### Fullerenes

# Highly Efficient Cu(OAc)<sub>2</sub>-Catalyzed Dimerization of Monofunctionalized Hydrofullerenes Leading to Single-Bonded [60]Fullerene Dimers\*\*

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The single-bonded fullerene dimer RC<sub>60</sub>-C<sub>60</sub>R, which has a direct covalent bond between two C60 cages, is an interesting and unusual structure that is expected to display interesting optical and electronic properties through the interaction of two adjacent fullerene cages.<sup>[1]</sup> Since the pioneering work by Krusic and co-workers,<sup>[2]</sup> studies on ESR and X-ray crystalstructure analysis revealed that singly bonded fullerene dimers consist of racemic and meso isomers, which are in equilibrium with the monomer radical  $(RC_{60})$  in solution.<sup>[3]</sup> Some experimental and theoretical studies on these singlebonded fullerene dimers demonstrated that they were usually formed by dimerization of RC60 radicals, which were generated by various radical reactions;<sup>[4]</sup> for example, the photoirradiation of C<sub>60</sub> with perfluoroalkyl iodides in the presence of  $(R_3Sn)_{2,1}^{[3a]}$  Mn(OAc)<sub>3</sub>-mediated radical reaction of C<sub>60</sub> with phosphonate esters<sup>[3c]</sup> or dialkyl malonates,<sup>[5a]</sup> and one-electron oxidation of the monoanion  $RC_{60}^{-}$  by oxidants.<sup>[3b,5b-d]</sup> However, their application to the elaborated fullerene dimers is generally limited by low functional-group tolerance, low yield, and the use of large excess amounts of reagents. Functionalization of fullerene by transition-metal catalysis has recently been considered to be a promising and innovative strategy in fullerene chemistry, which offers advantages for high chemical yield, selectivity control, and high functional-group compatibility under mild reaction

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conditions.<sup>[6]</sup> However, examples of catalytic dimerization for the synthesis of single-bonded fullerene dimers have never been reported.<sup>[6f]</sup>

Recently, we developed the cobalt-catalyzed hydroalkylation of C<sub>60</sub> with active alkyl bromides at ambient temperature to give monoalkylated hydrofullerenes in good to high yields.<sup>[7]</sup> Our interest in catalytic C-H bond activation led us to consider the possibility of catalytic C-H bond functionalization of the monosubstituted hydrofullerenes toward the construction of fullerene dimers.<sup>[8]</sup> A study by Komatsu and co-workers revealed that  $RC_{60}$  could be formed from full-erenyl radical cation ( $RHC_{60}$  +), which in turn was generated from monofunctionalized hydrofullerene by one-electron oxidation in sulfuric and sulfonic acids.<sup>[9]</sup> In addition, Yu and co-workers reported the Cu<sup>II</sup>-catalyzed aryl C-H bond functionalization by using  $O_2$ ;<sup>[10]</sup> the reaction was proposed to proceed through the formation of an aryl radical cation (Ar<sup>+</sup>) species by one electron transfer from the aryl ring to the Cu<sup>II</sup> catalyst followed by formation of an aryl radical (Ar). Taking these results into consideration, we turned our attention to metal oxidants as catalysts. Herein, we report a novel and efficient Cu(OAc)2-catalyzed homo-dimerization of various monofunctionalized hydrofullerenes that affords the singlebonded fullerene dimers 2 as a mixture of racemic and meso isomers in excellent yields in the presence of a small amount of dimethylformamide (DMF) at room temperature under air [Eq. (1); ODCB = 1,2-dichlorobenzene]. Notably, the crossee below) were prepared for the first time through rization of two different hydrofullerenes.



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We initiated this unprecedented but highly promising catalytic dimerization by examining solvents and catalysts at room temperature under air. The yields in Table 1 were

**Table 1:** Screening of catalysts and solvents for the homo-dimerization of monofunctionalized [60]hydrofullerenes.<sup>[a]</sup>



