JOC The Journal of Organic Chemistry

NOTE

pubs.acs.org/joc

Synthesis of Oxosumanenes through Benzylic Oxidation

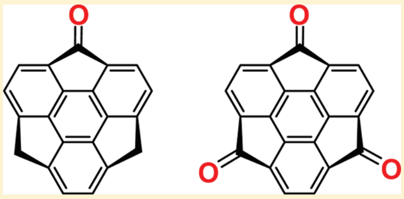
Toru Amaya,[†] Maiko Hifumi,[†] Michiaki Okada,[†] Yasutomo Shimizu,[†] Toshiyuki Moriuchi,[†] Kouji Segawa,[‡] Yoichi Ando,[‡] and Toshikazu Hirao*[,†]

[†]Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Yamada-oka, Suita, Osaka 565-0871, Japan

[‡]Institute of Scientific and Industrial Research, Osaka University, Mihogaoka, Ibaraki, Osaka 567-0047, Japan

S Supporting Information

ABSTRACT: Oxosumanenes were synthesized through benzylic oxidation. The electronic and redox properties were revealed to exhibit the expanded π-conjugation compared to sumanene. Single-crystal X-ray analysis of monooxosumanene showed columnar π-stacking in a concave−convex fashion. Stereoselective trimethylation of the trioxo derivative was performed via 1,2-addition to the carbonyl groups.



Bowl-shaped π-conjugated carbon molecules (geodesic polyarenes, buckybowls, or π bowls, here we use π bowls) are considered to be key materials in addition to fullerenes and carbon nanotubes in the curved π-conjugated carbon systems. Most of the investigation in π-bowl chemistry has been performed on corannulene ($C_{20}H_{10}$, Figure 1) and its derivatives.[1] However, the methods to prepare functionalized corannulenes are still limited because the rim of corannulene consists of aromatic double bonds.[2] On the other hand, sumanene (**1**), a C_{3v} partial symmetric structure of C_{60}, is characterized by three benzylic positions, which may allow facile functionalization. In 2003, a synthesis of **1** under nonpyrolytic conditions was developed by our group.[3] From a material viewpoint, the needle-like single crystal of **1** was revealed to show high electron mobility with large anisotropy.[4] Stereoselective trisilylation at the benzylic positions via the corresponding trianion was achieved to afford a single diastereoisomer.[5] A series of π-extended bowl-shaped π-conjugated compounds were also synthesized from **1** via the benzyl anion.[6,7] In this context, oxosumanenes such as **3** are thought to be important key scaffolds to introduce nucleophiles. Furthermore, they should be potential bowl-shaped electrical materials with larger π-conjugation and stronger electron acceptors relative to **1**. During our investigation,[8] trimethylsumanenetrione was reported.[9] However, the above-mentioned properties have not been investigated. Herein, we report the synthesis, derivatization, and characterization of monooxo- and trioxosumanenes **2** and **3**.

In order to oxidize benzylic carbons, various conditions were examined. Use of chromium trioxide with 3,5-dimethylpyrazole gave **3** in 14% yield. Benzeneseleninic anhydride with *t*-BuOK was also employed to afford **3** in 8% yield. Condensation reaction with nitrosobenzene via benzyl anion was attempted to produce triimine as a synthetic equivalent to the trione. However, two-step yield of **3** after the acid hydrolysis remained low. Gif-type oxidation conditions were investigated. In the presence of *t*-BuOOH and pyridine,[10] not only the typical $FeCl_3$ but also various metal catalysts were examined, such as $RuCl_3$, phosphotungstic acid, $VOSO_4$, $CoCl_2$, $CuCl_2$, $Mn(OAc)_4$, etc. Ultimately, a satisfactory yield of **3** was obtained under the conditions using $RuCl_3$ (73%, Scheme 1A). On the other hand, the conditions using phosphotungstic acid made the reaction slow enough to isolate monooxosumanene **2** in 51% (Scheme 1B). Meanwhile, the dione was only occasionally found during a series of investigation and identified by ^1H NMR and GC−MS analysis as follows: ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 7.8 Hz, 2H), 7.35 (s, 2H), 7.30 (d, J = 7.8 Hz, 2H), 4.74 (d, J = 20.2 Hz, 1H), 3.59 (d, J = 20.2 Hz, 2H); MS(EI) m/z 292. However, the oxidation reaction was likely to be too fast to isolate a sufficient amount of the dione.

