doi:10.1246/cl.2010.1323
Published on the web November 13, 2010

Hybrid Inorganic–Organic Crystals Composed of Octamolybdate Isomers and Pyridinium Surfactant

Takeru Ito,*[1] Keisuke Mikurube,[1] Yukihiro Abe,[1] Takahisa Koroki,[2] Masaki Saito,[2]
Jun Iijima,[3] Haruo Naruke,[3] and Tomoji Ozeki*[2]
[1]*Department of Chemistry, School of Science, Tokai University, 4-1-1 Kitakaname, Hiratsuka, Kanagawa 259-1292*
[2]*Department of Chemistry and Materials Science, Tokyo Institute of Technology,*
2-12-1-H-63 O-okayama, Meguro-ku, Tokyo 152-8551
[3]*Chemical Resources Laboratory, Tokyo Institute of Technology,*
4259-R1-23 Nagatsuta, Midori-ku, Yokohama, Kanagawa 226-8503

(Received September 30, 2010; CL-100843; E-mail: takeito@keyaki.cc.u-tokai.ac.jp, tozeki@cms.titech.ac.jp)

Hybrid inorganic–organic crystals containing α- and β-type octamolybdates (α-Mo_8 and β-Mo_8) were successfully prepared by using hexadecylpyridinium (C_{16}py). Although both hybrid crystals consisted of alternate stacking patterns of monolayers of Mo_8 anions and interdigitated bilayers of C_{16}py cations, the Mo_8 inorganic monolayers had different packing patterns between the hybrid C_{16}py–α-Mo_8 and C_{16}py–β-Mo_8 crystals. Each α-Mo_8 was isolated by the inserted C_{16}py cations, while β-Mo_8 formed one-dimensional chains together with sodium cations.

Hybrid inorganic–organic layered crystals exhibit higher structural flexibility than purely inorganic compounds owing to organic components. Conductive hybrid crystals[1–3] composed of organic molecules and inorganic anions have potential as solid electrolyte. In such hybrid layered crystals, molecular structure and arrangement of components should be precisely controlled for the emergence of conductive functions.

A combination of polyoxometalate anions and surfactant cations is promising for functional layered inorganic–organic hybrids. Polyoxometalates can add various physicochemical properties for an inorganic component,[4,5] and surfactants lead to controllable layered structures as a structure-directing organic component.[6–8] Several hybrid polyoxometalate–surfactant materials[9] and hybrid layered crystals[10–16] have been reported. Some kinds of polyoxometalates have isomers.[17–21] Selective usage of suitable isomers could allow finer design of the structures and functions of the hybrid crystals.

Here, we report the structures of hybrid layered crystals containing hexadecylpyridinium (C_{16}py) and octamolybdate isomers, α-$Mo_8O_{26}{}^{4-}$ (α-Mo_8) and β-$Mo_8O_{26}{}^{4-}$ (β-Mo_8). The difference in the Mo_8 structure induced the different composition and structure of the hybrid crystals.

The hybrid crystal containing α-Mo_8 (C_{16}py–α-Mo_8) was synthesized by a modified procedure in the literature.[22,23] The crystal structure of C_{16}py–α-Mo_8, $[C_5H_5N(C_{16}H_{33})]_4[\alpha$-$Mo_8O_{26}]$, was determined by X-ray structure analysis.[24,25] C_{16}py–α-Mo_8 consists of alternating α-Mo_8 inorganic monolayers and C_{16}py organic layers (Figure 1a). The periodicity of the layers is 23.0 Å. The hexadecyl chains of C_{16}py interdigitate in the bilayers of C_{16}py, and all C–C bonds except one terminal C–C bond (C41–C42) have anti-conformation. The hydrophilic heads of C_{16}py penetrate into the α-Mo_8 inorganic monolayers (Figure 1b) as in the C_{16}py–hexamolybdate crystal[13] and isolate each α-Mo_8 anion. There are two independent pairs of pyridine rings with a slight overlap, suggesting the presence of weak π–π stacking interaction (distance between pyridine rings: 3.24–3.64 Å).

