ORGANIC LETTERS

2005
Vol. 7, No. 1
115−118

Preparation, Properties, and Reduction of Heteroaromatic Quinoids with 1,4-Diazacyclopentadien-2-ylidene Terminals

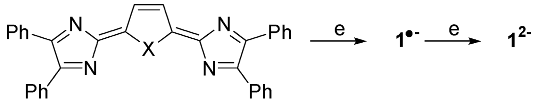
Masatoshi Kozaki, Asuka Isoyama, Kogen Akita, and Keiji Okada*

Department of Chemistry, Graduate School of Science, Osaka City University,
3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan

okadak@sci.osaka-cu.ac.jp

Received November 10, 2004

ABSTRACT



1

X = S, NCH_3, CH=CH

New n-type heteroaromatic quinoids with 1,4-diazacyclopentadien-2-ylidene terminals were prepared. These quinoids possess strong electron-accepting properties, comparable to dicyanomethylene analogues. Both the radical anions and dianions were generated by metal reduction using 3% Na–Hg in THF and were spectroscopically characterized.

Considerable work has been done on charged species of conjugated oligomers and dendrimers to obtain insights on doped and conducting species.[1] Many spectroscopic and crystallographic methods have been used to study cationic species of thiophene-based oligomers, which are used as models for polythiophene.[2,3] In contrast to p-type materials, there are only a limited number of n-type molecular assemblies, and only a few anionic species of those have been characterized.[4−6] Quinoidal oligothiophene with dicyanomethylene terminals is one such compound and its reduced species has been spectroscopically characterized.[6]

In the course of our studies of charged and spin systems of molecular assemblies[3,7] we have been interested in development of new redox systems applicable to molecular assemblies. 1,4-Diazacyclopentadienylidene (DACP) seems to be an attractive functional group to form an aromatic 6π

---

[1] (a) Mullen, K.; Wegner, G. *Electronic Materials: The Oligomer Approach*; Wiley-VCH: Weinheim, Germany, 1998. (b) Newcome, G. R.; Moorefield, C. N.; Vögtle, F. *Dendrimers and Dendrons: Concepts, Syntheses, Applications*; Wiley-VCH: Weinheim, Germany, 2001.

[2] (a) Miller, L. L.; Mann, K. R. *Acc. Chem. Res.* **1996**, *29*, 417−423. (b) van Haare, J. A. E. H.; Havinga, E. E.; van Dongen, J. L. J.; Janssen, R. A. J.; Cornil, J.; Brédas, J.-L. *Chem. Eur. J.* **1998**, *4*, 1509−1522. (c) Aso, Y.; Takimiya, K.; Otsubo, T. *J. Synth. Org. Chem., Jpn. (Yuki Gousei Kagaku Kyokaishi)* **2002**, *60*, 52−61. (d) Nishinaga, T.; Wakamiya, A.; Yamazaki, D.; Komatsu, K. *J. Am. Chem. Soc.* **2004**, *126*, 3163−3174.

[3] Kozaki, M.; Yonezawa Y.; Okada, K. *Org. Lett.* **2002**, *4*, 4535−4538.

[4] Nishida, J.; Naraso; Murai, S.; Fujiwara, E.; Tada, H.; Tomura, M.; Yamashita, Y. *Org. Lett.* **2004**, *6*, 2007−2010 and references therein.

[5] For some selected papers for n-dopable oligothiophenes, see: (a) Takahashi, K.; Fujita, S.; Akiyama, K.; Miki, M.; Yanagi, K. *Angew. Chem. Int. Ed.* **1998**, *37*, 2484−2487. (b) Sakamoto, Y.; Komatsu, S.; Suzuki, T. *J. Am. Chem. Soc.* **2001**, *123*, 4643−4644. (c) Yonezawa, Y.; Kozaki, M.; Okada, K. *Synth. Met.* **2001**, *119*, 99−100. (d) Ohnishi, H.; Kozaki, M.; Okada, K. *Synth. Met.* **2003**, *135*, 85−86. (e) Tarutani, S.; Takahashi, K. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 463−475.

