn(TPP)$(OH)_2$, **SnP1**]. So far, tin(IV) porphyrin complexes with weakly coordinating anions such as perchlorate,[10] trifluoromethanesulfonate,[11] and tetrafluoroborate[12] have been used only as mild Lewis acids in organic transformation.

The reaction of **SnP1** with acetylacetone (**1**) was taken to study the C–C bond cleavage of β-diketones. A preliminary reaction was performed with **SnP1** and 10 times excess of **1** in $CHCl_3$ at room temperature for 3 days.[13] The reaction proceeded more efficiently when the reaction was carried out in neat **1** at higher temperature. Typically, the reaction using a mixture of **SnP1** and 10 times excess of **1** without any solvents was accomplished within 3–4 h at 90–100 °C.

The resulting tin porphyrin complex was characterized by ^{1}H NMR spectroscopy. As shown in Figure S1, this compound displays very similar ^{1}H NMR spectroscopic properties to acetato-tin(IV) porphyrin Sn(TPP)$(O_2CCH_3)_2$ (**SnP2**) reported earlier.[14] We evidently proved the formation of acetato-tin(IV) porphyrin **SnP2** by X-ray crystallography. X-ray crystal structure of [Sn(TPP)$(O_2CCH_3)_2$]·$CHCl_3$ shown in Figure 1 is similar as reported earlier by Liu et al. where two molecules of CH_3COOH are additionally present in a unit cell.[15]

The production of **SnP2** from the reaction implies that the degradation of **1** can be engaged in generating acetate species during

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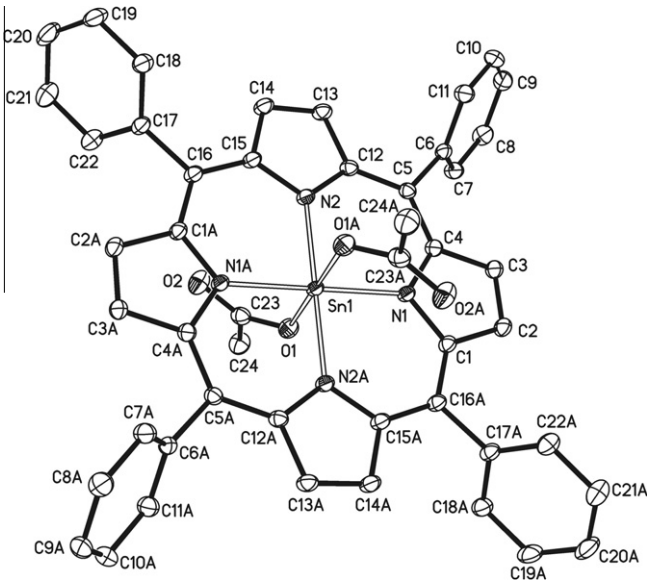


Figure 1. X-ray crystal structure of $[Sn(TPP)(O_2CCH_3)_2]\cdot CHCl_3$ with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms and solvate $CHCl_3$ molecule are omitted for clarity.

the course of reaction, as shown in Scheme 1. The enzymatic cleavage reaction of acetylacetone by Dke1 affords equimolar amounts of acetate and methylglyoxal.[2] The alkaline hydrolysis of β-diketones in aqueous alkali solutions also gives carboxylic acids and ketones as products.[4] Our further study was thus directed to uncover reaction pathways for the degradation of acetylacetone mediated by **SnP1**.

The incorporation of molecular O_2 was examined firstly to find out possible reaction routes. The cleavage of acetylacetone catalyzed by enzyme Dke1 produces methylglyoxal as well as acetic acid due to the incorporation of molecular O_2.[2] We thus conducted two different reaction conditions for the cleavage of acetylacetone mediated by **SnP1**: in the presence and absence of molecular O_2. We could not find methylglyoxal compound in the products obtained from either reactions, judged by ^{1}H NMR spectroscopy and ESI mass spectrometry. These results provide a substantial ground that the C–C bond cleavage of **1** mediated by **SnP1** does not follow the oxidative reaction pathway involving the incorporation of molecular O_2.