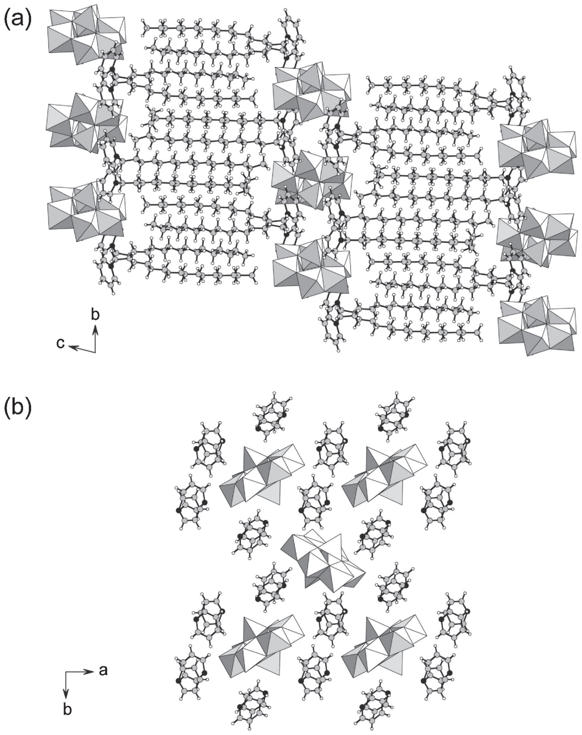

Figure 1. Crystal structure of C_{16}py–α-Mo_8 (C: gray, N: black, H: white; α-Mo_8 in polyhedral representations): (a) *a* axis projection and (b) molecular arrangement in the *ab* plane. The hexadecyl groups are omitted for clarity.

C_{16}py–α-Mo_8 has C–H···O hydrogen bonds[26,27] at the interface between the α-Mo_8 and C_{16}py layers. The C···O distances of the hydrogen bonds are 3.23–3.98 Å (mean value: 3.64 Å). Most hydrogen bonds are formed between oxygen atoms of α-Mo_8 and the hydrophilic head of C_{16}py (i.e., pyridine rings or methylene groups near nitrogen).

Powder X-ray diffraction patterns[28] of C_{16}py–α-Mo_8 (Figure 2b) are identical to the pattern calculated from the results of single-crystal X-ray analysis (Figure 2a, Supporting Information[34]), indicating that C_{16}py–α-Mo_8 is formed as a single phase.

Figure 3 shows the structure of hybrid crystal composed of C_{16}py and β-Mo_8 measured at 173 K (C_{16}py–β-Mo_8-173).[29]

© 2010 The Chemical Society of Japan

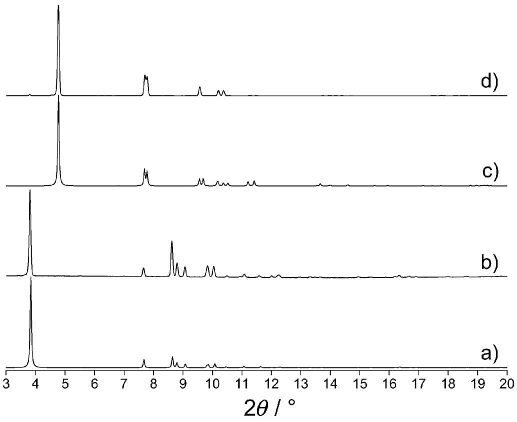

Figure 2. Powder X-ray diffraction patterns of a) simulation from single-crystal data of C_{16}py–α-Mo_8, b) observed data for C_{16}py–α-Mo_8, c) simulation from single-crystal data of C_{16}py–β-Mo_8-273, and d) observed data for C_{16}py–β-Mo_8. All the measurements were carried out at ambient temperature with Cu Kα radiation.

