Cyanide ion complexation by a cationic borane†‡

Ching-Wen Chiu and François P. Gabbaï*

Received 9th October 2007, Accepted 8th November 2007
First published as an Advance Article on the web 4th December 2007
DOI: 10.1039/b715534d

While we have previously reported that [1-(Mes_2B)-8-(Me_3NCH_2)-$C_{10}H_6$]$^+$ ([**2**]$^+$) complexes fluoride ions to form [1-(Mes_2FB)-8-(Me_3NCH_2)-$C_{10}H_6$] (**2-F**), we now show that this cationic borane also complexes cyanide to form [1-(Mes_2(NC)B)-8-(Me_3NCH_2)-$C_{10}H_6$] (**2-CN**). This reaction also occurs under biphasic conditions (H_2O–$CHCl_3$) and may serve to transport cyanide in organic phases. The zwitterionic cyanoborate **2-CN** has been fully characterized and its crystal structure determined. UV-vis titration experiments carried out in THF indicate that [**2**]$^+$ has a higher affinity for fluoride ($K > 10^8\ M^{-1}$) than cyanide ($K = 8.0\ (\pm 0.5) \times 10^5\ M^{-1}$). Steric effects which impede cyanide binding to the sterically congested boron center of [**2**]$^+$ are most likely at the origin of this selectivity. Finally, electrochemical studies indicate that [**2**]$^+$ is significantly more electrophilic than its neutral precursor 1-(Mes_2B)-8-(Me_2NCH_2)-($C_{10}H_6$) (**1**). These studies also show that reduction of [**2**]$^+$ is irreversible, possibly because of elimination of the NMe_3 moiety under reductive conditions. In fact, [**2**]OTf reacts with $NaBH_4$ to afford 1-(Mes_2B)-8-(CH_3)-($C_{10}H_6$) (**4**) which has also been fully characterized.

Introduction

In the past few years, a great deal of attention has been devoted to the use of cationic boranes[1] for the molecular recognition of fluoride anions.[2–10] Because of favorable Coulombic effects, such boranes are sometimes able to overcome the hydration energy of fluoride to form the corresponding zwitterionic fluoroborate derivative in aqueous solutions.[3,4] These reactions are quite useful because they lay the basis for the development of new fluoride ion probes that can operate in aqueous solutions. In a recent development, our group has demonstrated that a similar approach could be used for the sensing of cyanide in water at neutral pH.[3] For example, the ammonium borane [*p*-(Mes_2B)C_6H_4(NMe_3)]$^+$ captures cyanide ions in aqueous solutions to form a very stable zwitterionic ammonium cyanoborate complex.[3]

In a previous communication, we reported the synthesis of the cationic borane [1-(Mes_2B)-8-(Me_3NCH_2)-$C_{10}H_6$]$^+$ ([**2**]$^+$) by reaction of 1-(Mes_2B)-8-(Me_2NCH_2)-($C_{10}H_6$) (**1**) with MeOTf. We also reported that this cationic borane has a high affinity for fluoride whose complexation results in the formation of [1-(Mes_2(F)B)-8-(Me_3NCH_2)-$C_{10}H_6$] (**2-F**).[2] In this paper, we now report on the cyanide binding affinity of [**2**]$^+$. We also report on the unusual electrochemical properties of [**2**]$^+$ which can be used to monitor cyanide binding. Ultimately, these studies may result in the development of new methods for sensing or complexing the toxic cyanide anion whose use for harmful purposes is a growing concern.