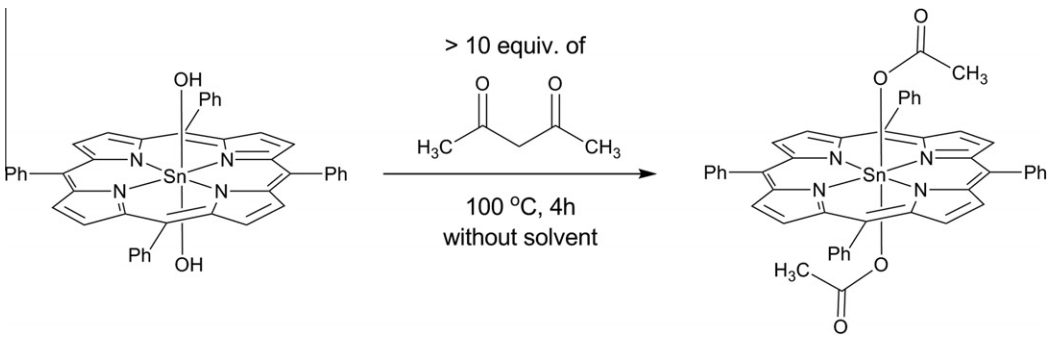
To further seek out plausible mechanisms for the cleavage, we have herein proposed a reaction pathway via the nucleophilic attack by the hydroxo ligands in **SnP1**. As presented in Scheme 2, four centered intermediate species provides a platform for the C–C and O–H bond cleavage along with the simultaneous O–C and H–C bond formation.

But even after best efforts, we could not observe the ^{1}H NMR signals and ESI-MS cluster bands related to acetone, most probably due to its low boiling point and high vapor pressure. To prove the mechanism and validate the generation of acetone as by-product from the reaction, we opted dibenzoylmethane (**2**) as a reactant in place of **1**. It was speculated that if it would follow the proposed route then the generation of acetophenone would be more feasible. The higher boiling point and lower vapor pressure of acetophenone are vital to prove the generation of this ketonic compound by means of ^{1}H NMR and ESI mass spectral studies. Indeed, the ^{1}H NMR spectrum of the crude reaction mixture exhibits the presence of a singlet at 2.50 ppm for CH_3 group of acetophenone while signals related to phenyl groups merge with the phenyl signals of TPP ligand in $Sn(TPP)(O_2CPh)_2$ (**SnP3**) and residue **2** (Fig. S2). Furthermore, chemical shifts of the signals of **SnP3** are identical to those reported earlier.[16] This crude material was further subjected to ESI mass spectral study, in which several diagnostic peaks appear at m/z 105.1, 121.2, and 123.1 corresponding to $[PhCO]^+$ (C_7H_5O requires 105.03), $[PhC(O)CH_3+H]^+$ (C_8H_9O requires 121.07), and $[PhCOOH+H]^+$ ($C_7H_7O_2$ requires 123.04) fragments, respectively (Fig. S4). These results provide sufficient base to anticipate that the hydroxo ligands are playing a crucial role in the bond cleavage via attacking on the electron-deficient carbonyl carbons and promoting the C–C bond cleavage adjacent to the carbonyl groups.

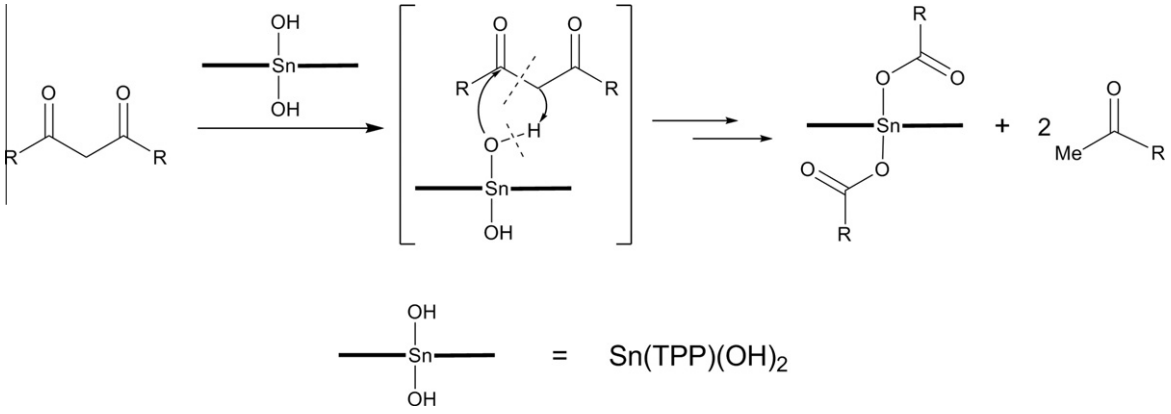
We also examined the reactivity of **SnP1** toward unsymmetrical β-diketones such as 1-phenylbutane-1,3-dione (R1 = Ph, R2 = Me; **3**) or 4,4-dimethyl-1-phenylpentane-1,3-dione (R1 = Ph, R2 = ^{t}Bu; **4**). Reactions with the two unsymmetrical β-diketones proceeded slowly compared to those with the symmetrical β-diketones under similar reaction condition. The reactions for the unsymmetrical β-diketones were almost completed after heating up to 200–250 °C. Based on our proposed mechanism, the reaction of **SnP1** with unsymmetrical β-diketones can produce a mixture of three porphyrin complexes as shown in Scheme 3. As shown in Figure S5, the ^{1}H NMR spectrum for a reaction mixture obtained from a reaction of **SnP1** with **3** indeed exhibits three sets of signals attributed to the ligated acetate and benzoate groups of expected porphyrinic products.