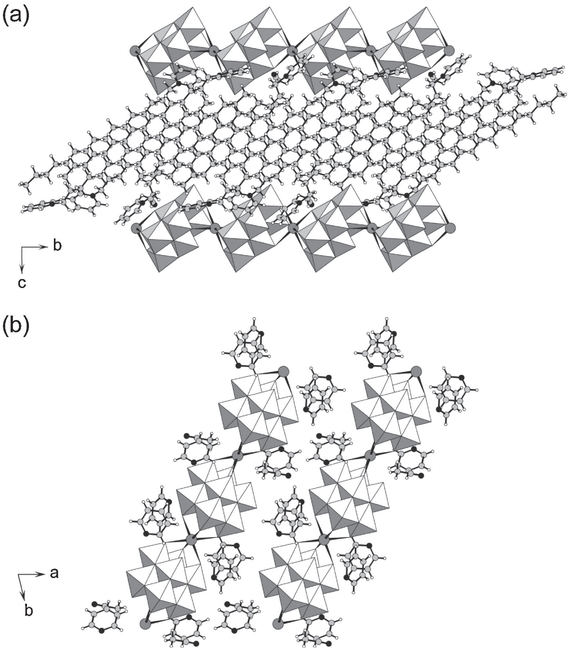

Figure 3. Crystal structure of C_{16}py–β-Mo_8 at 173 K (C: gray, N: black, H: white; Na: gray (larger spheres); β-Mo_8 in polyhedral representations): (a) *a* axis projection and (b) molecular arrangement in the *ab* plane. The hexadecyl groups are omitted for clarity.

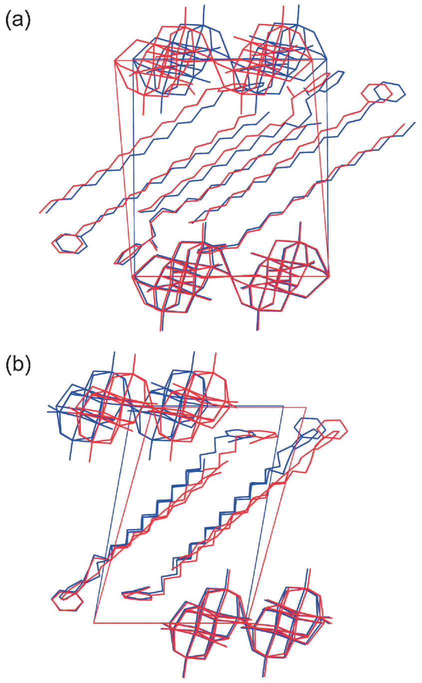

Figure 4. Crystal packing of C_{16}py–β-Mo_8 at 173 (blue) and 273 K (red) in wireframe representations: (a) *a* axis and (b) *b* axis projection. The hydrogen atoms are omitted for clarity.

Single-crystal X-ray analysis revealed the composition of C_{16}py–β-Mo_8 to be $[C_5H_5N(C_{16}H_{33})]_3Na[\beta\text{-}Mo_8O_{26}]\cdot CH_3CN$.[29,30] The crystal structure of C_{16}py–β-Mo_8-173 consists of alternate stacking of β-Mo_8 inorganic monolayers and C_{16}py organic layers with a periodicity of 18.6 Å (Figure 3a). As in the C_{16}py–α-Mo_8 crystal, the hexadecyl chains of C_{16}py interdigitate, and all C–C bonds except one (C7–C8) have anti-conformation. C_{16}py–β-Mo_8-173 also has C–H···O hydrogen bonds at the interface between the β-Mo_8 and C_{16}py layers (C···O distance: 3.28–3.96 Å; mean value: 3.61 Å). Observed and calculated powder diffraction patterns of C_{16}py–β-Mo_8 are shown in Figures 2d and 2c, respectively.

The β-Mo_8 anions are considered to be formed by the isomerization of α-Mo_8. C_{16}py–β-Mo_8 was obtained by keeping the C_{16}py–α-Mo_8 powder in acetonitrile. Therefore, slightly dissolved C_{16}py–α-Mo_8 seems to isomerize into β-Mo_8 to reprecipitate as C_{16}py–β-Mo_8. Such isomerization between α-Mo_8 and β-Mo_8 in acetonitrile has been reported.[17,18]

C_{16}py–β-Mo_8 contains Na^+ as counter cation as observed in other salts of β-Mo_8.[31,32] The Na^+ cations connect β-Mo_8 anions to form one-dimensional β-Mo_8–Na^+ chains (Figure 3b). The inorganic monolayers of C_{16}py–β-Mo_8-173 are composed of the one-dimensional β-Mo_8–Na^+ chains, inserted C_{16}py cations and acetonitrile molecules (solvent of crystallization). The space between the β-Mo_8–Na^+ chains are filled by pyridine rings of C_{16}py and acetonitrile molecules, which are located in the vicinity of Na^+ cations. There seems to be no interaction between pyridine rings nor between pyridine ring and acetonitrile.