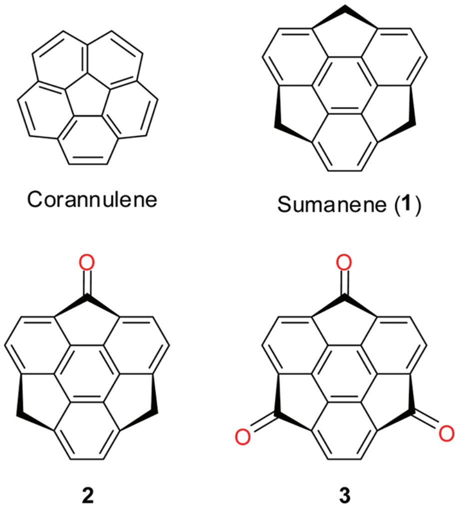
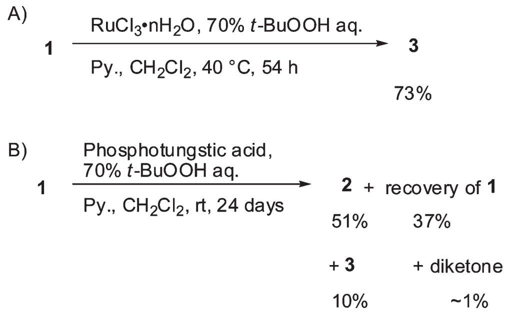


Figure 1. Corannulene, sumanene (**1**), monooxosumanene **2**, and trioxosumanene **3**.

Structure of **2** was revealed by the X-ray crystallographic analysis. The single crystal was obtained by sublimation under

Received: June 16, 2011
Published: August 29, 2011

Scheme 1. Synthesis of Trioxosumanene 3 and Monooxosumanene 2



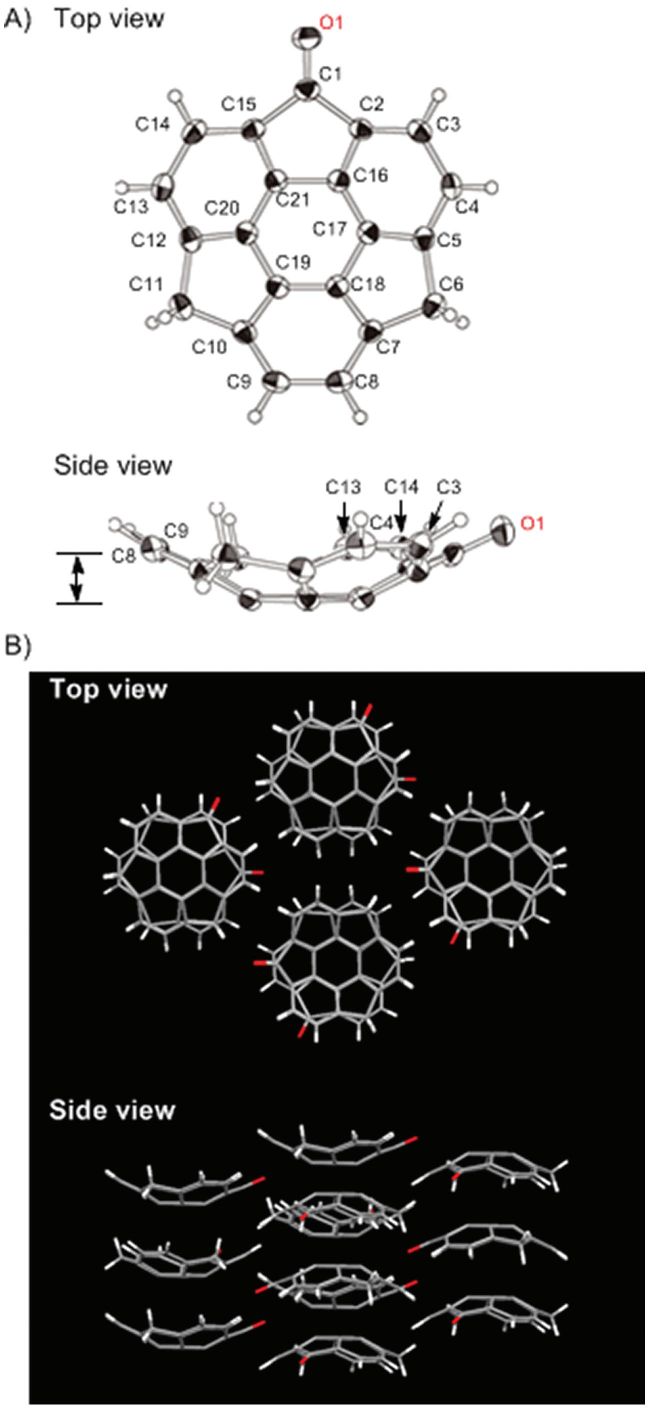


Figure 2. ORTEP drawings and packing structure of **2**.