[6] (a) Gronowitz, S.; Uppström, B. *Acta Chem. Scand.* **1974**, *B28*, 981−985. (b) Yui, K.; Aso, T.; Otsubo, T.; Ogura, F. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 1539−1546. (c) Pappenfus, T. M.; Chesterfield, R. J.; Frisbie, C. D.; Mann, K. R.; Casado, J.; Raff, J. D.; Miller, L. L. *J. Am. Chem. Soc.* **2002**, *124*, 4184−4185. (d) Pappenfus, T. M.; Raff, J. D.; Hukkanen, E. J.; Burney, J. R.; Casado, J.; Drew, S. M.; Miller, L. L.; Mann, K. R. *J. Org. Chem.* **2002**, *67*, 6015−6024. (e) Chesterfield, R. J.; Newmann, C. R.; Pappenfus, T. M.; Ewbank, P. C.; Haukaas, M. H.; Mann, K. R.; Miller, L. L.; Frisbie, C. D. *Adv. Mater.* **2003**, *15*, 1278−1282.

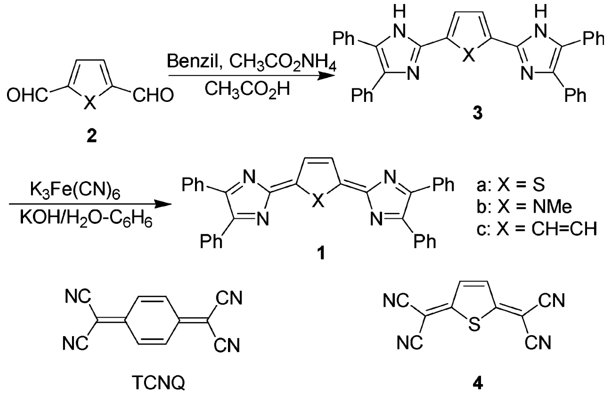
[7] (a) Okada, K. In *Molecular Magnetism*; Itoh, K., Kinoshita, M., Eds.; Kodansha-Gordon and Breach: Tokyo, 2000; pp 264−277. (b) Okamoto, T.; Kozaki, M.; Yamashita, Y.; Okada, K. *Tetrahedron Lett.* **2001**, *42*, 7591−7594. (c) Hiraoka, S.; Okamoto, T.; Kozaki, M.; Shiomi, D.; Sato, K.; Takui, T.; Okada, K. *J. Am. Chem. Soc.* **2004**, *126*, 58−59. (d) Okamoto, T.; Kuratsu, M.; Kozaki, M.; Hirotsu, K.; Ichimura, A.; Matsushita, T.; Okada, K. *Org. Lett.* **2004**, *6*, 3493−3496.

10.1021/ol0476927 CCC: $30.25

system upon one-electron reduction.[8] However, until now, there has been no report on the reduction of DACP-quinoidal compounds. Here, we report on the preparation, properties, and reduction of a series of heteroaromatic qunoids with DACP-terminals **1**.

The heteroaromatic quinoids **1a** and **1b** were synthesized by applying the method of synthesis for the known **1c** (Scheme 1).[9,10] Condensation of **2** with benzil in the presence of ammonium acetate in acetic acid gave compounds **3** (**3a**; 54%, **3b**; 90% yields). Oxidation of **3** using $K_3Fe(CN)_6$ in benzene–aqueous KOH solution afforded compounds **1** (**1a**; 70%, **1b**; 74% yields) as deeply colored stable solids (λ_{max}, nm (log ϵ) in CH_2Cl_2, **1a**; 632 (5.01), **1b**; 669 (5.16)).

