1,2-Azaboratabenzene: A Heterocyclic π -Ligand with an **Adjustable Basicity at Nitrogen**

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Summary: 1,2-Dihydro-2-phenyl-1,2-azaborine (6a) has been prepared by a multistep synthesis from the readily available 2,2-dibutyl-2,5-dihydro-1-trimethylsilyl-1H-1,2-azastannole (7). Deprotonation of 6a affords 1-phenyl-1,2-azaboratabenzene 1a, which on reaction with $[Cp*RuCl]_4$ gives the sandwich compound 5. 5 has been shown to function as a nucleophilic catalyst for the acylation of benzyl alcohol by phenylethylketene.

There is considerable interest in the chemistry of π -coordinated nitrogen-containing heterocycles that retain their N-basicity.¹⁻⁵ Most noteworthy are the observations by Fu and co-workers that azaruthenocenes and azaferrocenes are good nucleophilic catalysts.² In this context, we have become interested in the novel heterocycle 1,2-azaboratabenzene 1. 1,2-Azaboratabenzene is a potentially aromatic ligand that is closely related to boratabenzenes 2 and to pyridines 3. Boratabenzenes have a particularly rich π -coordination chemistry,⁶ while pyridine forms rather few π -coordinated metal complexes.^{3,7} On the other hand, pyridines usually bind metals via the nitrogen atom in an η^{1} manner.⁸ Pyridine is also a good σ -base/nucleophile, and electron-rich pyridines such as 4-(dimethylamino)pyridine (DMAP) are widely used as nucleophilic catalysts.⁹ We felt that **1** might π -coordinate to various metals to afford complexes 4, which retain their σ -basicity. Indeed, it is our hope that the complexes 4 might have an adjustable basicity/nucleophilicity, which might be tunable by the judicious choice of the coordinating metal and its ancillary ligands. Herein we report on the synthesis of 1-phenyl-1,2-azaboratabenzene 1a and its $Ru(II)Cp^*$ complex 5. The marked decrease in the pK_a

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values of 5 relative to 1a demonstrates that the basicity of azaboratabenzene can be modulated by π -complexation.

1-Phenyl-1,2-azaboratabenzene 1a should be available by deprotonation of its conjugate acid, 1,2-dihydro-2phenyl-1,2-azaborine **6a**. Although **6a** was reported by White in 1963, the extremely low yield makes this preparation unsuitable for our purposes.¹⁰ Instead, we find that **6a** can be prepared in good yield via a route involving a ring expansion of a 1,2-azaborolide¹¹ (see Scheme 2). The B/Sn exchange reaction of the readily available 2,2-dibutyl-2,5-dihydro-1-trimethylsilyl-1,2azastannole¹² (7) with PhBCl₂ gave a 95% conversion to the corresponding 2,5-dihydro-1-trimethylsilyl-2phenyl-1H-1,2-azaborole (8).¹³ Deprotonation of 8 with LDA afforded an 89% yield of the lithium 1,2-azaborolide 9, which can be isolated as a white solid. Treatment of 9 with LDA/CH₂Cl₂ in ether gave the ring-expanded product 6b in 41% yield. Desilylation of 6b with Bu₄-NF in THF/H₂O gave the desired **6a** as a white crystalline solid with a mp identical to that reported by White. An X-ray structure of **6a** (in the Supporting Information) unambiguously identifies the compound. Since **6a** is isostructural with biphenyl,¹⁴ the phenyl and 1,2dihydro-1,2-azaborine rings are crystallographically equivalent. Thus accurate bond distances could not be obtained.

Deprotonation of **6a** with potassium bis(trimethylsilyl)amide in toluene gave K-1a, which can be isolated as a white powder. Alternatively treatment of **6a** with LDA in THF afforded Li-1a, which can be isolated as a pale yellow powder on removal of the solvent. The ¹H NMR spectrum of 1a in either THF- d_8 or DMSO- d_6 shows a first-order pattern which is consistent with the assigned structure. The observed ¹H, ¹¹B, and ¹³C NMR

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^a Key: a, PhBCl₂; b, LDA; c, LDA/CH₂Cl₂; d, Bu₄NF/THF-H₂O; e, base; f, acid; g, MeI; h, [Cp*RuCl]₄.