The hybrid crystal of C_{16}py–β-Mo_8 exhibited a phase transition, which is common for compounds with long aliphatic chain.[33] Figure 4 shows the crystal packing of C_{16}py–β-Mo_8 measured at 173 and 273 K (C_{16}py–β-Mo_8-173 and C_{16}py–β-Mo_8-273). The *c* axis is more tilted with respect to the *ab* plane in C_{16}py–β-Mo_8-273. The packing features and molecular conformations are similar, while slight expansion in each axis of the lattice is observed in C_{16}py–β-Mo_8-273. Several torsion angles in the C_{16}py tails and tilt angles of the hexadecyl tail to the pyridine ring in the C_{16}py cations are different between C_{16}py–β-Mo_8-173 and C_{16}py–β-Mo_8-273, which may cause the phase transition. The structures of the one-dimensional β-Mo_8–Na^+ chains are identical before and after the phase transition,

© 2010 The Chemical Society of Japan

suggesting the stability of the β-Mo_8–Na^+ chains. C_{16}py–β-Mo_8-273 has similar C–H···O hydrogen bonds (C···O distance: 3.13–3.97 Å; mean value: 3.65 Å) to C_{16}py–β-Mo_8-173. As for C_{16}py–α-Mo_8, it was not possible to find appropriate conditions for the observation of phase transition.

In conclusion, we have reported hybrid layered inorganic–organic crystals composed of polyoxomolybdate isomers, $[C_5H_5N(C_{16}H_{33})]_4[\alpha\text{-}Mo_8O_{26}]$ (C_{16}py–α-Mo_8) and $[C_5H_5N(C_{16}H_{33})]_3Na[\beta\text{-}Mo_8O_{26}]\cdot CH_3CN$ (C_{16}py–β-Mo_8). Both had the alternate stacking of polyoxomolybdate monolayers and C_{16}py interdigitated bilayers. The difference in the molecular structure of Mo_8 led the change in the composition and Mo_8 arrangement. The crystal structure of hybrid polyoxometalate–surfactant crystals is controllable by changing the isomer structure of polyoxometalate.

The synchrotron radiation experiment was performed under the approval of the Photon Factory Program Advisory Committee (Proposal No. 2007G639). This study was supported in part by Research and Study Program of Tokai University Educational System General Research Organization, and The Murata Science Foundation.

References and Notes

1 P. Batail, *Chem. Rev.* **2004**, *104*, 4887.

2 a) E. Coronado, C. J. Gómez-García, *Chem. Rev.* **1998**, *98*, 273. b) E. Coronado, C. Giménez-Saiz, C. J. Gómez-García, *Coord. Chem. Rev.* **2005**, *249*, 1776. c) L. Ouahab, *Chem. Mater.* **1997**, *9*, 1909.

3 D. B. Mitzi, *Prog. Inorg. Chem.* **1999**, *48*, 1.

4 C. L. Hill, *Chem. Rev.* **1998**, *98*, 1.

5 D.-L. Long, E. Burkholder, L. Cronin, *Chem. Soc. Rev.* **2007**, *36*, 105.

6 Q. Huo, D. I. Margolese, U. Ciesla, D. G. Demuth, P. Feng, T. E. Gier, P. Sieger, A. Firouzi, B. F. Chmelka, F. Schüth, G. D. Stucky, *Chem. Mater.* **1994**, *6*, 1176.

7 Y. Yamauchi, K. Kuroda, *Chem. Asian J.* **2008**, *3*, 664.

8 T. Yokoi, T. Tatsumi, *J. Jpn. Pet. Inst.* **2007**, *50*, 299.

9 a) A. Stein, M. Fendorf, T. P. Jarvie, K. T. Mueller, A. J. Benesi, T. E. Mallouk, *Chem. Mater.* **1995**, *7*, 304. b) G. G. Janauer, A. Dobley, J. Guo, P. Zavalij, M. S. Whittingham, *Chem. Mater.* **1996**, *8*, 2096. c) A. Taguchi, T. Abe, M. Iwamoto, *Adv. Mater.* **1998**, *10*, 667. d) J. Do, A. J. Jacobson, *Chem. Mater.* **2001**, *13*, 2436. e) S. Polarz, B. Smarsly, M. Antonietti, *ChemPhysChem* **2001**, *2*, 457. f) G. Zhang, H. Ke, T. He, D. Xiao, Z. Chen, W. Yang, J. Yao, *J. Mater. Res.* **2004**, *19*, 496. g) K. N. Rao, L. D. Dingwall, P. L. Gai, A. F. Lee, S. J. Tavener, N. A. Young, K. Wilson, *J. Mater. Chem.* **2008**, *18*, 868. h) S. Landsmann, C. Lizandara-Pueyo, S. Polarz, *J. Am. Chem. Soc.* **2010**, *132*, 5315.

