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Template Effects in the Formation of [2]Pseudo-rotaxanes Containing Diazapyrenium Units

Giancarlo Doddi,*,† Gianfranco Ercolani,‡ Paolo Mencarelli,*,† and Giuseppe Papa†

Dipartimento di Chimica e CNR-IMC, Università di Roma La Sapienza, P. le Aldo Moro, 5, 00185 Rome, Italy, and Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata, Via della Ricerca Scientifica, 00133 Rome, Italy

paolo.mencarelli@uniroma1.it

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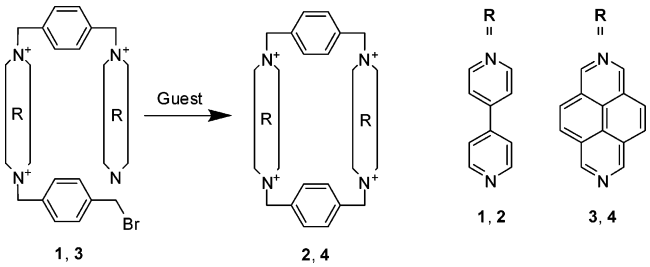

The template effects exerted by guests **14** and **15** in the ring closure reaction of **3** have been quantitatively evaluated. The rate largely increases in the presence of the two templates. The results are compared with those relative to the ring closure reaction of **1** yielding cyclobis(paraquat-*p*-phenylene), **2**. The comparison indicates that the formation of tetracationic aromatic cycles templated by aromatic donors benefits from the use of extended π surfaces both in the acceptor and in the donor components.

Template effects exerted by suitable guests have often been invoked as determinant factors in the successful synthesis of many macrocycles.[1] In spite of their practical importance, however, there are only a few kinetic studies in the literature that have put such phenomena on a quantitative scale, notably, the studies of Masci et al. on the template effects exerted by alkali and alkaline earth metal ions in the synthesis of crown ethers,[2] and those of our group dealing with the template effects exerted by a number of aromatic guests in the synthesis of cyclobis(paraquat-*p*-phenylene),[3] **2**, the well-known tetracationic host devised by Stoddart and largely used for the preparation of a variety of catenanes, rotaxanes, pseudorotaxanes, molecular switches, shuttles, and machines.[4]

Up to now, the focus of our research has been on investigating the kinetics of the reaction **1** → **2** (see the Table of Contents graphic) on varying the nature of the aromatic guest;[3] however, following the observation of Stoddart and co-workers that noncovalent bonding interactions are reinforced significantly when diazapyrenium, instead of bipyridinium, recognition sites are employed in the π-electron deficient aromatic component,[5] we decided to synthesize the precursor **3** and to study the template effect of some linear guests on the kinetics of its ring closure to yield **4** (see the Table of Contents graphic). The results of this investigation are reported here.

The synthesis of the precursor **3** was carried out according to an improved strategy with respect to that previously followed for the synthesis of **1**. Indeed, **1** was prepared by us according to the synthetic route illustrated in Scheme 1 in a 7% overall yield.[3a] Such a low yield was mainly due to the statistical nature of the second step in which the two reactants, **7** and **8**, are reacted in a 1:1 molar ratio. Purification of the desired tricationic ester **9**, accompanied by substantial amounts of the unreacted bifunctional substrate **7** and the disubstitution product, required repeated column chromatography separations that further lowered the yield to a bare 14%.

On account of the low yield obtained, we resorted to a different strategy for the preparation of **3** (Scheme 2). In the first three steps of Scheme 2, the corresponding bifunctional reagent is always present in large excess so as to avoid statistical reactions. Being that each bifunctional reagent is neutral, its unreacted excess at the end of the reaction could be easily separated from the insoluble saline product by filtration. The

* Corresponding author. Tel.: 39-6-4991-3697. Fax: 39-6-490-631.
† Università di Roma La Sapienza.
‡ Università di Roma Tor Vergata.