Entry	Catalyst	Solvent (1:3)	<i>t</i> [h]	<b>2</b> a $[\%]^{[b]}$	<b>1</b> a [%] <sup>[b]</sup>
1	Cu(OAc) <sub>2</sub>	ODCB	24	trace	97
2	Cu(OAc) <sub>2</sub>	1,4-dioxane/ODCB	24	trace	96
3	Cu(OAc) <sub>2</sub>	THF/ODCB	24	20	78
4	Cu(OAc) <sub>2</sub>	CH <sub>3</sub> CN/ODCB	4	92	4
5	Cu(OAc) <sub>2</sub>	DMF/ODCB	4	94	4
6	Cu(OAc) <sub>2</sub>	DMF/ODCB (1:10)	4	97 (92)	2
7 <sup>[c]</sup>	Cu(OAc) <sub>2</sub>	DMF/ODCB	4	14	84
8 <sup>[c,d]</sup>	Cu(OAc) <sub>2</sub>	DMF/ODCB	2	93	2
9	Cu(OCH <sub>3</sub> ) <sub>2</sub>	CH <sub>3</sub> CN/ODCB	48	66	25
10	AgOAc	CH <sub>3</sub> CN/ODCB	48	81	13
11	CuCl <sub>2</sub>	CH <sub>3</sub> CN/ODCB	48	trace	96
12	Cu(OTf)₂	CH <sub>3</sub> CN/ODCB	48	0	94
13	Au(OAc) <sub>3</sub>	CH <sub>3</sub> CN/ODCB	48	86	11
14	Pd(OAc) <sub>2</sub>	CH <sub>3</sub> CN/ODCB	48	12	85
15	Ni(OAc) <sub>2</sub>	CH <sub>3</sub> CN/ODCB	48	20	78
16	Zn(OAc) <sub>2</sub>	CH <sub>3</sub> CN/ODCB	24	0	98
17	Mn(OAc)₃	CH <sub>3</sub> CN/ODCB	24	14	82
18	none	CH <sub>3</sub> CN/ODCB	24	0	99

[a] Conditions: The catalyst (10 mol%) was added to a solution (10 mL) of **1a** (0.1 mmol) and additives in ODCB under air. The resulting mixture was stirred at room temperature for the times shown. [b] Yields determined by HPLC by using  $C_{60}$  as an internal standard. Yield of product isolated by silica-gel chromatography is shown in parentheses. [c] Reaction was conducted under argon atmosphere. [d] 1.0 equivalent of Cu(OAc)<sub>2</sub> was used.

determined by HPLC analysis using  $C_{60}$  as an internal standard. Homo-dimerization of the monofunctionalized hydrofullerene  $1a^{[7]}$  in the presence of  $Cu(OAc)_2$  (10 mol%) by using ODCB as a sole solvent afforded only trace amounts of the corresponding dimer 2a, and 1a was recovered almost quantitatively (Table 1, entry 1). The remarkable enhancement of efficiency on addition of organometal reagents to  $C_{60}$  by adding pyridine or DMF reported by the Nakamura group<sup>[11]</sup> led us to examine polar solvents mixed with ODCB. The addition of 1,4-dioxane did not affect the yield of 2a, whereas the use of tetrahydrofuran afforded 2a in 20% yield (Table 1, entries 2 and 3). We further examined more-polar additives. To our delight, the addition of CH<sub>3</sub>CN or DMF improved the yields of 2a to 92% and

94%, respectively, within 4 h (Table 1, entries 4 and 5). A decrease of the amount of DMF resulted in slightly increased yield (Table 1, entry 6).

It should be noted that, in the absence of air, the present reaction produced the corresponding dimer 2a in only 14% yield under a catalytic amount of Cu(OAc)<sub>2</sub> (Table 1, entry 7). This result indicates that air has an important role, which is indispensable for achieving high catalytic activity. Moreover, recent studies on the formation of the single-bonded fullerene dimers show that the fullerene radical  $(R^1C_{60})$  is almost certainly a key intermediate, which can be formed from the corresponding fullerene anion  $(R^1C_{60}^{-})$  by  $O_2$  or  $I_2$  oxidant.<sup>[3b,5b-d]</sup> If this is the case, the fact that a stoichiometric amount of Cu(OAc)<sub>2</sub> affords 2a in 93% yield in the absence of air means that  $Cu(OAc)_2$  can generate  $R^1C_{60}$  under the present solvent systems (Table 1, entry 8). To gain further insight into the role of the metal oxidant, we examined various metal catalysts. Other coinage-metal catalysts with lower acidity than Cu(OAc)<sub>2</sub>, such as Cu(OMe)<sub>2</sub> and AgOAc, are also active, but the yields are lower than that with  $Cu(OAc)_2$  and longer reaction times are needed (Table 1, entries 9 and 10). Lewis acidic metal catalysts, such as CuCl<sub>2</sub> and Cu(OTf)<sub>2</sub>, are totally inactive, although Au(OAc)<sub>3</sub> showed good catalytic activity notwithstanding its higher acidity (Table 1, entries 11-13). In contrast, several other transition-metal acetates, such as Pd(OAc)<sub>2</sub>, Ni(OAc)<sub>2</sub>, Zn- $(OAc)_2$ , and  $Mn(OAc)_3$ , are less active or completely ineffective (Table 1, entries 14-17). It is clear that the reaction did not proceed without metal catalysts (Table 1, entry 18). In addition, under optimized conditions (10 mol% of Cu(OAc)<sub>2</sub> in a 1:10 mixture of DMF and ODCB at room temperature under air for 4 h), the reaction proceeded with similar efficiency on a one-gram scale, giving 2a in 90% yield.