Scheme 1



X-ray crystallographic analysis of **1a** showed a highly planar quinoid structure except for four terminal phenyl groups (Figure 1).[11] The bond lengths and angles are consistent with the reported thienoquinoids.[6d,12]

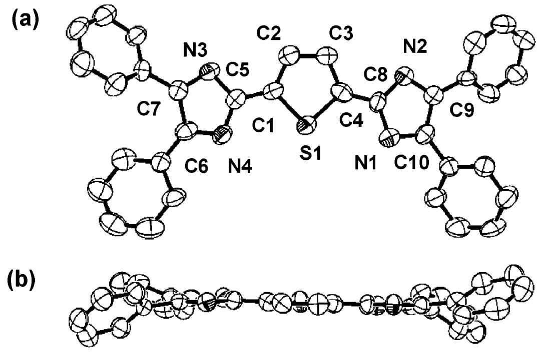


Figure 1. Molecular structures (ORTEP) of **1a**: (a) overview; (b) side view and labeling. Selected bond lengths (Å): S1–C1, 1.757(8); S1–C4, 1.742(7); N1–C8, 1.377(9); N1–C10, 1.305(9); N2–C8, 1.383(9); N2–C9, 1.313(9); N3–C5, 1.373(9); N3–C7, 1.311(9); N4–C5, 1.371(9); N4–C6, 1.328(9); C1–C2, 1.441(10); C1–C5, 1.377(10); C2–C3, 1.365(10); C3–C4, 1.410(10); C4–C8, 1.382(10); C6–C7, 1.469(10); C9–C10, 1.483(10).

The electron-accepting ability of **1** was estimated by means of cyclic voltamogram. The half-wave potentials of **1** are summarized in Table 1, along with those of TCNQ and **4**. Compounds **1a** showed two reversible one-electron reduction waves at close potentials (−0.04 and −0.14 V vs SCE) (Figure 2). The reduction potential shifts to a lower value as the central ring of the quinoid becomes electron-rich. The reduction potential of **1c** is a little higher than that of **1a**, whereas the difference is much larger between TCNQ and **4**. The difference between the first and second reduction potentials (ΔE, 0.1–0.2 V) observed for **1** is significantly smaller than those of TCNQ and **4**. The smaller ΔE values

Table 1. Reduction Potentials[a] of **1**, **TCNQ**, and **4**

	(V vs SCE)		
	$E^1_{1/2}$	$E^2_{1/2}$	ΔE (V)
1a	−0.04	−0.14	0.10
1b	−0.25	−0.45	0.20
1c	0.01	−0.09	0.10
TCNQ	0.27	−0.45	0.72
4[b]	0.07	−0.54	0.61

[a] In CH_2Cl_2 in the presence of 0.1 M $(n\text{-}C_4H_9)_4NClO_4$ at 50 mV/s with a SCE reference using a glassy carbon working electrode and a Pt-counter electrode. [b] Reference 6b.

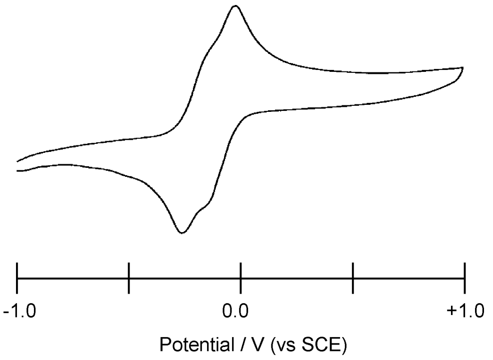


Figure 2. Cyclic voltammogram of **1a** measured in CH_2Cl_2 containing 0.1 M $(n\text{-}C_4H_9)_4NClO_4$.

---

(8) (a) Dedik, S. G.; Orlov, V. D.; Édzhinya, A. S.; Khodorkovskii, V. Yu.; Neiland, O. Ya. *Khim. Geterotsikl. Soedin.* **1989**, *10*, 1421. (b) Prasanna, S.; Radhakrishnan, T. P. *Synth. Met.* **1996**, *78*, 127–130. (c) Aqad, E.; Leriche, P.; Mabon, G.; Gorgues, A.; Khodorkovsky, V. *Tetrahedron Lett.* **2001**, *42*, 2813–2815.