Figure 1. Comparison of the ¹H NMR, ¹³C NMR (in parentheses), and ¹¹B NMR (in circles) chemical shift values of **1a** and **2a** in THF- d_8 .

chemical shift values of K-1a are quite similar to those shown for Li-2a,^{15,16} as illustrated in Figure 1. The spectra exhibit high-field ¹¹B chemical shift values that are consistent with strong stabilization by π -bonding to boron. The ¹H and ¹³C NMR chemical shift values of CH groups that are α and γ to boron are shifted upfield from the signals for the CH groups that are β to boron. This is consistent with a greater carbanionic character of the α - and γ -carbon atoms.^{17,18} Overall the great similarity of the spectra imply a similarity in the electronic structure of **1a** and **2a**.



Figure 2. Molecular structure of 5 (ORTEP). Thermal ellipsoids are at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å): B–N, 1.450(2), B–C (4), 1.504(3), B–C(5), 1.594(2), B–Ru, 2.2967(17), C(4)–Ru, 2.1950(19), N–Ru, 2.155(3).

Although we lack the means to experimentally probe the charge density of **1a** at nitrogen, the nitrogen atom is nucleophilic. Quenching the solution of K-**1a** with excess methyl iodide afforded the known N-methyl derivative **6c**.¹¹ Deprotonation of **6a** is reversible in either THF or DMSO. Bracketing experiments in DMSO indicate that the acidity of **6a** is comparable with pentamethylcyclopentadiene (p $K_a \approx 26$).¹⁹

The reaction of K-1a with [Cp*RuCl]₄ gives adduct **5** as amber crystals in 51% yield. The ¹H, ¹¹B, and ¹³C NMR signals of the C₄BN-ring atoms are shifted upfield relative to those of K-1a, indicating π -complexation, which was confirmed by obtaining the X-ray crystal structure. The molecular structure of **5** illustrated in Figure 2 shows that the C₄BN ring is η^6 -coordinated to the Ru atom. On addition of 1 equiv of HOAc to the THF solution of **5**, it forms salt **10**. Therefore **10** has an acidity less than that of common carboxylic acids (pK_a \approx 5). Potentiometric titration of **5** in 80% CH₃OH/H₂O gave a pK_a of 9.21 \pm 0.10. Thus the basicity of **5** is comparable with that of DMAP (pK_a = 9.0) under the same conditions.²⁰

It was of considerable interest to examine whether complex **5** could serve as a nucleophilic catalyst. Initially we have chosen to look for catalysis of the acylation of benzyl alcohol by phenylethylketene, which had previously been studied by Fu and Ruble.^{2a} It was found that **5** is an effective catalyst, accelerating the reaction by a factor of approximately 13. Under identical conditions the rate of catalysis is 1/26th that of DMAP. Nucleophilic pyridine catalysts including DMAP derivatives show a marked decrease in catalytic activity where there is steric hindrance α to the nitrogen.²¹ Thus the lower activity of **5** relative to DMAP is an expected consequence of the large phenyl substituent at boron. We speculate that derivatives of **5** with smaller B substituents will show much higher catalytic activity.

In summary 2-phenyl-1,2-azaboratabenzene is easily prepared and can be converted to π -coordinated Ru(II) complex 5. The marked decrease in basicity between 1a and 5 is likely to be a general feature on π -coordination and is apparently due to electron withdrawal from the

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ligand by the metal. This modulation of basicity on π -complexation is complementary to the adjustment of the basicity of pyridines on ring substitution. The observation that **5** is a nucleophilic catalyst is significant. We suggest that coordinated azaboratabenzenes may find a role as catalysts with a tunable nucleophilicity.