The structure for the *meso* isomer of **2a** was unambiguously confirmed by single-crystal X-ray diffraction analysis (Figure 1).<sup>[12]</sup> A crystal of the *meso* isomer was grown as the predominant component in CHCl<sub>3</sub>/CS<sub>2</sub> at -15 °C from a mixture of *meso* and racemic products. The fullerene–fullerene C–C bond (1.53(2) Å) is slightly shorter than the reported one.<sup>[3b,c]</sup> The UV/Vis spectrum of **2a** in chloroform showed a broad absorption band at 445 nm, which is red-shifted relative to that of the corresponding hydrofullerene **1a** (433 nm). The cyclic voltammogram (CV) of **2a** in ODCB



*Figure 1.* ORTEP of the *meso* isomer of **2a** and CVs of **1a** and **2a** in ODCB.

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exhibited three reversible waves on reduction, which would correspond to the formation of monoanion, dianon, and trianion of its monomer (Figure 1).<sup>[3b]</sup> The different values between dimer **2a** and monomer **1a** on half-wave potentials  $(E_{1/2}^{\text{red}})$  clearly indicate the electronic interaction between the two C<sub>60</sub> cages of **2a**.

The present Cu(OAc)<sub>2</sub>-catalyzed dimerization of monosubstituted hydrofullerenes **1** showed high compatibility with a variety of functional groups, producing the corresponding single-bonded dimers **2** in very high yields (Table 2; THP = tetrahydropyranyl). All of the reactions were monitored by TLC and HPLC analysis, and the corresponding dimers **2** were isolated by silica gel column chromatography as a mixture of *meso* and racemic isomers. In each case, a very small amount of recovered **1** and unidentified products was observed, but these impurities could be removed by silica gel column chromatography. An *n*-Butyl (**1b**) or a methoxy group (**1c**) on the benzene ring of monobenzyl-substituted hydrofullerenes was tolerated, affording the corresponding dimers **2b,c** in excellent yields (Table 2, entries 1 and 2).<sup>[7]</sup> It is

**Table 2:** Cu(OAc)<sub>2</sub>-catalyzed homo-dimerization of monosubstituted hydrofullerenes.<sup>[a]</sup>



Entry	1	t [h]	2	Yield <b>2</b> [%] <sup>10</sup>	Yield 1 [%] <sup>[9]</sup>
1	1 b	4	2 b	90	2
2	lc	4	2 c	96	trace
3	٦d	4	2 d	88	2
4	le	4	2 e	90	trace
5	1 f	4	2 f	94	3
6 <sup>[c]</sup>	lg	24	2 g	70	3
7	1h	5	2 h	81	trace
8	1i	5.5	2 i	84	2
9	1j	4.5	2j	91	trace
10	1k	5	2 k	79	trace

[a] Conditions: Cu(OAc)<sub>2</sub> (10 mol%) was added to a solution of 1 (0.1 mmol) and DMF (1 mL) in ODCB (10 mL) under air. The resulting mixture was stirred at room temperature for the times shown. [b] Yields of isolated product. [c] 30 mol% of Cu(OAc)<sub>2</sub> was used.