Results and discussion

Although both **1** and [**2**]OTf have been previously characterized, the crystal structure of **1** had not been determined. This compound crystallizes in the monoclinic space group $P2_1/c$ with four molecules in the unit cell (Fig. 1, Table 1). The carbon–boron bond lengths of **1** are unremarkable and the boron adopts a trigonal planar geometry ($\sum_{\text{angles}} = 359.0°$). The methylene carbon atom C(01) of the CH_2NMe_2 moiety is separated from the boron atom B(1) by only 3.121 Å indicating significant steric congestion. As a result, the B(1)–C(1)–C(9) (128.7(2)°) and C(01)–C(8)–C(9) (123.7(2)°) angles substantially deviate from the ideal value of 120°. These distortions are comparable to those observed in the structure of [**2**]OTf.[2]

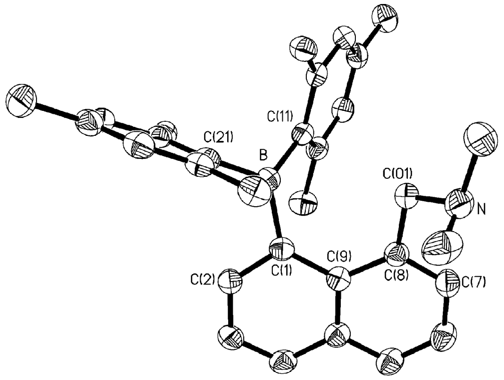


Fig. 1 ORTEP plot of the molecular structure of **1** with thermal ellipsoids set at 50% probability level. Hydrogen atoms are omitted for clarity. Selective bond distances [Å] and bond angles [°]: B–C(1) 1.570(3), B–C(11) 1.576(3), B–C(21) 1.587(3), C(1)–C(2) 1.385(3), C(1)–C(9) 1.450(3), C(7)–C(8) 1.379(3), C(8)–C(9) 1.428(3), C(8)–C(01) 1.516(3); C(1)–B–C(11) 122.0(2), C(1)–B–C(21) 116.5(2), C(11)–B–C(21) 120.5(2), C(2)–C(1)–C(9) 117.3(2), C(2)–C(1)–B 111.9(2), C(9)–C(1)–B 128.7(2), C(7)–C(8)–C(9) 119.4(2), C(7)–C(8)–C(01) 116.9(2), C(9)–C(8)–C(01) 123.7(2).

Department of Chemistry, Texas A&M University, College Station, Texas, 77843, USA. E-mail: francois@tamu.edu; Fax: +1 979 845 4719; Tel: +1 979 862 2070

† This paper is dedicated to Professor Ken Wade on the occasion of his 75th birthday.

‡ CCDC reference numbers 663259 and 663260. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b715534d

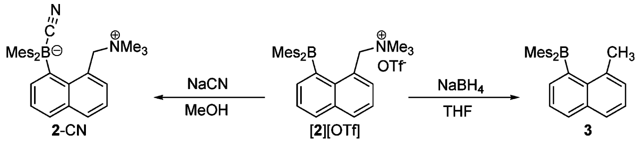
Table 1 Crystal data and structure refinement for **1** and **2-CN**

Crystal data	**1**	**2-CN**
Formula	$C_{31}H_{36}BN$	$C_{33}H_{39}BN_2$
M_r	433.42	474.47
Crystal size/mm	0.42 × 0.27 × 0.16	0.21 × 0.06 × 0.03
Crystal system	Monoclinic	Monoclinic
Space group	*P*2(1)/*c*	*P*2(1)/*c*
a/Å	15.8202(13)	16.009(3)
b/Å	10.2595(8)	10.329(2)
c/Å	17.3207(14)	17.540(4)
α/°	90.00	90.00
β/°	116.620(1)	111.12(3)
γ/°	90.00	90.00
V/Å^3	2513.5(3)	2705.5(9)
Z	4	4
ρ_{calc}/g cm^{-3}	1.145	1.165
μ(Mo-K$_\alpha$)/mm^{-1}	0.064	0.066
F(000)	936	1024
Data collection		
T/K	110	110
Scan mode	ω	ω
hkl range	$-19 \rightarrow 15, -12 \rightarrow 11, -20 \rightarrow 20$	$-19 \rightarrow 19, -11 \rightarrow 12, -14 \rightarrow 20$
Measured refl.	12734	13047
Unique refl., [R_{int}]	4544, [0.0660]	4757, [0.0763]
Refl. used for refinement	4544	4757
Refined parameters	295	326
R_1,[a] wR_2[b] [all data]	0.0815, 0.1399	0.1393, 0.1961
ρ_{fin} (max/min)/e Å^{-3}	0.417/−0.358	0.444/−0.594