reduced pressure (sealed tube, ∼180 °C, 0.015 MPa under argon). ORTEP diagrams clearly show the bowl-shaped structure (Figure 2A, side view).[11] The bowl depth, which is defined as the perpendicular distance from the center of the hub benzene ring (C16−C21) to the rim carbon atoms (C3, C4, C8, C9, C13, and C14), is 1.11−1.13 Å. These values are comparable to that of sumanene (1.11 Å).[5] Deep bowl-shaped π-aromatics sometimes favor a stacking structure in a concave−convex fashion.[5,12] Such an arrangement was observed in an intermolecular packing structure of **2** (Figure 2B). The stacking distance is 3.82−3.87 Å (between the hub benzene rings), which is similar to that of sumanene although it is relatively larger than that of ordinary π-stacking. Each layer of the column is stapled in a staggered fashion. The carbonyl moiety alternates between two molecules piled together as shown in Figure 2B, top view, which may be due to a steric and electronic repulsive effect of the two methylene units and carbonyl group. Neighboring columns are oriented in opposite directions (Figure 2B, side view). It contrasts to the stacking of **1**, where all columns are oriented in the same direction.[5] It suggests that **2** may also be of potential utility as electrically active materials in a solid state like **1**.

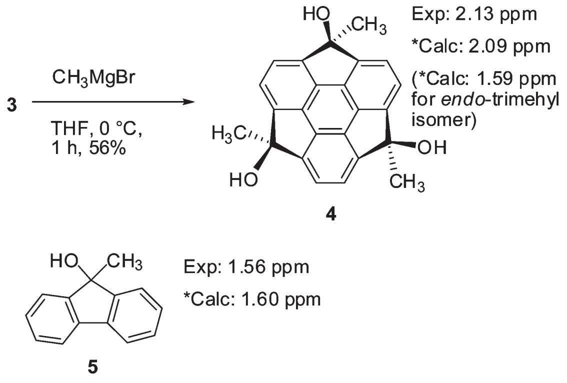
Introduction of nucleophiles via 1,2-addition was demonstrated by the treatment of **3** with methylmagnesium bromide (Scheme 2). The reaction was performed at 0 °C to give the trimethylated product **4** in 56% yield as a single isomer. The chemical shift of the methyl group in **4** is 2.13 ppm in DMSO-d_6, which is lower than the corresponding peak of the fluorene derivative **5** (1.56 ppm). This is likely to be caused by the deshielding effect of ring current from the bowl-shaped aromatic skeleton, indicating the *exo*-trimethyl substitution. To support the assignment, prediction of chemical shift of the methyl group was also carried out using GIAO method based on DFT calculation (B3LYP6-31G(d,p)//B3LYP6-31G(d,p)). The shift of the *exo*-methyl groups for **4** was reproduced well by the calculation (2.13 and 2.09 ppm for the experimental and calculated values, respectively), showing the downfield shift from the calculated values of **5** and the *endo*-trimethyl isomer of **4** as well ($\Delta\delta = 0.49$ and 0.50 ppm, respectively).

The UV−vis absorption spectra of **2** and **3** in 5.0×10^{-6} and 1.0×10^{-4} M (inset) CH_2Cl_2 solution are shown in Figure 3. Monooxosumanene **2** has maximum absorptions at 252, 274, 329, 344, and 400 nm, and a shoulder peak was observed around 295 nm. Trioxosumanene **3** has a strong peak at 243, a peak at 299 nm with a shoulder peak around 320 nm, and a broad weak peak at 443 nm with a shoulder peak around 480 nm. The end of absorptions for **2** and **3** reach around 495 and 550 nm, respectively, whereas that for sumanene (**1**) is around 375 nm (see the Supporting Information of ref 4 for the corresponding spectrum). Thus, as the number of the carbonyl group increases, the absorption end is red-shifted. In a solid state, the color of **2** and **3** are yellow and orange, respectively, in contrast to **1**, of which is white. These results indicate the expansion of π-conjugation by the carbonyl groups.