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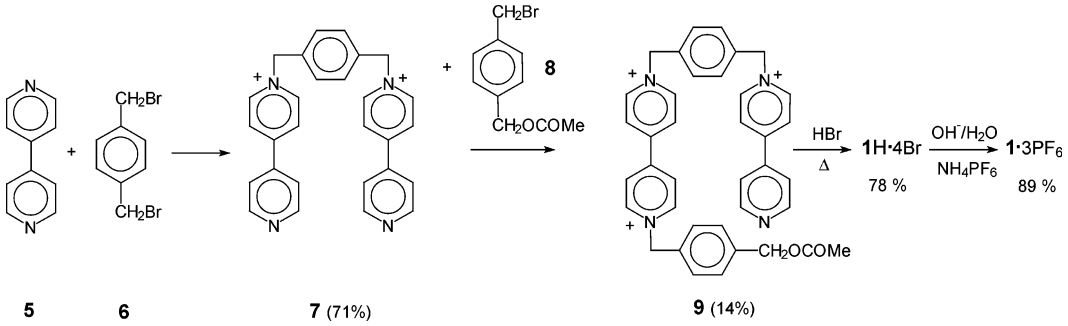
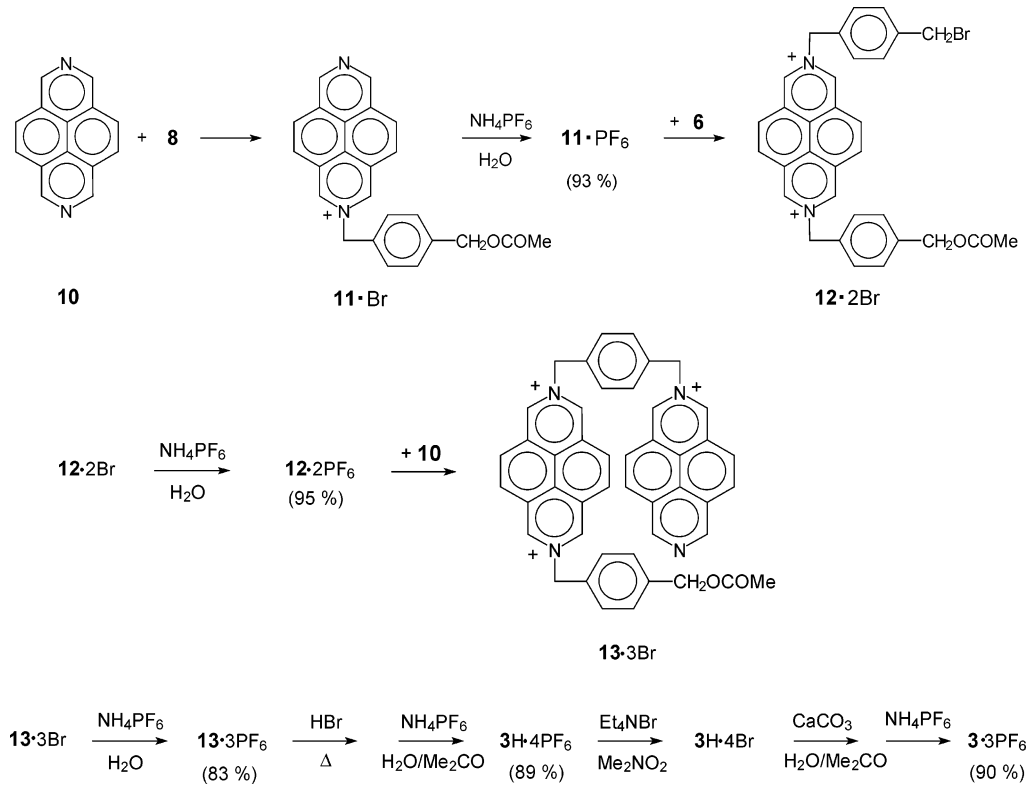
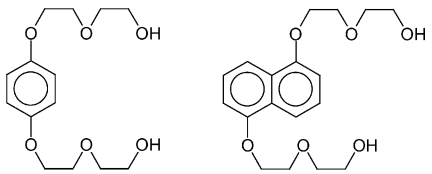
SCHEME 1



SCHEME 2



change in the synthetic strategy resulted in a dramatic improvement of the overall yield of **3** with respect to **1**: 59 versus 7%. Template effects in the ring closure reaction of **3** exerted by the linear guests **14** and **15** were successively evaluated.