[a] $R1 = \sum\|F_o| - |F_c\|/\sum|F|$. [b] $wR2 = \{[\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$; $a = 0.0$ (**1**), 0.49 (**2-CN**); $b = 3.8$ (**1**), 12.73 (**2-CN**).

In an attempt to better understand the chemical properties of **1** and [**2**]OTf, we have studied their electrochemistry (Fig. 2). The cyclic voltammogram of **1** in THF shows a reversible reduction wave at $E_{1/2}$ −2.53 V (*vs.* Fc/Fc$^+$) which is followed by undefined irreversible processes. The redox behavior of this derivative is similar to that of other triarylboranes which typically display a single reversible reduction wave corresponding to the formation of a radical anion.[11–20] The reduction potential of **1** is slightly more negative than that reported for dimesityl-1-naphthylborane (−2.41 V, *vs.* Fc/Fc$^+$) in agreement with the electron releasing properties of the CH_2NMe_2 substituent present at the 8-position.[21] Interestingly, the cyclic voltammogram of [**2**]$^+$ in THF only shows an irreversible wave at E_{peak} −2.18 V (*vs.* Fc/Fc$^+$). A comparison with the reduction peak potential of −2.48 V recorded for **1** indicate that [**2**]$^+$ is substantially more electrophilic than **1**. This observation can be easily reconciled by considering the fact that [**2**]$^+$ is a cation which is therefore expected to be more electrophilic. The irreversibility of the reduction of [**2**]$^+$ suggested that the resulting radical anion decomposes possibly through loss of NMe_3.

Interestingly, reduction of [**2**]OTf with $NaBH_4$ in methanol produces 1-(Mes_2B)-8-(CH_3)–($C_{10}H_6$) (**3**) (Scheme 1). This reaction most likely proceeds by nucleophilic displacement of the NMe_3 group by a hydride. The spectroscopic features of **3** are similar to those of **1**. The ^1H NMR spectrum of **3** exhibits six distinct resonances that correspond to the aromatic CH groups of the unsymmetrically substituted naphthalene backbone. In addition, the methyl groups of the mesityl substituents give rise to broadened multiple resonances indicating that **3** has a highly congested structure. The resonance of the methyl group bound to the 8-position appears at 2.29 ppm as a broad singlet. Finally, the presence of a trigonal planar boron center is confirmed by the ^{11}B NMR signal detected at 70 ppm.



Scheme 1

Encouraged by the high affinity that [**2**]$^+$ displays for fluoride,[2] we decided to investigate its reaction with cyanide ions. This cationic borane is swiftly converted into zwitterionic **2-CN** when treated with NaCN in MeOH (Scheme 1). The ^{11}B NMR signal of **2-CN** appears at −12.2 ppm as expected for a tetrahedral boron atom. Formation of this cyanide complex noticeably affects the ^1H NMR resonances of the diastereotopic methylene hydrogen atom. The two resonances are shifted downfield and appear at 4.66 and 5.46 ppm (*vs.* 3.69 and 4.81 ppm in [**2**]$^+$). In the IR spectrum, the cyanide stretching band appears at 2163 cm^{-1}. Formation of **2-CN** can also be monitored using differential pulsed voltammetry. Indeed, addition of cyanide ions to a solution of [**2**]OTf in THF with nBu$_4$NPF$_6$ as a supporting electrolyte leads to a progressive decrease of the peak corresponding to the reduction of the boron center (Fig. 3). This decrease is caused by binding of the cyanide