The redox properties were also studied electrochemically. Potentials were obtained by cyclic voltammetry with a scan rate of 100 mV s^{-1} under argon (Table 1, see Figure S1, Supporting Information, for cyclic voltammograms). Monooxosumanene **2** in CH_2Cl_2 showed a reduction wave at −1.28 V ($E_{1/2}$ versus Ag/AgCl) assignable to the one-electron reduction processes of the carbonyl group, which is comparable to that of fluorenone (-1.27 V). Compared to sumanene (-2.54 V versus Ag/AgCl in DMF at 253 K, a partially chemically reversible reduction is observed),[13] monooxosumanene **2** is apparently reduced more readily. In the case of trioxosumanene **3** in CH_2Cl_2, two separate reduction waves were observed at -0.46 and -0.77 V, which could be assigned to the successive one-electron reduction processes of two carbonyl groups. The third carbonyl group was not reduced under these conditions. The reduction potential of **3** exhibits an anodic shift from **2**, which is accounted for by the electron deficiency.

In summary, mono- and trioxosumanenes **2** and **3** were synthesized and characterized. Monooxosumanene **2** was found to exhibit columnar stacking in a crystal state. Stereoselective trimethylation of **3** was demonstrated. UV–vis absorption spectroscopy and cyclic voltammetry experiments revealed the expansion of π-conjugation and high electron acceptance by lowering of LUMO levels. Investigation for further derivatization and electrical materials application is now in progress.

Scheme 2. Synthesis of 4 and the Experimental and Estimated ^{1}H NMR Chemical Shifts for the Methyl Protons in 4 and 5



*GIAO/B3LYP6-31G(d,p)//OPT/B3LYP6-31G(d,p)

■ EXPERIMENTAL SECTION

Synthesis of 4,7-Dihydro-1*H*-tricyclopenta[*def*,*jkl*,*pqr*]triphenylen-1-one (2). To a CH_2Cl_2 (23 mL) solution of sumanene (**1**, 150 mg, 0.57 mmol) were added pyridine (6 mL), phosphotungstic acid (300 mg), and 70% aqueous solution of *t*-BuOOH (2.1 mL) at room temperature. After being stirred for 24 days, the reaction mixture was poured into 1 M HCl solution and ether. The aqueous layer was extracted twice with ether. The combined organic layer was washed with water, aqueous saturated $Na_2S_2O_3/NaHCO_3$ (1:2) solution, water, and brine, dried over $MgSO_4$, and evaporated in vacuo. The residue was purified by silica gel column chromatography to give monooxosumanene **2** (81.1 mg, 0.29 mmol, 51%) as a yellow solid: mp ~300 °C (dec in a sealed capillary under nitrogen, uncorrected); IR (ATR, powder) 1697 (C=O) cm^{-1}; UV–vis λ_{max} (CH_2Cl_2) nm (ε) 252 (42400), 274 (38800), 329 (2160), 344 (2230), 400 (1430); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, $J = 7.8$ Hz, 2H), 7.19 (s, 2H), 7.16 (d, $J = 7.8$ Hz, 2H), 4.73 (d, $J = 19.7$ Hz, 2H), 3.52 (d, $J = 19.7$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 190.0, 156.1, 149.4, 148.9, 148.7, 148.1, 139.0, 124.9, 124.4, 124.1, 42.0 ppm; HRMS(FAB) calcd for $C_{21}H_{10}O_1$ 278.0732, found 278.0733 $(M)^+$.

Synthesis of 1*H*-Tricyclopenta[*def*,*jkl*,*pqr*]triphenylene-1,4,7-trione (3). To a CH_2Cl_2 (11 mL) solution of sumanene (**1**, 50.4 mg, 0.19 mmol) were added pyridine (2 mL), $RuCl_3 \cdot nH_2O$ (85 mg), and a 70% aqueous solution of *t*-BuOOH (0.5 mL) at room temperature. The reaction mixture was warmed to 40 °C. After being stirred for 54 h, five

Table 1. Electrochemical Data[a] of 2, 3, and Fluorenone

compd	E_{red1}	E_{red2}
2	−1.28	
3	−0.46	−0.77
fluorenone	−1.27	

[a] $E_{1/2}$/V (vs Ag/AgCl); [compound] = 1.0×10^{-3} M; solvent CH_2Cl_2.