14 **15**

Before investigating the effect of the templates, we measured the first-order rate constant for the ring closure reaction of the precursor **3** in the absence of any added template (k_0). The kinetics was studied at 62 °C in acetonitrile following, by ^{1}H NMR, the disappearance of the CH_2Br signal. The concentration of **3** was kept as low as possible (ca. 3×10^{-3} M) to avoid polymerization reactions. The obtained value of k_0 (2.1×10^{-6} s^{-1}) is of the same order of magnitude of that previously obtained for the uncatalyzed ring closure reaction of **1** ($k_0 = 8.3 \times 10^{-7}$ s^{-1}).[3a] The kinetic measurements in the presence of the templates **14** and **15** were carried out at 62 °C in acetonitrile following, by UV−vis spectroscopy at λ 502 and 520 nm, respectively, the appearance of the charge-transfer band of the corresponding [2]pseudo-rotaxane. First-order rate constants (k_{obs}) for the reaction of **3** (1 to 6×10^{-4} M) were obtained in the presence of variable excess amounts of the templates **14** and **15**. The ratios k_{obs}/k_0, plotted in Figure 1 against the concentration of **14** and **15**, respectively, provide a measure of the rate enhancements produced by the presence of the templates.

Rate enhancements up to a spectacular factor of about 450 were recorded in the case of **15.** For the sake of comparison, the previously obtained catalytic profiles relative to the ring closure reaction of the precursor **1** with the same guests[3a,e] are also reported.

It is evident from Figure 1 that, at a given concentration of each guest, the ring closure reaction of precursor **3** features a greater rate enhancement.

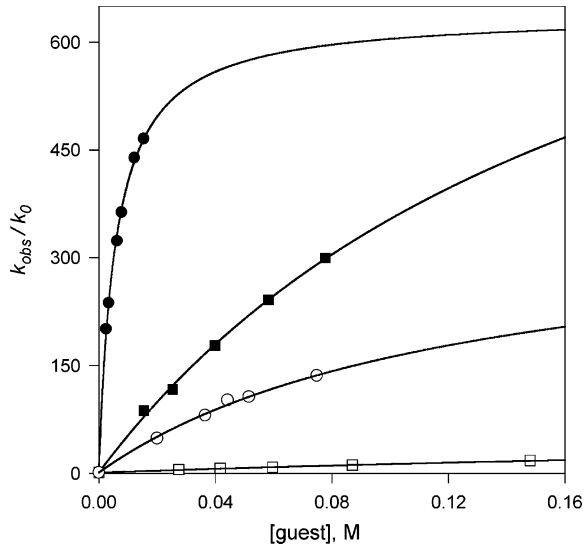


FIGURE 1. Rate enhancements produced by the guests **14** (squares) and **15** (circles) on the ring closure reaction of the precursors **1** (open symbols) and **3** (filled symbols). The points are experimental, and the curves are calculated (see text).

TABLE 1. Association Constants, in CH_3CN at 62 °C, Obtained for Guests 14 and 15 in the Ring Closure Reaction of the Precursors 3 and 1

reactant	guest	K_{sub} (M^{-1})	$K_{T\#}$ (M^{-1})	$K_{T\#}/K_{sub}$
3	**14**	5.4 (±1)	5.43 (±0.26) × 10^3	1.00 (±0.15) × 10^3
	15	172 (±10)	1.10 (±0.04) × 10^5	640 (±14)
1	**14**[a]	1.9 (±0.5)	144 (±7)	76 (±16)
	15[b]	8 (±2)	2900 (±200)	360 (±70)

[a] Ref 3a. [b] Ref 3e.

The kinetic profiles reported in Figure 1 can be analyzed by eq 1, which is obtained from a distribution scheme that takes into account the association of the guest with the substrate (K_{sub}) and with the transition state of the ring closure reaction ($K_{T\#}$).[3a]

$$\frac{k_{obs}}{k_0} = \frac{1 + K_{T\#}[guest]}{1 + K_{sub}[guest]} \quad (1)$$

Eq 1 shows that a rate enhancement will be observed if the template binds the transition state more strongly than the reactant.[6,7] Nonlinear least-squares fits to eq 1 of the k_{obs}/k_0 ratios provided the association constants K_{sub} and $K_{T\#}$ reported in Table 1. For the sake of comparison, the corresponding data relative to the ring closure reaction of precursor **1** are also reported.