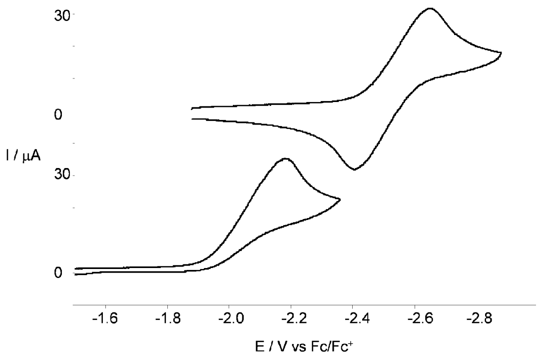


Fig. 2 Cyclic voltammograms of **1** (top) and [**2**]$^+$ (bottom) in THF with a glassy-carbon working electrode (0.1 M nBu$_4$NPF$_6$). Scan rates: $v = 300$ mV s^{-1} for **1** and 100 mVs^{-1} for [**2**]$^+$.

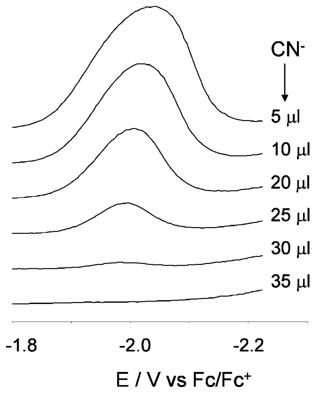


Fig. 3 Changes in the differential pulsed voltammogram of [**2**]OTf (0.001 M) observed upon the addition of nBu$_4$NCN (0.087 M in CH_2Cl_2) to a THF solution.

ion to the boron center which can no longer be reduced because of its coordinative saturation. Similar observations have been made upon addition of fluoride ions to bidentate boranes.[22]

The crystal structure of **2-CN** has been determined (Table 1, Fig. 4). This compound crystallizes in the monoclinic space group $P2_1/c$ with four molecules in the unit cell. The sum of the C_{aryl}–B–C_{aryl} angles ($\sum_{(C-B-C)} = 343.5°$) indicates substantial pyramidalization of the boron atom which is more acute than that observed in **2-F** ($\sum_{(C-B-C)} = 340.7°$).[2] The B(1)–C(30) bond connecting the carbon atom of the cyanide anion to the boron center (1.527(6) Å) is significantly shorter than those typically found in triarylcyanoborate anions such as $[Ph_3BCN]^-$ (1.65 Å).[23] It is also important to note that the B(1)–C(1) bond length of 1.791(7) Å is abnormally long, especially when compared to the B(1)–C(1) bond lengths of 1.678(5) Å measured in **2-F** and 1.573 Å measured in [**2**]OTf. The B(1)–C(1)–C(9) angle of 132.8(4)° in **2-CN** is also larger than that present in **2-F** (130.6(3)°). These unusual metrical parameters and, in particular, the length of the B(1)–C(1) bond indicates that the steric congestions present in **2-CN** are more important than in **2-F**. The larger size of the cyanide anion is certainly responsible for this effect.