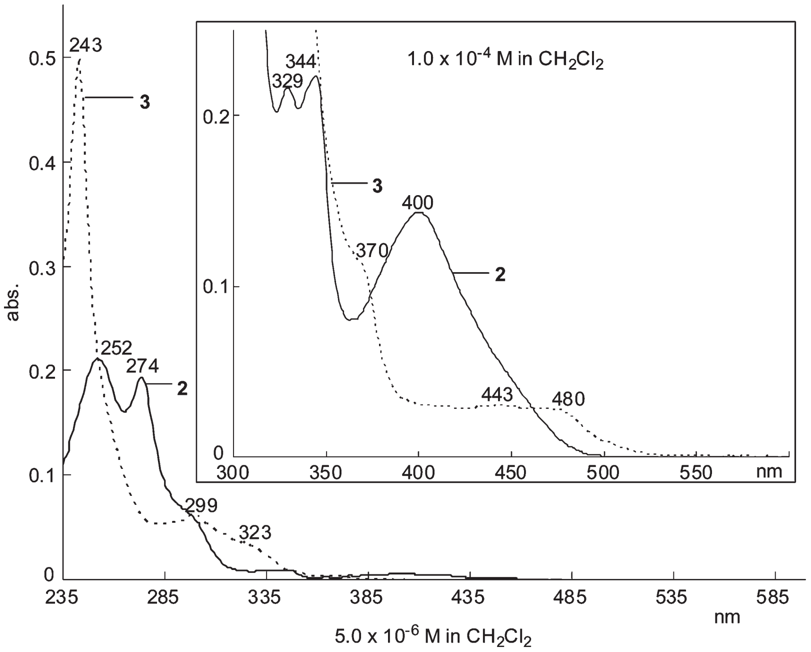


Figure 3. UV–vis absorption spectra of **2** (solid line) and **3** (dotted line) in 5.0×10^{-6} and 1.0×10^{-4} M (inset) CH_2Cl_2 solution.

portions of silica gel were added. Almost half of the solvent was evaporated very carefully, and then the mixture was purified by silica-gel column chromatography to give trioxosumanene **3** (42.9 mg, 0.14 mmol, 73%) as an orange solid: mp ~280 °C (dec in a sealed capillary under nitrogen, uncorrected); IR (ATR, powder) 1712 (C=O) cm^{-1}; UV−vis λ_{max} (CH_2Cl_2) nm (ε) 243 (100000), 299 (12600), 443 (310); ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 188.2, 149.7, 143.6, 126.6 ppm; HRMS(FAB) calcd for $C_{21}H_6O_3$ 306.0317, found 306.0312 $(M)^+$.

Synthesis of (1*S*,4*S*,7*S*)-1,4,7-Trimethyl-4,7-dihydro-1*H*-tricyclopenta[*def*,*jkl*,*pqr*]triphenylene-1,4,7-triol (4). To a THF (3 mL) solution of trioxosumanene **3** (20 mg, 0.065 mmol) was added a 1.06 M THF solution of MeMgBr (0.308 mL, 0.33 mmol) at 0 °C under argon. After being stirred for 1 h, the reaction mixture was poured into aqueous saturated NH_4Cl solution and ether. The aqueous layer was extracted twice with ether. The combined organic layer was washed with brine, dried over $MgSO_4$, and evaporated in vacuo. The residue was purified by silica gel column chromatography to give **4** (13.0 mg, 0.37 mmol, 56%): mp ~250 °C (dec in a sealed capillary under nitrogen, uncorrected); IR (ATR, powder) 3358 (OH), 3220 (OH) cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 6.97 (s, 6H, Ar-*H*), 5.60 (s, 3H, −O*H*), 2.13 (s, 9H, −C*H*$_3$); ^{13}C NMR (100 MHz, DMSO-d_6) 160.3, 146.1, 120.5, 88.4, 29.0 ppm; HRMS(FAB) calcd for $C_{24}H_{18}O_3$ 354.1256, ound 354.1257 $(M)^+$.

Electrochemical Experiments. The cyclic voltammetry was performed on a BAS CV-50W voltammetry analyzer in deaerated CH_2Cl_2 containing 0.1 M Bu_4NClO_4 as a supporting electrolyte under argon at room temperature with a three-electrode system consisting of a glassy-carbon working electrode (BAS), a platinum auxiliary electrode (BAS), and an Ag/AgCl (0.01 M) reference electrode (BAS) at 100 mV/s scan rate.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Cyclic voltammograms of **2**, **3**, and fluorenone, optimized structure and Cartesian coordinates of **4**, the *endo*-trimethyl isomers of **4** and **5**, ^1H and ^{13}C NMR spectra of **2**−**4**, IR spectra of **2**−**4**, and X-ray data for **2** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: hirao@chem.eng.osaka-u.ac.jp.