A mixture of porphyrin products after preparative TLC was further characterized by ESI mass spectrometry to identify each porphyrin product. Several diagnostic peaks for **SnP3** appear in the ESI mass spectrum (Fig. S6). We suspect that other porphyrinic products may be less stable under the condition of ESI mass measurement. The reaction with **4** also showed the similar reaction pattern to produce $Sn(TPP)(O_2C^tBu)$ (**SnP4**), judged by ^{1}H NMR (Fig. S7) and ESI mass (Fig. S9) spectral studies.

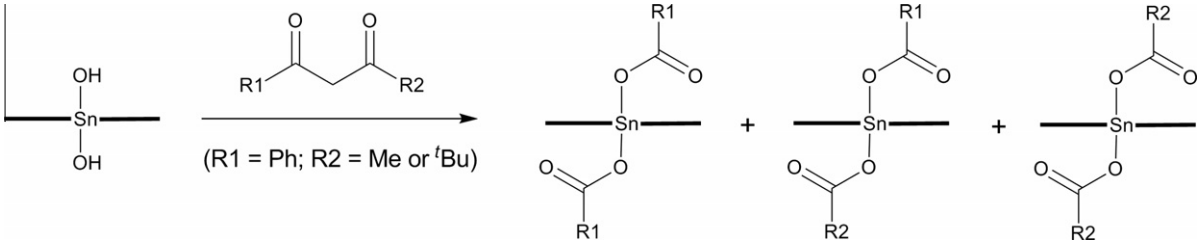
The basic nature of the hydroxo ligand bonded to tin(IV) center was found in the formation of (β-diketonato)organotin complexes. For example, the reaction of $R_2Sn(OH)(OSO_2R')$ (R = *n*-Pr, *n*-Bu; R′ = Me, Et, *n*-Pr) compounds with β-diketones produced



Scheme 1. Conversion of $Sn(TPP)(OH)_2$ to $Sn(TPP)(O_2CCH_3)_2$ by the reaction with acetylacetone.



Scheme 2. A possible reaction pathway for the C–C bond cleavage of β-diketones mediated by $Sn(TPP)(OH)_2$.



Scheme 3. Possible porphyrin products based on the proposed mechanism for the reaction of $Sn(TPP)(OH)_2$ with unsymmetrical β-diketones.

(β-diketonato)tin complexes, R_2Sn(β-diketonato)(OSO_2R') where the β-diketonates act as *O,O*-chelating ligands.[17] This report obviously shows the basicity of the hydroxo ligand coordinated to tin(IV) center to be able to accept protons, which is very similar to the reactivity found in the acidolysis of the hydroxo-tin(IV) porphyrin complexes. By comparison with the results of both studies, we thus believe that the enhanced nucleophilicity of hydroxo ligands in **SnP1** capable of the C–C bond cleavage of β-diketones is attributed to the electron-donating influence of porphyrin ligand to stabilize high-valent tin(IV) center besides the intrinsic basic nature of hydroxo ligands.