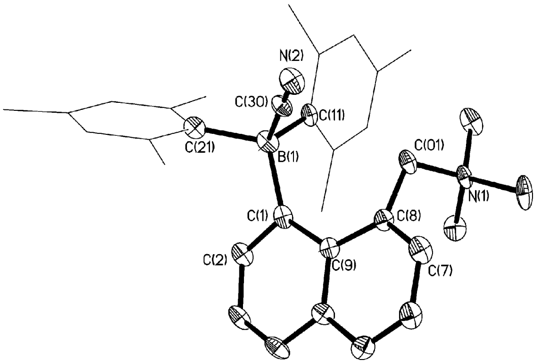


Fig. 4 ORTEP plot of the molecular structure of **2-CN** with thermal ellipsoids set at 50% probability level. Hydrogen atoms are omitted for clarity. Selective bond distances [Å] and bond angles [°]: B(1)–C(1) 1.791(7), B(1)–C(11) 1.633(6), B(1)–C(21) 1.726(7), B(1)–C(30) 1.527(6), N(2)–C(30) 1.074(5), C(1)–C(2) 1.354(6), C(1)–C(9) 1.457(6), C(7)–C(8) 1.328(6), C(8)–C(9) 1.405(6), C(8)–C(01) 1.527(6); B(1)–C(30)–N(2) 117.0(5), C(1)–B(1)–C(11) 113.1(4), C(1)–B(1)–C(21) 112.9(4), C(11)–B(1)–C(21) 117.5(4), C(2)–C(1)–C(9) 110.2(4), C(2)–C(1)–B(1) 116.3(4), C(9)–C(1)–B(1) 132.8(4), C(7)–C(8)–C(9) 117.0(4), C(7)–C(8)–C(01) 117.8(4), C(9)–C(8)–C(01) 125.0(4).

A UV titration experiment carried out by monitoring the absorption of $[\mathbf{2}]^+$ at λ_{max} 352 nm ($\varepsilon = 11435$ dm^3 mol^{-1} cm^{-1}) shows that the cyanide binding constant of $[\mathbf{2}]^+$ in THF is equal to $8.0 (\pm 0.5) \times 10^5$ M^{-1} (Fig. 5). Under the same conditions, the fluoride binding constant of $[\mathbf{2}]^+$ cannot be accurately measured and exceeds 10^8 M^{-1}. These results indicate that $[\mathbf{2}]^+$ shows a greater selectivity for fluoride than cyanide which is surprising since cyanide ($pK_a = 9.3$) is more basic than fluoride ($pK_a = 3.18$). Presumably, the larger size of the cyanide anion impedes binding to the sterically crowded boron center of $[\mathbf{2}]^+$. Similar effects have been observed in the case of $[o\text{-}Mes_2B\text{-}C_6H_4\text{-}NMe_3]^+$ which binds fluoride but not cyanide in aqueous media.[3] In an effort to assess the influence of the cationic nature of $[\mathbf{2}]^+$ on its cyanide binding ability, we have also studied the cyanide affinity of **1**. UV-vis titrations carried out in THF indicate that the cyanide binding constant of **1** is at least three orders of magnitude lower than that of $[\mathbf{2}]^+$ thus suggesting that favorable Coulombic effects are essential to the cyanide binding ability of $[\mathbf{2}]^+$. Although cation $[\mathbf{2}]^+$ does not react with cyanide in water, it is able to transport it into organic phases. For example, shaking a biphasic mixture consisting of NaCN in D_2O (0.5 ml, 7.6×10^{-2} M) and [**2**]OTf in $CDCl_3$ (0.5 ml, 7.21×10^{-2}M) results in a 32% conversion of [**2**]OTf into **2-CN** after a few minutes.

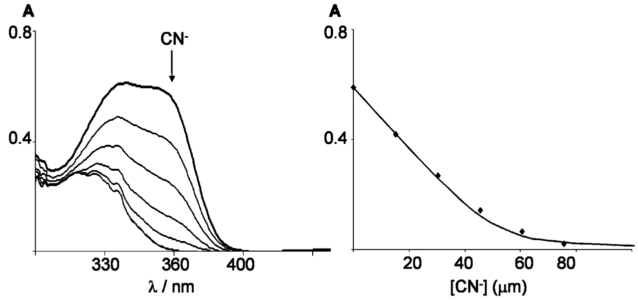


Fig. 5 Left: Changes in the UV-vis absorption spectra of a solution of $[\mathbf{2}]^+$ (5.16×10^{-5}M in THF) upon the addition of a NaCN solution (9.14×10^{-3}M in methanol); Right: resulting fluoride binding isotherm.