(9) (a) Rohr, W.; Staab, H. A. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 1073–1074. (b) Mayer, D.-C. U.; Baumugärtel, H. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 311. (c) Mayer, D.-C. U.; Baumugärtel, H.; Zimmermann, H. *Tetrahedron Lett.* **1966**, *42*, 5221–5223.

(10) (a) Krieg, B.; Manecke, G. Z. *Naturforsch., Teil B* **1967**, *22*, 132–141. (b) Krieg, B.; Manecke, G. *Makromol. Chem.* **1967**, *108*, 210–217. (c) Okada, K.; Imamura, K.; Oda, M.; Kozaki, M.; Isino, K.; Tashiro, K. *Chem. Lett.* **1998**, 891–892.

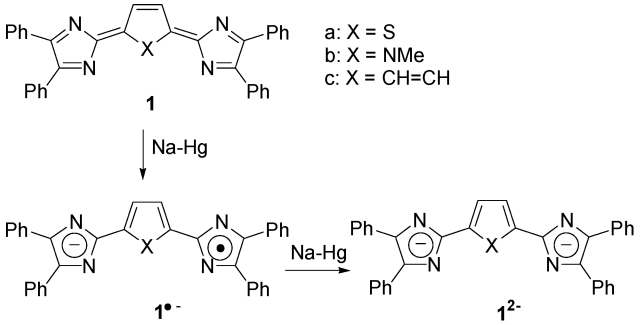
(11) Crystallographic data for **1a**: $C_{41}H_{36}N_4O_2S$, monoclinic, space group *C2/c* (#15), $a = 38.54(2)$ Å, $b = 8.216(7)$ Å, $c = 26.46(2)$ Å, $V = 7212.0(68)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.191$ g/cm^3, $T = 296$ K, $R = 0.075$, $R_w = 0.082$.

(12) (a) Hieber, G.; Hanack, M.; Wurst, K.; Strähle, J. *Chem. Ber.* **1991**, *124*, 1597–1605. (b) Takahashi, K.; Suzuki, T.; Akiyama, K.; Ikegami, Y.; Fukazawa, Y. *J. Am. Chem. Soc.* **1991**, *113*, 4576–4583. (c) Suzuki, K.; Tomura, M.; Yamashita, T. *J. Mater. Chem.* **1998**, *8*, 1117–1119.

shows a diminished on-site Coulombic repulsion in the dianionic species compared with **4**, due to the delocalization of negative charges in the larger DACP rings. The ΔE value of 0.1 V for **1a** and **1c** indicates that disproportionation of two radical anions to the neutral and dianion occurs to a small extent ($K_{\mathrm{disp}} \sim 0.02$ at 25 °C). Hence, both the radical anion and the dianion species would be stable and observable, provided that a suitable reducing method is used.

Metal reduction of **1** using 3% Na−Hg as a reducing agent in dry THF under degassed conditions was carried out (Scheme 2). The reduction was monitored by measuring the UV−vis−NIR spectrum. The spectrum change as a function of contact time with 3% of Na−Hg alloy can be separated in two stages, i.e, formation of the anion radical (Figure 3a) and the dianion formation (Figure 3b) for the reduction of **1a**.

Scheme 2



In the first stage, the intense original absorption ($\lambda_{\max} = 633$ nm, log $\epsilon = 4.96$) of **1a** disappeared and new absorption bands grew at 1033 (log $\epsilon = 4.05$)[13] and 1211 nm (4.39). Similar spectral changes were observed for the reduction of **1b** and **1c**, giving absorptions in the NIR region ($\lambda_{\max} = 892$ (log $\epsilon = 3.87$), 1020 (4.21) for **1b**$^{\bullet-}$, $\lambda_{\max} = 1185$ (log $\epsilon = 4.16$), 1423 (4.42) nm for **1c**$^{\bullet-}$). Obviously, these species are ascribed to the formation of the anion radical species as evidenced by the observation of the EPR signal [$g = 2.00234$ (**1a**$^{\bullet-}$), 2.00016 (**1b**$^{\bullet-}$), 2.00017 (**1c**$^{\bullet-}$)] in THF−toluene (1:1).