Experimental Section

General Procedures. Manipulations of air-sensitive compounds were performed under a nitrogen or argon atmosphere using standard Schlenk techniques or in a nitrogen-filled drybox. Tetrahydrofuran, diethyl ether, hexanes, and pentane were dried and deoxygenated by distillation from sodium/ benzophenone ketyl. Dichloromethane was dried by distillation from calcium hydride. Dichlorophenylborane (Aldrich), diisopropylamine (Aldrich), n-BuLi (Aldrich), tetrabutylammonium fluoride (Aldrich), iodomethane (Aldrich), dichloro(pentamethylcyclopentadienyl)ruthenium(III) polymer (Strem), and super-hydride (Aldrich) were used without further purification. LDA was prepared by reaction of diisopropylamine and *n*-BuLi in pentane followed by washing with pentane and drying under vacuum. 2,2-Dibutyl-2,5-dihydro-1-trimethylsilyl-1H-1,2-azastannole (7)¹² and chloro(pentamethylcyclopentadienyl)ruthenium(II) tetramer²² were prepared according to the literature procedures. ¹H, ¹³C, and ¹¹B NMR spectra were recorded on a Varian Inova 400 or 500 NMR spectrometer at ambient temperature. Chemical shifts are reported in parts per million (δ). Proton and carbon chemical shifts are relative to respective solvent internal standards shown below: CDCl₃ δ 7.26⁽¹H), 77.23 (¹³C); C₆D₆ δ 7.16 (¹H), 128.39 (¹³C); DMSO $d_6 \delta 2.50$ (¹H), 39.57 (¹³C); THF- $d_8 \delta 3.58$ (¹H), 67.40 (¹³C). The coupling constants (J) are reported in hertz. The following abbreviations are used to describe peak patterns: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, and m =multiplet. All ¹³C and ¹¹B NMR spectra were determined with complete proton decoupling. UV-visible spectra were recorded on a Shimadzu UV-160U spectrometer. High-resolution mass spectra were recorded on a VG-250S spectrometer with an electron-impact at 70 eV. Elemental analyses were conducted on a Perkin-Elmer 240 CHN analyzer by the Analytical Service Department of the Chemistry Department at the University of Michigan, Ann Arbor. Melting points were recorded on a MEL-TEMP Laboratory Devices melting point apparatus with an uncorrected thermometer.

2,5-Dihydro-2-phenyl-1-trimethylsilyl-1H-1,2-azaborole (8). A solution of PhBCl₂ (97.46 g, 0.61mol) in 200 mL of hexane was gradually added to a solution of 7 (221.28 g, 0.61mol) in 500 mL of hexane at 0 °C. After stirring at 0 °C for 15 min, the reaction mixture was allowed to warm to room temperature and then refluxed for 24 h. Once the solvent had been removed, the residue was vacuum distilled to give the product as a colorless liquid (125.66 g, 95%), bp 48-52 °C at 0.05 Torr. ¹H NMR (500 MHz, C₆D₆): δ 0.05 (s, 9H, SiMe₃); $3.67 (t, J = 1.7 Hz, 2H, CH_2); 6.57 (d, J = 7.8 Hz, 1H, CHB);$ 7.12 (d, J = 7.8 Hz, 1H, CH); 7.22 (m, 3H, ArH); 7.61 (d, J =6.6 Hz, 2H, ArH). ¹³C NMR (100.6 MHz, CDCl₃): δ 1.5 (SiMe₃); 60.2 (CH₂); 127.4 (Ar); 128.1 (Ar); 132.6 (Ar); 136 (br, CHB); 153.9 (CH). Signal for C_{ipso}, not observed. ¹¹B NMR (160.4 MHz, CDCl₃): δ 45.9. HRMS (EI, *m/z*): calcd for C₁₂H₁₈¹¹BNSi (M⁺), 215.1302; found, 215.1301.

2,3-Dihydro-1-trimethylsilyl-2-phenyl-1H-1,2-azaborol-3-yllithium (9). A solution of **8** (47.3 g, 0.22 mol) in 100 mL of diethyl ether was slowly added to a solution of LDA (25.9 g, 0.24 mol) in 250 mL of diethyl ether at -78 °C. The mixture was stirred at -78 °C for 2 h and at room temperature for 10 h. After removal of the solvent under reduced pressure, the residue was washed with 3 \times 20 mL of pentane and then dried under vacuum, leaving lithium salt **9** as a white solid (43.2 g, 89%). ¹H NMR (500 MHz, DMSO-d_6): δ 0.12 (s, 9H, SiMe_3); 4.30 (dd, J = 4.8, 1.7 Hz, 1H, CHB); 5.75 (t, J = 2.2 Hz, 1H, CHN); 5.83 (dd, J = 4.8, 2.7 Hz, 1H, CH); 6.80 (t, J = 7.3 Hz, 1H, ArH); 6.99 (t, J = 7.3 Hz, 2H, ArH); 7.40 (d, J = 7.3 Hz, 2H, ArH). ¹³C NMR (100.6 MHz, DMSO-d_6): δ 2.9 (SiMe_3); 88 (br, CHB); 111.0 (CHN), 117.5 (CH), 121.8 (Ar), 125.8 (Ar), 133.3 (Ar). Signal for C_{ipso}, not observed. ¹¹B NMR (160.4 MHz, DMSO-d_6): δ 30.3.