noteworthy that hydrofullerene 1j with a propargyl ester group on the benzyl moiety produced the desired dimer 2j in 91% yield without the formation of any conjugated divnes generated from the Glaser reaction (Table 2, entry 9).<sup>[13]</sup> Alkyl-substituted hydrofullerenes with an ester group (1d)<sup>[7]</sup> as well as benzyl- and THP-protected alcohols (1e and 1f) are also active substrates, producing the corresponding dimers 2d-f in high yields, whereas hydrofullerene 1g with an unprotected hydroxy group showed a lower activity, giving 2g in 70% yield in the presence of 30 mol% of Cu(OAc)<sub>2</sub> catalyst under longer reaction times (24 h) (Table 2, entries 3-6). The reaction also proceeded well with hydrofullerenes with a benzene ring substituted directly to the C<sub>60</sub> moiety, giving 2h and 2i in 81% and 84% yield, respectively (Table 2, entries 7 and 8). The present copper catalysis was applied to the construction of a fullerene-bound macromolecule, which may be useful for versatile electronic materials. For example, under the standard conditions, the fullerene-bound dendrimer 1k afforded the corresponding dendritic dimer **2k** in 79% yield (Table 2, entry 10).<sup>[7]</sup> It should be mentioned that the prepared dimers, except for 2d and 2h, showed good solubility in toluene and ODCB. In particular, the dendritic dimer 2k exhibited dramatically improved solubility in various organic solvents.

This method also provides an interesting opportunity for the synthesis of novel cross-dimers containing two different functionalized C<sub>60</sub> units (Table 3). Under the standard conditions, cross-dimerization of two different hydrofullerenes 1a and 1f proceeded smoothly to produce the desired crossdimer 3a in 31% yield together with the two homodimers 2a and **2 f** in 26% and 30% yield, respectively (Table 3, entry 1). Cross-dimer 3a was speculated to consist of four isomers according to the four possible kinds of monoradicals (Figure 2),<sup>[3b,c]</sup> although the individual isomers cannot be completely identified from <sup>1</sup>H NMR spectra and HPLC analysis. Similarly, cross-dimerizations of 1a and 1e, as well as 1e and 1 f, afforded the cross-dimers 3b and 3c, respectively, in similar yields together with the corresponding homodimers (Table 3, entries 2 and 3). All products were isolated by silica gel chromatography. Interestingly, the cross-dimers 3 are in equilibrium with homodimers 2 in solution. For example, monitoring by <sup>1</sup>H NMR spectroscopy showed that the pure

Table 3: Cu(OAc)<sub>2</sub>-catalyzed cross-dimerization.<sup>[a]</sup>

B	R	1 +	H H Cu(OAc) <sub>2</sub> (10 m DMF/ODCB = air, RT, 5	nol%) ► 1:10 h	cross-dimer 3 + homo-dimers 2
Entry	<b>1</b> (R <sup>1</sup> )	1 (R <sup>2</sup> )	Homo-dimer <b>2</b> [%] <sup>[b]</sup>	Cro	ss-dimer <b>3</b> [%] <sup>[b]</sup>
1	1a	1f	26 ( <b>2 a</b> ); 30 ( <b>2 f</b> )	31	(3 a)
2	la	le	25 (2a); 31 (2e)	32	(3 b)
3	le	1f	29 (2e); 31 (2f)	33	(3 c)

[a] Conditions: To a solution of two different hydrofullerenes **1** (0.1 mmol) and DMF (1 mL) in 1,2-dichlorobenzene (ODCB, 10 mL) under an air atmosphere was added  $Cu(OAc)_2$  (10 mol%). The resulting mixture was stirred at room temperature for 5 h. [b] Dimers **2** and **3** were isolated by silica-gel chromatography.

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*Figure 2.* Four plausible isomers of cross-dimers **3** speculated from their four different radical monomers.

dimer **3a** was gradually converted into **2a** and **2f** in CDCl<sub>3</sub>/ CS<sub>2</sub> at ambient temperature and reached equilibrium after 12 h, although this interconversion rate between the crossdimer and homodimers was slow enough to identify its <sup>1</sup>H and <sup>13</sup>C NMR spectra. Furthermore, **3a** was obtained by mixing of the two homodimers 2a and 2f in CDCl<sub>3</sub>/CS<sub>2</sub> at ambient temperature through similar interconversion. In sharp contrast, **3a** is very stable in the solid state; it can be stored for several months at ambient temperature without any structural changes. The single-bonded dimers dissociate to the stable monoradicals in solution, followed by recombination of the resulting monoradicals to form various dimers, which was in good agreement with the previous studies reported by the groups of Komatsu and Wang.<sup>[3b,c]</sup> This interconversion provides an alternative approach for the construction of cross-dimers from various homodimers in solution.

A plausible mechanism for the present catalytic dimerization based on our experimental observations, as well as works on the generation of radical cation species by the groups of Komatsu<sup>[9]</sup> and Yu,<sup>[10]</sup> is shown in Scheme 1. Initially, the one-electron oxidation of hydrofullerene **1** takes place through the single-electron transfer from the  $C_{60}$ 



**Scheme 1.** A plausible mechanism for the Cu(OAc)<sub>2</sub>-catalyzed dimerization of monosubstituted hydrofullerenes.