In conclusion, we have demonstrated the facile C–C bond cleavage of β-diketones such as acetylacetone, dibenzomethane, 1-phenylbutane-1,3-dione, and 4,4-dimethyl-1-phenylpentane-1,3-dione by tin(IV) porphyrin complex, $Sn(TPP)(OH)_2$. The investigated reaction pathway implies that the cleavage phenomenon apparently proceeds via simultaneous C–C and O–H bond cleavage through four-centered intermediate species. The C–C bond cleavage of β-diketones is not unprecedented, but the use of metalloporphyrin in the C–C bond cleavage of β-diketones is a new finding. To the best of our knowledge, our result is the first example showing that metalloporphyrin complexes cleave the C–C bond of β-diketones. It has been studied in recent years that metalloporphyrin complexes of trivalent group 9 (Rh(III)[18] and Ir(III)[19]) undertake the cleavage of the carbonyl carbon and α-carbon bond of ketones in very harsh conditions. Our study offers a new insight into organic transformation by using tin(IV) porphyrin complexes as nucleophiles, sharply contrasting with previous utilization[10–12] of tin(IV) porphyrins as Lewis acids. At present, there is a single report on the C–C bond cleavage of vicinal diol mediated by tin(IV) porphyrins, in which diolato tin porphyrin intermediates seem to undergo oxidative cleavage to release carbonyl compounds and tin(II) porphyrins.[20] We can propose further synthetic routes for unsymmetrical ketones involving alkyl group transfer from $Sn(TPP)(OR)_2$ to the C_α-position of β-diketones. More studies on the alkyl group transfer as well as the reactions of $Sn(TPP)(OH)_2$ with a variety of symmetrical and unsymmetrical β-diketones are in progress.

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Supplementary data

Crystallographic data for the structural analysis have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK with the deposition numbers CCDC 882215 for $[Sn(TPP)(O_2CCH_3)_2]\cdot CHCl_3$. Copies of this information can be obtained free of charge via, e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk; fax: +44 1223 336 033.

Supplementary data (experimental details) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2012.09.075.

References and notes

1. Ballantyne, B.; Cawley, T. *J. Appl. Toxicol.* **2001**, *21*, 165–171.
2. (a) Straganz, G. D.; Glieder, A.; Brecker, L.; Ribbons, D. W.; Steiner, W. *Biochem. J.* **2003**, *369*, 573–581; (b) Straganz, G. D.; Hofer, H.; Steiner, W.; Nidetzky, B. *J. Am. Chem. Soc.* **2004**, *126*, 12202–12203.
3. (a) Sakai, K.; Hamada, N.; Watanabe, Y. *Agric. Biol. Chem.* **1986**, *50*, 989–996; (b) Kawagoshi, Y.; Fujita, M. *J. Microbiol. Biotechnol.* **1998**, *14*, 95–100.
4. (a) Bickel, C. L. *J. Am. Chem. Soc.* **1945**, *67*, 2204–2206; (b) Pearson, R. G.; Mayerle, E. A. *J. Am. Chem. Soc.* **1951**, *73*, 926–930; (c) Hauser, C. R.; Swamer, F. W.; Ringler, B. I. *J. Am. Chem. Soc.* **1948**, *70*, 4023–4026.
5. Poncelet, O.; Hubert-, P. L. G.; Daran, J.-C. *Polyhedron* **1990**, *9*, 1305–1310.
6. Pradilla, S. J.; Chen, H. W.; Koknat, F. W.; Fackler, J. P. *Inorg. Chem.* **1979**, *18*, 3519–3522.
7. Huang, L.; Cheng, K.; Yao, B.; Xie, Y.; Zhang, Y. *J. Org. Chem.* **2011**, *76*, 5732–5737.
8. (a) Arnold, D. P.; Blok, J. *Coord. Chem. Rev.* **2004**, *248*, 299–319; (b) Sanders, J. K. M.; Bampos, N.; Clyde-Watson, Z.; Darling, S. L.; Hawley, J. C.; Kim, H.-J.; Mak, C. C.; Webb, S. J. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, 2000; vol. 3, pp 1–48.
9. (a) Kim, S. H.; Kim, H.; Kim, K.; Kim, H.-J. *J. Porphyrins Phthalocyanines* **2009**, *13*, 805–810; (b) Kim, H. J.; Jang, J. H.; Choi, H.; Lee, T.; Ko, J.; Yoon, M.; Kim, H.-J. *Inorg. Chem.* **2008**, *47*, 2411–2415; (c) Kim, H. J.; Jeon, W. S.; Lim, J. H.; Hong, C. S.; Kim, H.-J. *Polyhedron* **2007**, *26*, 2517–2522; (d) Kim, H.-J.; Jo, H. J.; Kim, J.;

Kim, S.-Y.; Kim, D.; Kim, K. *CrystEngComm* **2005**, *7*, 417–420; (e) Kim, H. J.; Park, K.-M.; Ahn, T. K.; Kim, S. K.; Kim, K. S.; Kim, D.; Kim, H.-J. *Chem. Commun.* **2004**, 2594–2595.