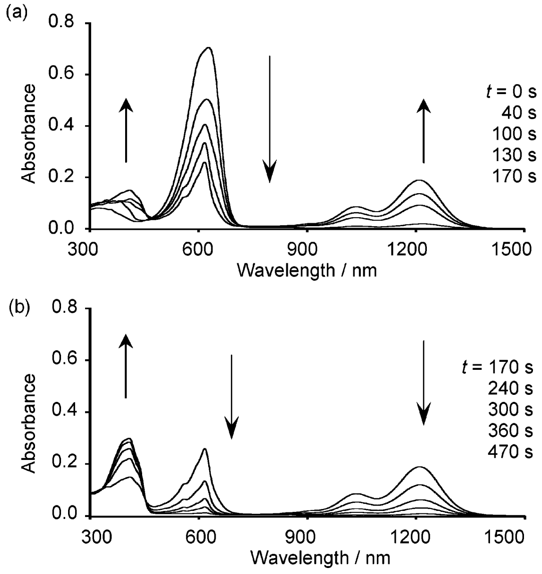


Figure 3. UV−vis−NIR spectral change for **1a**, plotted as a function of contact time (*t*) with 3% Na−Hg in THF. Arrows indicate the direction of changes. Reduction of **1a** to the radical anion **1a**$^{\bullet-}$ (a) and **1a**$^{\bullet-}$ to the dianion **1a**$^{2-}$ (b).

The observed NIR absorptions are characteristic of intervalence bands in class II or charge resonance bands in class III compounds according to the classification of Robin and Day.[14] The observed absorptions accompany vibrational progressions and the bandwidth for the 1211 nm (8258 cm^{-1}) absorption is about 720 cm^{-1}, which is considerably smaller than the theoretical minimum value for intervalence bands, $\nu_{1/2}$(HTL) = 4254 cm^{-1},[15] indicating the observed absorption is a charge resonance band rather than an intervalence band. Theoretical calculations using the ZINDO method using the Gaussian program package[16] gave a 1149 nm absorption (osillator strength = 0.66 with 96% contribution of HOMOβ → LUMOβ transition to the first excited state). The MO diagram and the MO shapes are depicted in Figure 4. Both orbitals are well delocalized in the whole molecule, compatible with these anion radicals being categorized as class III (Robin and Day) species.

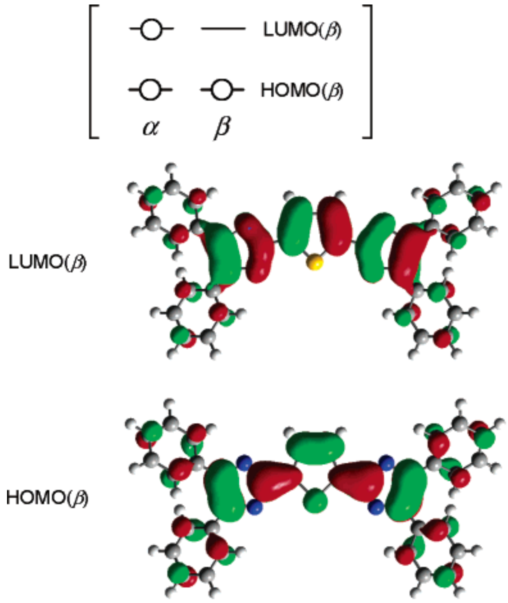


Figure 4. Orbital diagram and the shape of HOMO(β) and LUMO(β) for the radical anion **1a**$^{\bullet-}$ calculated at the ZINDO/S level theory.

---

[13] The molar absorptivities for the radical anions and dianions were calculated by assuming clean conversion.

[14] Robin, M. B.; Day, P. *Adv. Inorg. Chem., Radiochem.* **1967**, *10*, 247−422.