■ ACKNOWLEDGMENT

This work was partially supported by Grants-in-Aid for Scientific Research (A) (22245007) and Young Scientists (A) (22685006) from Japan Society for the Promotion of Science. Financial support from the Japan Science and Technology Agency (A-STEP, No AS2211281D) and Nissan Science Foundation are also acknowledged.

■ REFERENCES

(1) For an account and reviews, see: (a) Rabideau, P. W.; Sygula, A. *Acc. Chem. Res.* **1996**, *29*, 235. (b) Mehta, G.; Rao, H. S. P. *Tetrahedron* **1998**, *54*, 13325. (c) Wu, Y.-T.; Siegel, J. S. *Chem. Rev.* **2006**, *106*, 4843. (d) Tsefrikas, V. M.; Scott, L. T. *Chem. Rev.* **2006**, *106*, 4868.

(2) Functionalization of corannulenes: (a) Seiders, T. J.; Elliott, E. L.; Grube, G. H.; Siegel, J. S. *J. Am. Chem. Soc.* **1999**, *121*, 7804. (b) Sygula, A.; Xu, G.; Marcinow, Z.; Rabideau, P. W. *Tetrahedron* **2001**, *57*, 3637. (c) Preda, D. V.; Scott, L. T. *Tetrahedron Lett.* **2000**, *41*, 9633. (d) Grube, G. H.; Elliott, E. L.; Steffens, R. J.; Jones, C. S.; Baldridge, K. K.; Siegel, J. S. *Org. Lett.* **2003**, *5*, 713. (e) Pappo, D.; Mejuch, T.; Reany, O.; Solel, E.; Gurram, M.; Keinan, E. *Org. Lett.* **2009**, *11*, 1063.

(3) Sakurai, H.; Daiko, T.; Hirao, T. *Science* **2003**, *301*, 1878.

(4) Amaya, T.; Seki, S.; Moriuchi, T.; Nakamoto, K.; Nakata, T.; Sakane, H.; Saeki, A.; Tagawa, S.; Hirao, T. *J. Am. Chem. Soc.* **2009**, *131*, 408.

(5) Sakurai, H.; Daiko, T.; Sakane, H.; Amaya, T.; Hirao, T. *J. Am. Chem. Soc.* **2005**, *127*, 11580.

(6) Amaya, T.; Mori, K.; Wu, H.-L.; Ishida, S.; Nakamura, J.; Murata, K.; Hirao, T. *Chem. Commun.* **2007**, 1902.

(7) Amaya, T.; Nakata, T.; Hirao, T. *J. Am. Chem. Soc.* **2009**, *131*, 10810.

(8) Amaya, T.; Okada, M.; Wu, H.-L.; Hirao, T. 12th International Symposium on Novel Aromatic Compounds (ISNA-12), Awaji Island, Japan, 22−27 July, 2007 (abstract: p 177).

(9) Tsuruoka, R.; Higashibayashi, S.; Ishikawa, T.; Toyota, S.; Sakurai, H. *Chem. Lett.* **2010**, *39*, 646.

(10) Nakanishi, M.; Bolm, C. *Adv. Synth. Catal.* **2007**, *349*, 861.

(11) Crystal data for **2**: monoclinic, space group $P2_1/a$ (#14), a = 7.68545(15) Å, b = 16.9437(3) Å, c = 9.7925(2) Å, β = 103.0492(12)°, V = 1242.25(4) Å^3, Z = 2; $R1$ = 0.0404; $wR2$ = 0.1266. The data have been deposited with the Cambridge Crystallographic Data Centre: CCDC-805907.

(12) (a) Sygula, A.; Folsom, H. E.; Sygula, R.; Abdourazak, A. H.; Marcinow, Z.; Fronczek, F. R.; Rabideau, P. W. *J. Chem. Soc., Chem. Commun.* **1994**, 2571. (b) Forkey, D. M.; Attar, S.; Noll, B. C.; Koerner, R.; Olmstead, M. M.; Balch, A. L. *J. Am. Chem. Soc.* **1997**, *119*, 5766. (c) Imamura, K.; Takimiya, K.; Aso, Y.; Otsubo, T. *Chem. Commun.* **1999**, 1859. (d) Petrukhina, M. A.; Andreini, K. W.; Peng, L.; Scott, L. T. *Angew. Chem., Int. Ed.* **2004**, *43*, 5477.

(13) Zanello, P.; Fedi, S.; de Biani, F. F.; Giorgi, G.; Amaya, T.; Sakane, H.; Hirao, T. *Dalton Trans.* **2009**, 9192.