1,2-Dihydro-1-trimethylsilyl-2-phenyl-1,2-azaborine (6b). A solution of LDA (8.82 g, 82.3 mmol) in 100 mL of diethyl ether was added gradually to a suspension of 9 (18.20 g, 82.3 mmol) in 70 mL of CH₂Cl₂ at -78 °C. The mixture was stirred at -78 °C for 2 h and at room temperature for 10 h. Once the solvent was removed under reduced pressure, the residue was extracted with 3×150 mL of pentane. After filtration and removal of the solvent, the dark red oily residue was vacuum distilled to give the product 6b as a colorless oil (7.77 g, 41%), bp 70-74 °C at 0.05 Torr. ¹H NMR (500 MHz, DMSO- d_6): δ 0.14 (s, 9H, SiMe₃); 6.49 (t, J = 6.6 Hz, 1H, C(5)H; 6.57 (d, J = 10.9 Hz, 1H, C(3)H); 7.33 (m, 5H, ArH); 7.55(d, J = 6.8 Hz, 1H, C(6)H); 7.60 (dd, J = 10.9, 6.4 Hz, 1H,C(4)H). $^{13}\mathrm{C}$ NMR (100.6 MHz, CDCl_3): δ 2.3, 112.4, 127.2, 127.3, 131.0 (br), 132.5, 137.6, 143.5. Signal for Cipso not observed. ¹¹B NMR (160.4 MHz, DMSO- d_6): δ 38.9. HRMS (EI, *m/z*): calcd for C₁₃H₁₈¹¹BNSi (M⁺), 227.1302; found, 227.1297. Anal. Calcd for C13H18BNSi: C, 68.73; H, 7.99; N, 6.17. Found: C, 68.98; H, 8.24; N, 6.01.

1,2-Dihydro-2-phenyl-1,2-azaborine (6a). A 1.0 M solution of Bu₄NF (36 mL, 36 mmol) in THF was added slowly to a solution of **6b** (6.84 g, 30 mmol) in 25 mL of THF at 0 °C. The mixture was stirred at 0 °C for 4 h and at room temperature for 10 h. After reducing the volume of THF to 10 mL in vacuo, 50 mL of ice water was added and the mixture was extracted with 3×50 mL of pentane. The pentane extracts were washed with 3 \times 30 mL of H_2O and dried over anhydrous Na₂SO₄. After filtration and removal of the solvent, the product **6a** was obtained as a white powder (3.82 g, 82%), mp 117–9 °C. ¹H NMR (500 MHz, DMSO- d_6): δ 6.37 (t, J =6.5 Hz, 1H, C(5)H); 7.09 (d, J = 11.2 Hz, 1H, C(3)H); 7.33-7.41 (m, 3H, ArH); 7.48 (t, J = 7.1 Hz, C(6)H); 7.69 (dd, J =11.2, 6.5 Hz, 1H, C(4)H); 7.88 (d, J = 6.4 Hz, 2H, ArH); 10.61 (br, 1H, NH). ¹³C NMR (100.6 MHz, DMSO-*d*₆): δ 110.3, 127.3 (br), 127.8, 128.7, 132.5, 135.4, 144.3. Signal for C_{ipso} not observed. ¹¹B NMR (160.4 MHz, DMSO- d_6): δ 33.4. HRMS (EI, m/z): calcd for C₁₀H₁₀¹¹BN (M⁺), 155.0906; found, 155.0908. Anal. Calcd for C₁₀H₁₀BN: C, 77.49; H, 6.50; N, 9.04. Found: C, 77.14; H, 6.23; N, 8.92. UV (λ_{max}) in hexanes: 241 nm, 287 nm.