Conclusions

The results presented in this paper provide additional evidence for the suitability of cationic boranes for the complexation of cyanide ions. The relatively high cyanide binding affinity of $[\mathbf{2}]^+$ can be assigned to favorable Coulombic effects which increase the anion affinity of the receptor. This conclusion is also in agreement with the redox properties of $[\mathbf{2}]^+$ which is more easily reduced than its neutral precursor **1**. Last but not least, these results allow us to establish that $[\mathbf{2}]^+$ has a higher affinity for fluoride than cyanide. Keeping in mind that cyanide is much more basic than fluoride, the observed selectivity arises, at least in part, from steric effects which impede cyanide binding to the boron center of $[\mathbf{2}]^+$.

Experimental

Materials and methods

[**2**]OTf was synthesized according to the published procedure. UV-vis spectra were recorded on HP8453. IR spectra were obtained using a Bruker Tensor 37 infrared spectrophotometer. NMR spectra were recorded on Varian Unity Inova 400 FT NMR (399.63 MHz for ^{1}H, 128.2 MHz for ^{11}B, and 100.50 MHz for ^{13}C) spectrometer. Chemical shifts δ are given in ppm and are referenced against external Me_4Si (^{1}H, ^{13}C), and $BF_3 \cdot OEt_2$ (^{11}B).

Crystallography

Single crystals of **1** were obtained from evaporation of a CH_2Cl_2–hexane solution. Colorless crystals of **2-CN** were obtained from slow evaporation of the methanol solution. The crystallographic measurement of **1** and **2-CN** were performed using a Siemens SMART-CCD area detector diffractometer with a graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The crystal was mounted onto a nylon loop with Apiezon grease. The structure was solved by direct methods, which successfully located most of the non-hydrogen atoms. Subsequent refinement on F^2 with the SHELXTL/PC package (version 5.1) allowed location of the remaining non-hydrogen atoms.

Synthesis of 3

Excess $NaBH_4$ was added into a methanol solution of the [**2**]OTf salt (100 mg, 0.17 mmol) at room temperature and stirred for 10 min. After reaction, the solvent was removed under reduced pressure and the white solid residue was extracted with 10 ml of hexane three times. By removing the hexane, compound **3** was obtained as a light yellow solid (24 mg, yield = 36%). ^1H NMR ($CDCl_3$, 400 MHz, 213 K): δ 0.92 (s, 3H), 1.89 (s, 3H), 2.03 (s, 3H), 2.17 (s, 3H), 2.31 (bs, 9H), 6.47 (s, 1H), 6.75 (s, 1H), 6.82 (s, 1H), 6.90 (s, 1H), 7.29 (d, 1H, $^3J_{H-H} = 7.2$ Hz), 7.35 (t, 1H, $^3J_{H-H} = 8$ Hz), 7.40 (t, 1H, $^3J_{H-H} = 7.6$ Hz), 7.45 (d, 1H, $^3J_{H-H} = 7.2$ Hz), 7.74 (d, 1H, $^3J_{H-H} = 7.6$ Hz), 7.92 (d, 1H, $^3J_{H-H} = 8$ Hz). ^{13}C NMR ($CDCl_3$, 100.5 MHz, 213K) δ 21.2, 21.3, 22.7, 23.3, 23.6, 24.3, 25.0, 124.9, 125.3, 127.0, 127.8, 128.4, 128.7, 128.8, 128.9, 132.7, 133.0, 133.6, 135.8, 135.9, 138.6, 139.0, 140.7, 141.0. ^{11}B NMR ($CDCl_3$, 128.2 MHz, 213K): δ 69.6.