[15] Hush, N. S. *Coord. Chem. Rev.* **1985**, *64*, 135−157.

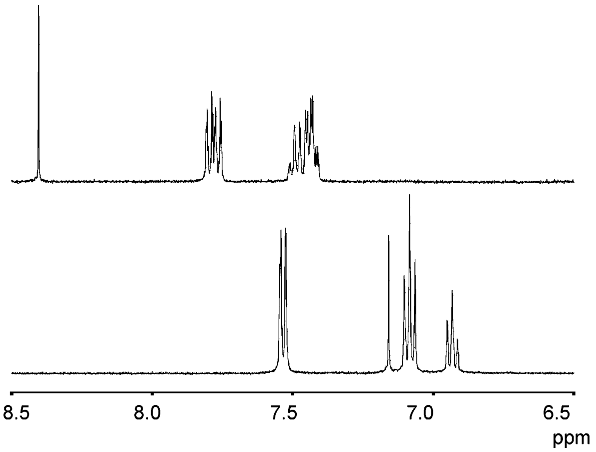


Figure 5. ^{1}H NMR spectra of neutral **1a** (top) and dianion $\mathbf{1a}^{2-}$ (bottom) measured in THF-d_8.

Further reduction resulted in a decrease of the radical anion bands and growth of a new band assignable to dianion at $\lambda_{max} = 400$ nm ($\log \epsilon = 4.59$) for $\mathbf{1a}^{2-}$ (Figure 3b), and 342 (4.41) and 382 nm (4.70) for $\mathbf{1b}^{2-}$ and $\mathbf{1c}^{2-}$, respectively.

Figure 5 shows ^{1}H NMR spectra for the neutral **1a** and the dianion $\mathbf{1a}^{2-}$.[17] All the protons appear at higher fields in the dianion; the protons on the central ring received the largest upfield shift to the normal region of the heteroaromatic ring. There are obviously two kinds of phenyl groups in **1a**, whereas they are equivalent in $\mathbf{1a}^{2-}$. A similar spectral change was also observed for the reduction of **1b** and **1c** (Table 2).

A study on oligomeric heteroaromatic-quinoids with DACP-terminals is in progress.

Table 2. Selected ^{1}H NMR Data[a] of Dianion $\mathbf{1}^{2-}$[b] (δ/ppm)

	H (central rings)	H (Ph-*o*)	H (Ph-*m*)	H (Ph-*p*)
1a	8.40	7.74−7.82	7.40−7.51	
$\mathbf{1a}^{2-}$	7.16	7.52	7.08	6.93
1b	8.04	7.78, 7.74	7.38−7.46	
$\mathbf{1b}^{2-}$	6.28	7.64	7.09	6.90
1c	8.58	7.83	7.45	7.51
$\mathbf{1c}^{2-}$	7.88	7.59	7.11	6.95

[a] 400 MHz, in THF-d_8. [b] Obtained by the reduction with Na mirror ($\mathbf{1a}^{2-}$ and $\mathbf{1c}^{2-}$) and K mirror ($\mathbf{1b}^{2-}$).

Supporting Information Available: Detailed synthetic procedure for **1a** and **1b**, crystallographic data (CIF), and spectroscopic data (UV−vis−NIR including line-shape analysis, EPR, and NMR). These materials are available free of charge via the Internet at http://pubs.acs.org.

OL0476927

---

(16) The geometrical optimization (UB3LYP/6-31G*) was carried out using the X-ray structure of **1a** as an initial input. In the ZINDO/S-CI calculation, 20 highest occupied and 20 lowest vacant orbitals were considered. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E. Yazyev, O.; Austin, A.; Cammi, R.; Pomelli, C.; Ochterski, J.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian 03, revision B.01; Gaussian Inc.: Pittsburgh, PA, 2003.

(17) Dianions for the ^{1}H NMR specta were generated with Na mirror for $\mathbf{1a}^{2-}$ and $\mathbf{1c}^{2-}$ and K mirror for $\mathbf{1b}^{2-}$.