10 G. G. Janauer, A. D. Dobley, P. Y. Zavalij, M. S. Whittingham, *Chem. Mater.* **1997**, *9*, 647.

11 N. Fosse, L. Brohan, *J. Solid State Chem.* **1999**, *145*, 655.

12 T. Ito, K. Sawada, T. Yamase, *Chem. Lett.* **2003**, *32*, 938.

13 T. Ito, T. Yamase, *Chem. Lett.* **2009**, *38*, 370.

14 T. Ito, T. Yamase, *Materials* **2010**, *3*, 158.

15 M. Nyman, D. Ingersoll, S. Singh, F. Bonhomme, T. M. Alam, C. J. Brinker, M. A. Rodriguez, *Chem. Mater.* **2005**, *17*, 2885.

16 M. Nyman, M. A. Rodriguez, T. M. Anderson, D. Ingersoll, *Cryst. Growth Des.* **2009**, *9*, 3590.

17 W. G. Klemperer, W. Shum, *J. Am. Chem. Soc.* **1976**, *98*, 8291.

18 J. J. Cruywagen, *Adv. Inorg. Chem.* **1999**, *49*, 127.

19 S. Himeno, H. Niiya, T. Ueda, *Bull. Chem. Soc. Jpn.* **1997**, *70*, 631.

20 R. N. Devi, J. Zubieta, *Inorg. Chim. Acta* **2002**, *332*, 72.

21 Y.-Q. Lan, S.-L. Li, X.-L. Wang, K.-Z. Shao, Z.-M. Su, E.-B. Wang, *Inorg. Chem.* **2008**, *47*, 529.

22 N. H. Hur, W. G. Klemperer, R.-C. Wang, *Inorg. Synth.* **1990**, *27*, 78.

23 C_{16}py–α-Mo_8: $Na_2MoO_4\cdot 2H_2O$ (1.9 g, 8 mmol) was dissolved in H_2O (5 mL), and the pH level was adjusted to 3.0–4.5 with 6 M HCl. To the acidified solution was added a water/ethanol (10 mL, 7:3 or 1:1 (v/v)) solution of $C_{16}pyCl\cdot H_2O$ (1.1 g, 3 mmol) and stirred for 10 min. The resultant suspension was filtered and dried in dark place. Hot acetonitrile solution of the crude product was kept at 315 K to give colorless plates. Anal. Calcd for $C_{84}H_{152}N_4Mo_8O_{26}$: C, 42.0; H, 6.4; N, 2.3%. Found: C, 41.2; H, 6.5; N, 2.3%. IR (KBr disk): 958 (m), 922 (s), 912 (s), 850 (m), 804 (s), 719 (w), 688 (m), 661 (s), 646 (m), 559 (w) cm^{-1}. C_{16}py–β-Mo_8: Colorless plates of C_{16}py–β-Mo_8 with different shape were obtained as the mixture by keeping acetonitrile containing the recrystallized powder of C_{16}py–α-Mo_8 in a glass vial, which seems to be a source of Na^+ in C_{16}py–β-Mo_8.

24 a) X-ray diffraction data for C_{16}py–α-Mo_8 and C_{16}py–β-Mo_8-173 were collected with a Rigaku MERCURY CCD diffractometer using Mo Kα radiation. Those for C_{16}py–β-Mo_8-273 were measured with a Rigaku MERCURY CCD diffractometer using synchrotron radiation from the NW2A beamline of the Advanced Ring, Photon Factory (PF) of High Energy Accelerator Research Organization (KEK). Diffraction data were collected using Crystal Clear[24b] and processed with HKL2000.[24c] Structures were solved by the direct method using SHELXS97 and refined by the full-matrix least-squares using SHELXL97.[24d] b) *Crystal Clear: Molecular Structure Corporation*, Orem, UT, **2001**. c) Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307. d) G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112.