1,2-Dihydro-2-phenyl-1,2-azaborine-1-ylpotassium,K-(1a). A 0.5 M solution of potassium bis(trimethylsilyl)amide (22 mL, 11 mmol) in toluene was added gradually to a solution of **6a** (1.55 g, 10 mmol) in 20 mL of toluene at 0 °C. The mixture was stirred at 0 °C for 1 h and at room temperature for 4 h. After filtration and removal of the solvent, the residue was washed with 2 × 10 mL of toluene and 2 × 10 mL of pentane and dried in vacuo to give the product as a white powder (1.83 g, 95%). ¹H NMR (500 MHz, DMSO-*d*₆): δ 5.98 (t, *J* = 5.5 Hz, 1H, C(5)H); 6.40 (d, *J* = 10.5 Hz, 1H, C(3)H); 7.04 (t, *J* = 7.2 Hz, 1H, ArH); 7.15–7.21 (m, 3H, C(6)H, ArH); 7.96 (d, *J* = 7.1 Hz, 2H, ArH); 8.12 (d, *J* = 4.2 Hz, 1H, C(6)H). ¹³C NMR (100.6 MHz, DMSO-*d*₆): δ 110.0 (C5), 119.3 (br, C3), 125.0 (Ar), 126.6 (Ar), 132.3 (Ar), 138.7 (C4), 149.6 (C6). Signal for C_{ipso} not observed. ¹¹B NMR (160.4 MHz, DMSO-*d*₆): δ 34.9.

1,2-Dihydro-1-methyl-2-phenyl-1,2-azaborine (6c). In the NMR tube, 14 mg of CH_3I (0.1 mmol) was added to a solution of K-1a (19 mg, 0.1 mmol) in 1 mL of DMSO- d_6 . The resulting NMR spectra were identical with that of the known compound **6c**.

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[η⁶-1,2-Dihydro-2-phenyl-1,2-azaborine-1-yl][pentamethylcyclopentadienyl]ruthenium(II) (5). A solution of 1a (785 mg, 4.07 mmol) in 5 mL of THF was slowly added to a suspension of $[Cp*RuCl]_4$ (1.11 g, 4.08 mmol) in 25 mL of THF at -78 °C. The mixture was stirred at -78 °C for 2 h and room temperature for 10 h. The solvent was removed in vacuo, and the residue was extracted with 3×10 mL of hot hexanes. After filtration and removal of the solvent, the crude product was obtained as an amber powder, which was washed with 3×10 mL of pentane at -78 °C to give the product as a sand color powder (810 mg, 51%). ¹H NMR (500 MHz, DMSO-*d*₆): δ 1.66 (s, 15H, Cp*Me); 4.63 (d, J = 8.3 Hz, 1H, C(3)H); 5.25 (dd, J= 5.4, 2.9 Hz, 1H, C(5)H); 5.37 (dd, J = 8.3, 5.4 Hz, C(4)H); 6.37 (m, 1H, C(6)H); 7.22 (t, J = 7.3 Hz, 1H, ArH); 7.29 (t, J= 7.3 Hz, 2H, ArH); 7.86 (d, J = 7.9 Hz, 1H, ArH). ¹³C NMR $(100.6 \text{ MHz}, \text{DMSO-}d_6): \delta 10.4, 76.5 (br), 81.7, 89.8, 93.8,$ 106.3, 126.9, 127.4, 132.9. ¹¹B NMR (160.4 MHz, DMSO-d₆): δ 15.2. HRMS (EI, *m/z*): calcd for C₂₀H₂₃¹¹BN¹⁰²Ru [M - H]⁺, 390.0967; found, 390.0969. Anal. Calcd for $C_{20}H_{24}BNRu$: C, 61.55; H, 6.20; N, 3.59. Found: C, 61.42; H, 6.48; N, 3.50.