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moiety to  $Cu(OAc)_2$ , leading to radical cation **B**. We assume that coordination of  $Cu(OAc)_2$  to the  $C_{60}$  moiety to form intermediate **A** may accelerate the one-electron oxidation, wherein polar solvents such as DMF and CH<sub>3</sub>CN stabilize **A**. Elimination of a proton on the radical cation **B** by the acetate anion forms the monoradical **C**, which produces the corresponding single-bonded dimers. Dimerization of two monoradicals with *R* and *S* configuration gives the *meso* isomer (*R*– *S*), whereas dimerization of two monoradicals with the same configuration affords a racemic mixture of *R*–*R* and *S*–*S* isomers.<sup>[3c]</sup> We also speculate that polar solvents stabilize the radical cation **B** to assist the subsequent release of the proton. Finally, the Cu(OAc)<sub>2</sub> catalyst is regenerated by oxidation of CuOAc under an air atmosphere and in the presence of acetic acid.

In conclusion, we have demonstrated for the first time that single-bonded fullerene dimers can be synthesized in excellent yields through the catalytic dimerization of monosubstituted hydrofullerenes. A wide range of functional groups are tolerated. In contrast to the previously reported methods, the present catalytic reaction can be carried out under very mild conditions with remarkably higher yields. Fullerenebound dendritic homodimers and various cross-dimers, which are otherwise difficult to obtain, were synthesized in good to high yields for the first time. The present catalytic dimerization of monosubstituted hydrofullerenes seems to proceed through Cu(OAc)<sub>2</sub>-catalyzed generation of a fullerenyl radical cation species followed by formation of a fullerenyl radical. The Cu(OAc)<sub>2</sub> catalyst combined with a small amount of DMF under air is crucial for the efficient formation of the corresponding single-bonded fullerene dimers. Investigation on further catalytic functionalization of fullerenes and application to materials science are in progress.

#### **Experimental Section**

**2a**: To a solution of **1a** (87 mg, 0.1 mmol) in DMF and ODCB (1:10, 11 mL) was added Cu(OAc)<sub>2</sub> (1.8 mg, 0.01 mmol) at room temperature under air. The reaction mixture was stirred at room temperature for 4 h. The reaction was monitored by HPLC analysis (elution with toluene at 0.6 mLmin<sup>-1</sup> flow rate, detection at 320 nm). The mixture was subjected directly with silica gel chromatography (toluene/hexane = 1:1). A solution of **2a** in toluene and hexane was evaporated at below 60 °C, and the residue was washed with acetone to afford **2a** in 92% yield (80 mg).

**3a**: To a solution of **1a** (44 mg, 0.05 mmol) and **1f** (46 mg, 0.05 mmol) in DMF and ODCB (1:10, 11 mL) was added  $Cu(OAc)_2$  (1.8 mg, 0.01 mmol) at room temperature under air. The reaction mixture was stirred at room temperature for 5 h. The reaction was monitored by HPLC analysis (elution with toluene at 0.6 mLmin<sup>-1</sup> flow rate, detection at 320 nm). The mixture was subjected directly with silica gel chromatography using toluene as an eluent. Product **2a** was isolated as the first fragment, followed by **3a** and **2f**. A solution of **3a** in toluene was evaporated at below 60 °C, and the residue was washed with acetone to remove the remaining toluene, affording **3a** in 31% yield (28 mg). Similarly, **2a** and **2f** were obtained in 26% (23 mg) and 30% (26 mg) yield, respectively, after evaporation of toluene and washing with acetone.