10. (a) Tangestaninejad, S.; Habibi, M. H.; Mirkhani, V.; Moghadam, M. *Synth. Commun.* **2002**, *32*, 1337–1343; (b) Tangestaninejad, S.; Habibi, M. H.; Mirkhani, V.; Moghadam, M. *J. Chem. Soc. (S)* **2001**, 365–367; (c) Tangestaninejad, S.; Mirkhani, V. *Synth. Commun.* **1999**, *29*, 2079–2083.
11. (a) Gharaati, S.; Moghadam, M.; Tangestaninejad, S.; Mirkhani, V.; Mohammadpoor-Baltork, I.; Kosari, F. *Inorg. Chim. Acta* **2010**, *363*, 1995–2000; (b) Moghadam, M.; Tangestaninejad, S.; Mirkhani, V.; Mohammadpoor-Baltork, I.; Gharaati, S. *Appl. Organomet. Chem.* **2009**, *23*, 446–454; (c) Moghadam, M.; Tangestaninejad, S.; Mirkhani, V.; Shaibani, R. *Tetrahedron* **2004**, *60*, 6105–6111; (d) Moghadam, M.; Tangestaninejad, S.; Mirkhani, V.; Mohammadpoor-Baltork, I.; Shaibani, R. *J. Mol. Catal. A: Chem.* **2004**, *219*, 73–78.
12. (a) Moghadam, M.; Tangestaninejad, S.; Mirkhani, V.; Mohammadpoor-Baltork, I.; Taghavi, S. A. *J. Mol. Catal. A: Chem.* **2007**, *274*, 217–223; (b) Moghadam, M.; Tangestaninejad, S.; Mirkhani, V.; Mohammadpoor-Baltork, I.; Gharaati, S. *Catal. Commun.* **2007**, *8*, 2087–2095.
13. The reaction of $Sn(TPP)(OH)_2$ with acetylacetone proceeded very slowly at room temperature, and only up to 5–10% of $Sn(TPP)(OH)_2$ were converted even after 3 days. The reaction progress was monitored by ^1H NMR spectroscopy.
14. (a) Arnold, D. P. *Polyhedron* **1986**, *5*, 1957; (b) Crossley, M. J.; Thordarson, P.; Wu, R. A.-S. *J. Chem. Soc., Perkin Trans. 1* **2001**, 2294.
15. Liu, I.-C.; Lin, C.-C.; Chen, J.-H.; Wang, S.-S. *Polyhedron* **1996**, *15*, 459–463.
16. Smith, G.; Arnold, D. P.; Kennard, C. H. L.; Mak, T. C. W. *Polyhedron* **1991**, *10*, 509–516.
17. (a) Narula, S. P.; Kaur, S.; Shankar, R.; Verma, S.; Venugopalan, P.; Sharma, S. K. *Inorg. Chem.* **1999**, *38*, 4777–4783; (b) Shankar, R.; Singh, A. P.; Hundal, G.; Butcher, R. J. *J. Organomet. Chem.* **2007**, *692*, 5555–5562.
18. (a) Fung, H. S.; Li, B. Z.; Chan, K. S. *Organometallics* **2012**, *31*, 570–579; (b) Fung, H. S.; Li, B. Z.; Chan, K. S. *Organometallics* **2010**, *29*, 4421–4423; (c) Chan, Y. W.; Chan, K. S. *J. Am. Chem. Soc.* **2010**, *132*, 6920–6922; (d) Lai, T. H.; Chan, K. S. *Organometallics* **2009**, *28*, 6845–6846.
19. (a) Li, B. Z.; Fung, H. S.; Song, X.; Chan, K. S. *Organometallics* **2011**, *30*, 1984–1990; (b) Li, B. Z.; Song, X.; Fung, H. S.; Chan, K. S. *Organometallics* **2010**, *29*, 2001–2003.
20. Du, G.; Ellern, A.; Woo, L. K. *Inorg. Chem.* **2004**, *43*, 2379–2386.