[η° -1,2-Dihydro-2-phenyl-1,2-azaborine][pentamethylcyclopentadienyl]ruthenium(II) Acetate (10). Acetic acid (9 μ L) was added to a solution of 5 (20 mg) in 1 mL of benzene d_6 , and the yellow mixture immediately turned amber. No attempt was made to purify the resulting salt. ¹H NMR (500 MHz, Benzene- d_6): δ 1.42 (s, 15H, Cp*Me); 1.78 (s, 3H, CH₃COO⁻); 4.71 (d, J = 8.5 Hz, 1H, C(3)H); 4.94 (dd, J = 8.4, 5.5 Hz, 1H, C(4)H); 5.37 (t, J = 4.9 Hz, C(5)H); 7.29 (t, J = 7.4Hz,1H, ArH); 7.45 (t, J = 7.6 Hz, 2H, ArH); 7.82 (d, J = 4.2Hz, 1H, C(6)H); 7.86 (d, J = 6.6 Hz, 2H, ArH). ¹³C NMR (100.6 MHz, benzene- d_6): δ 10.4, 21.45, 78.9 (br), 82.4, 94.7, 97.2, 97.7, 128.7, 130.7, 134.4. ¹¹B NMR (160.4 MHz, benzene- d_6): δ 16.2.

Determination of the pK_a **Values. 1. The** pK_a **Value of 6a.** In the NMR tube, 14 mg of Cp*Li (0.1 mmol) was added to a solution of **6a** (15 mg, 0.1 mmol) in 1 mL of DMSO- d_6 . The resulting NMR spectrum showed the peaks of Cp*H as well as Cp*Li. In the reverse reaction, 19 mg of Li-1a (0.1 mmol), which had been prepared from **6a** and LDA, was added to a solution of Cp*H (14 mg, 0.1 mmol) in 1 mL of DMSO- d_6 . The resulting NMR spectrum also showed the peaks of Cp*H as well as Cp*Li. The above bracketing experiments indicate that the acidity of **6a** is comparable with that of pentamethylcyclopentadiene ($pK_a = 26$).

2. The pK_a Value of 5. The pK_a value of **5** was determined by the potentiometric titration of **5** in 80%(v) CH₃OH/20%(v) 0.1 N KCl aqueous solution with CF₃COOH, monitored by an Accumet AR20 pH/mV/conductivity meter. The pK_a of **5** is 9.21 \pm 0.10. The pK_a of DMAP is 9.00 \pm 0.03 under the same conditions.

Catalytic Acylation of Benzyl Alcohol with Phenylethylketene. The experimental procedure for the reaction of

Table 1.	Crystal and Data Collection Parameter	'n
	for 5	

10r 5			
C ₂₀ H ₂₄ BNRu			
390.28			
150(2)			
0.71073			
monoclinic			
P2(1)			
7.772(2)			
13.838(1)			
8.312(2)			
93.343(2)			
892.5(4), 2			
1.452			
0.876			
400			
0.42 imes 0.42 imes 0.14			
$-10 \le h \le 10, -18 \le k \le 18,$			
$-11 \leq l \leq 11$			
11 677/4372			
semiempirical fr equiv			
full-matrix least squares on F^2			
4372/1/310			
1.014			
R1 = 0.0274, wR2 = 0.0692			
R1 = 0.0286, wR2 = 0.0704			
0.746 and -0.459			

benzyl alcohol with phenylethylketene in C₆D₆ at 25.0 °C using 1% catalyst was identical to the procedure of Fu and Ruble.² The experiments were set up in a nitrogen-filled drybox. Two runs were measured for each catalyst. The results were $t_{1/2} = 0.084 \pm 0.005$ h. For DMAP, $t_{1/2} = 2.2 \pm 0.2$ h for **5** and $t_{1/2} = 27.5 \pm 0.7$ h without catalyst.

X-ray Crystallography. Crystals of 5 suitable for X-ray diffraction were obtained by recrystallization from hexanes. Crystallographic and data collection parameters are listed in Table 1. An ORTEP drawing of 5 showing the atom-numbering scheme used in the refinement is illustrated in Figure 2, respectively. Additional crystallographic data are available in the Supporting Information.

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Supporting Information Available: X-ray characterization of **5** and **6a** (CIF). Additional crystallographic information for **5** and copies of the NMR spectra of **8**, **9**, and K-**1a** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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