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- [1] a) J. S. Segura, N. Martin, *Chem. Soc. Rev.* 2000, 29, 13–25; b) H.
   Luo, Y. Araki, M. Fujitsuka, O. Ito, F. Cheng, Y. Murata, K.
   Komatsu, J. Phys. Chem. B 2004, 108, 11915–11920.
- [2] a) J. R. Morton, K. F. Preston, P. J. Krusic, E. Wasserman, J. Chem. Soc. Perkin Trans. 2 1992, 1425–1429; b) J. R. Morton, K. F. Preston, P. J. Krusic, S. A. Hill, E. Wasserman, J. Am. Chem. Soc. 1992, 114, 5454–5455; c) P. J. Fagan, P. J. Krusic, C. N. McEwen, J. Lazar, D. H. Parker, N. Herron, E. Wasserman, Science 1993, 262, 404–407.
- [3] a) M. Yoshida, F. Sultana, N. Uchiyama, T. Yamada, M. Iyoda, *Tetrahedron Lett.* **1999**, *40*, 735–736; b) F. Cheng, Y. Murata, K. Komatsu, Org. Lett. **2002**, *4*, 2541–2544; c) G.-W. Wang, C.-Z. Wang, S.-E. Zhu, Y. Murata, Chem. Commun. **2011**, *47*, 6111– 6113.
- [4] a) S. Ōsawa, E. Osawa, M. Harada, J. Org. Chem. 1996, 61, 257–265; b) T. Tanaka, K. Komatsu, J. Chem. Soc. Perkin Trans. 1 1999, 1671–1675.
- [5] a) T.-H. Zhang, P. Lu, F. Wang, G.-W. Wang, Org. Biomol. Chem.
  2003, 1, 4403 4407; b) P. J. Fagan, P. J. Krusic, D. H. Evans, S. A. Lerke, E. Johnston, J. Am. Chem. Soc. 1992, 114, 9697 9699;
  c) G. Schick, K.-D. Kampe, A. Hirsch, J. Chem. Soc. Chem. Commun. 1995, 2023 2024; d) Y. Zhang, Y. Matsuo, C.-Z. Li, H. Tanaka, E. Nakamura, J. Am. Chem. Soc. 2011, 133, 8086 8089.
- [6] a) N. Martín, M. Altable, S. Filippone, A. Martín-Domenech, A. Poater, M. Solà, *Chem. Eur. J.* 2005, *11*, 2716–2729; b) Y. Matsuo, A. Iwashita, E. Nakamura, *Chem. Lett.* 2006, *35*, 858–859; c) M. Nambo, R. Noyori, K. Itami, *J. Am. Chem. Soc.* 2007, *129*, 8080–8081; d) S. Mori, M. Nambo, L.-C. Chi, J. Bouffard, K.

Itami, Org. Lett. 2008, 10, 4609–4612; e) M. Nambo, A. Wakamiya, S. Yamaguchi, K. Itami, J. Am. Chem. Soc. 2009, 131, 15112–15113; f) M. Nambo, K. Itami, Chem. Eur. J. 2009, 15, 4760–4764; g) B. Zhu, G.-W. Wang, J. Org. Chem. 2009, 74, 4426–4428; h) B. Zhu, G.-W. Wang, Org. Lett. 2009, 11, 4334–4337; i) S. Filippone, E. E. Maroto, A. Martín-Domenech, M. Suarez, N. Martín, Nat. Chem. 2009, 1, 578–582; j) Z. Xiao, Y. Matsuo, E. Nakamura, J. Am. Chem. Soc. 2010, 132, 12234–12236; k) E. E. Maroto, A. de Cózar, S. Filippone, Á. Martín Domenech, M. Suarez, F. P. Cossío, N. Martín, Angew. Chem. 2011, 123, 6184–6188; Angew. Chem. Int. Ed. 2011, 50, 6060–6064; l) N. Martín, M. Altable, S. Filippone, Á. Martín Domenech, L. Echegoyen, C. M. Cardona, Angew. Chem. 2006, 118, 116–120; Angew. Chem. Int. Ed. 2006, 45, 110–114.

- [7] S. Lu, T. Jin, M. Bao, Y. Yamamoto, J. Am. Chem. Soc. 2011, 133, 12842–12848.
- [8] T. Jin, M. Himuro, Y. Yamamoto, J. Am. Chem. Soc. 2010, 132, 5590-5591.
- [9] Y. Murata, F. Cheng, T. Kitagawa, K. Komatsu, J. Am. Chem. Soc. 2004, 126, 8874–8875.
- [10] X. Chen, X.-S. Hao, C. E. Goodhue, J.-Q. Yu, J. Am. Chem. Soc. 2006, 128, 6790-6791.
- [11] a) Y. Matsuo, K. Tahara, K. Morita, K. Matsuo, E. Nakamura, Angew. Chem. 2007, 119, 2902–2905; Angew. Chem. Int. Ed. 2007, 46, 2844–2847; b) Y. Matsuo, A. Iwashita, Y. Abe, C.-Z. Li, K. Matsuo, M. Hashiguchi, E. Nakamura, J. Am. Chem. Soc. 2008, 130, 15429–15436.
- [12] CCDC 846755 (meso isomer of 2a) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.
- [13] C. Glaser, Ber. Dtsch. Chem. Ges. 1869, 2, 422-424.