Synthesis of 2-CN

[**2**]OTf (100 mg, 0.17 mmol) was mixed with eight equivalents of NaCN (66 mg, 1.35 mmol) in methanol at room temperature. After stirring for 1 h, the solvent was removed under reduced pressure and the residual white solid was extracted with diethyl ether. The combined ether solution was dried to give **2-CN** as a white powder (58 mg, yield 72%). Single crystals of **2-CN** were obtained from evaporation of a methanol solution. ^1H NMR ($CDCl_3$, 399.59 MHz, 263K): δ 1.21 (s, 3H, Mes–CH_3), 1.79 (s, 3H, Mes–CH_3), 2.15 (s, 3H, Mes–CH_3), 2.19 (s, 3H, Mes–CH_3), 2.20 (s, 3H, Mes–CH_3), 2.24 (s, 9H, NMe_3), 2.46 (s, 3H, Mes–CH_3), 4.66 (d, 1H, $^2J_{H-H} = 12.8$ Hz, nap-CH_2–NMe^{3+}), 5.46 (d, 1H, $^2J_{H-H} = 12.8$ Hz, nap-CH_2–NMe^{3+}), 6.55 (s, 2H, Mes–CH), 6.61 (s, 1H, Mes–CH), 6.90 (s, 1H, Mes–CH), 7.16–7.23 (m, 2H, nap–CH), 7.48 (d, 1H, $^3J_{H-H} = 6.4$ Hz, nap-CH), 7.54 (d, 1H, $^3J_{H-H} = 7.2$ Hz, nap-CH), 7.76 (d, 1H, $^3J_{H-H} = 6.4$ Hz, nap-CH), 7.85 (d, 1H, $^3J_{H-H} = 8.4$ Hz, nap-CH). ^{13}C NMR ($CDCl_3$, 100.5 MHz, 263K): δ 20.6 (Mes-*p*-CH_3), 23.8 (Mes-*o*-CH_3), 25.0 (Mes-*o*-CH_3), 25.8 (Mes-*o*-CH_3), 30.1 (d, $J_{C-F} = 13.0$ Hz, Mes-*o*-CH_3), 51.9 (NMe_3), 71.3 (nap-CH_2–N), 121.6, 125.0, 125.4, 126.9, 128.6, 129.0, 129.8, 132.7, 133.1, 133.8, 134.3, 138.3, 141.3, 142.9, 143.1, 143.4, 144.9. ^{11}B NMR ($CDCl_3$, 128.2 MHz, 263 K): δ −12.2. IR $\nu_{CN} = 2163$ cm^{-1}.

UV-vis titration in THF with fluoride

A THF solution of [**2**]OTf (4.95×10^{-5}M, 3 ml) was titrated with incremental amounts of fluoride by addition of TBAF in THF (4.46×10^{-3}M). The absorbance was monitored at $\lambda_{max} = 352$ nm ($\varepsilon = 11435$ dm^3 mol^{-1} cm^{-1} for [**2**]$^+$, $\varepsilon = 135$ dm^3 mol^{-1} cm^{-1} for **2-F**). The experimental data obtained were fitted to a 1 : 1 binding isotherm which indicated that the fluoride binding constant of [**2**]$^+$ is greater than 1×10^8 M^{-1}.

UV-vis titration in THF with cyanide

A THF solution of [**2**]OTf (5.16×10^{-5}M, 3 ml) was titrated with incremental amounts of cyanide by addition of NaCN in methanol (9.14×10^{-3}M). The absorbance was monitored at $\lambda_{max} = 352$ nm ($\varepsilon = 11435$ dm^3 mol^{-1} cm^{-1} for [**2**]$^+$, $\varepsilon = 394$ dm^3 mol^{-1} cm^{-1} for **2-CN**). The experimental data obtained were fitted to a 1 : 1 binding isotherm which indicated that the cyanide binding constant of [**2**]$^+$is 8.0 (± 0.5) × 10^5 M^{-1}.

Acknowledgements

This work was supported by NSF (CHE-0646916), the Welch Foundation (A-1423), the Petroleum Research Funds (Grant 44832-AC4) and the US Army Medical Research Institute of Chemical Defense.

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