25 Crystal data for C_{16}py–α-Mo_8: $C_{84}H_{152}N_4Mo_8O_{26}$, $M_r = 2401.62$, triclinic, space group $P\bar{1}$, $a = 12.6088(4)$, $b = 18.1104(6)$, $c = 23.8004(10)$ Å, $\alpha = 75.732(1)$, $\beta = 87.148(1)$, $\gamma = 89.366(2)°$, $V = 5260.7(3)$ Å^3, $Z = 2$, $T = 293(2)$ K, $\mu = 0.988$ mm^{-1}. 38458 reflections measured, 19817 reflections independent ($R_{int} = 0.0579$). $R_1 = 0.0503$ ($I > 2\sigma(I)$) and $wR_2 = 0.1257$ (all data). CCDC-797413.

26 a) G. R. Desiraju, *Acc. Chem. Res.* **1996**, *29*, 441. b) T. Steiner, *Chem. Commun.* **1997**, 727.

27 a) H. Chiba, A. Wada, T. Ozeki, *Dalton Trans.* **2006**, 1213. b) B. Xu, Z. Peng, Y. Wei, D. R. Powell, *Chem. Commun.* **2003**, 2562. c) Y. Xia, P. Wu, Y. Wei, Y. Wang, H. Guo, *Cryst. Growth Des.* **2006**, *6*, 253. d) H. Suzuki, M. Hashimoto, S. Okeya, *Eur. J. Inorg. Chem.* **2004**, 2632.

28 Powder X-ray diffraction patterns for C_{16}py–α-Mo_8 and C_{16}py–β-Mo_8 were measured with Cu Kα radiation using a Rigaku SmartLab diffractometer. Samples were sealed in glass capillaries to prevent efflorescence. Diffraction data were indexed and subjected to Pawley refinement using Diffrac plus TOPAS software.

29 Crystal data for C_{16}py–β-Mo_8-173: $C_{65}H_{117}N_4NaMo_8O_{26}$, $M_r = 2161.14$, triclinic, space group $P\bar{1}$, $a = 13.3332(4)$, $b = 17.0481(5)$, $c = 18.9193(7)$ Å, $\alpha = 87.202(1)$, $\beta = 79.651(1)$, $\gamma = 76.121(3)°$, $V = 4106.9(2)$ Å^3, $Z = 2$, $T = 173(2)$ K, $\mu = 1.259$ mm^{-1}. 36682 reflections measured, 20892 reflections independent ($R_{int} = 0.0679$). $R_1 = 0.0536$ ($I > 2\sigma(I)$) and $wR_2 = 0.1490$ (all data). CCDC-797414.

30 Crystal data for C_{16}py–β-Mo_8-273: $C_{65}H_{117}N_4NaMo_8O_{26}$, $M_r = 2161.14$, triclinic, space group $P\bar{1}$, $a = 13.6023(4)$, $b = 17.4964(6)$, $c = 19.4011(8)$ Å, $\alpha = 81.378(1)$, $\beta = 73.108(1)$, $\gamma = 74.594(1)°$, $V = 4246.1(3)$ Å^3, $Z = 2$, $T = 273(2)$ K, $\mu = 1.112$ mm^{-1}. 35427 reflections measured, 19963 reflections independent ($R_{int} = 0.1084$). $R_1 = 0.0901$ ($I > 2\sigma(I)$) and $wR_2 = 0.3212$ (all data). CCDC-797415.

31 M. McCann, K. Maddock, C. Cardin, M. Convery, V. Quillet, *Polyhedron* **1994**, *13*, 835.

32 a) S.-M. Chen, C.-Z. Lu, Y.-Q. Yu, Q.-Z. Zhang, X. He, *Inorg. Chem. Commun.* **2004**, *7*, 1041. b) H. Abbas, A. L. Pickering, D.-L. Long, P. Kögerler, L. Cronin, *Chem.—Eur. J.* **2005**, *11*, 1071. c) H. Abbas, C. Streb, A. L. Pickering, A. R. Neil, D.-L. Long, L. Cronin, *Cryst. Growth Des.* **2008**, *8*, 635.

33 For examples, see: a) M. Yano, T. Taketsugu, K. Hori, H. Okamoto, S. Takenaka, *Chem.—Eur. J.* **2004**, *10*, 3991. b) M. Maeda, M. Nagasawa, M. Tachibana, H. Kawaji, T. Atake, A. Iida, T. Ozeki, K. Hori, *Chem. Lett.* **2004**, *33*, 1566. c) G. Gbabode, P. Negrier, D. Mondieig, E. M. Calvo, T. Calvet, M. À. Cuevas-Diarte, *Chem.—Eur. J.* **2007**, *13*, 3150.

34 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

© 2010 The Chemical Society of Japan