The curves in Figure 1, calculated by inserting the values of K_{sub} and $K_{T\#}$ in eq 1, show a tendency to saturation. The saturation value, which is given by the ratio $K_{T\#}/K_{sub}$, is the maximum theoretical rate enhancement that would be attained when the substrate is completely bound to the template. These values, also reported in Table 1, indicate that the complexed form of **3** with **14**, and **15**, is ca. 1000, and 640 times, respectively, more reactive than the free one. Such rate enhancements are due to the fact that the association of the acyclic precursor **3** with templates **14** and **15** is rather weak, whereas the cyclic transition state shows a much greater binding affinity toward them. This is mainly due to the preorganization of the cyclic transition state and, secondarily, to the development of a further positive charge on the initially neutral nitrogen atom.

It is evident from Table 1 that all the association constants increase their values in going from **1** to **3**. This increase, which is directly attributable to the greater π-surface of the diazapyrenium unit, is much more pronounced for the cyclic transition states ($K_{T\#}$) than for the acyclic substrates (K_{sub}); for both guests, the $K_{T\#}$ value increases about 38 times, whereas the increases observed for K_{sub} are less pronounced and different for the two guests: about 3 times for guest **14** and about 22 times for guest **15**. This causes an inversion in the relative magnitude of the ratios $K_{T\#}/K_{sub}$ for the two guests in going from **1** to **3**. Judging from the ratios $K_{T\#}/K_{sub}$, it would seem that, in the case of the precursor **3**, guest **14** is a better template than **15**. However, the ratio $K_{T\#}/K_{sub}$ is a measure of the template effect under saturation conditions; conditions that in many cases are experimentally unattainable because of the limited solubility of templates. In fact, as shown in Figure 1, guest **15** is a far more efficient templating agent than **14** in the range of attainable guest concentrations. This fact points to the importance of the $K_{T\#}$ value as the best indicator for the templating ability of a guest, especially at low concentrations, where it determines the initial slope of the catalytic curve.

In conclusion, the results presented here indicate that the formation of tetracationic aromatic cycles templated by aromatic donors benefits from the use of extended π-surfaces both in the acceptor and in the donor components. This is evidenced by the kinetic advantage brought about by the substitution of the bipyridinium subunit with the diazapyrenium subunit in the acyclic precursor and by the substitution of the benzenic core with the naphthalenic core in the template structure. No doubt the kinetic advantage is due to the stronger $\pi-\pi$ interactions established between the more polarizable extended surfaces of the host and the guest in the cyclic transition state.

Experimental Section

Materials and Methods. 4-(Bromomethyl)benzyl acetate (**8**) was from our previous work.[3a]

2,7-Diazapyrene (**10**),[8] 1,4-bis[2-(2-hydroxyethoxy)ethoxy]benzene (**14**),[9] and 1,5-bis[2-(2-hydroxyethoxy)ethoxy]naphthalene (**15**)[10] were prepared according to literature procedures.

HPLC grade acetonitrile was used in the kinetic experiments without further purification.

2-[4-(Acetoxymethyl)benzyl]-2,7-diazapyrenium Hexafluorophosphate (11·PF_6) was prepared by adding dropwise, to a 100 mL solution of **10** (0.42 g, 2.06 mmol) in acetonitrile (HPLC grade) at refluxing temperature, 20 mL of an acetonitrile solution of **8** (0.10 g, 0.41 mmol). The solution was refluxed for 6 h. The solution was cooled to room temperature, and to complete the precipitation of the salt as bromide, a saturated solution of Et_4NBr in acetonitrile was added to the reaction mixture until no further precipitation was observed. The yellow precipitate was filtered off and dissolved in

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50 mL of water, and a saturated aqueous solution of NH_4PF_6 was added until no further precipitation was observed. After filtration, **11·PF$_6$** was obtained as a yellow solid (0.194 g, yield 93%). ^{1}H NMR (300 MHz, CD_3CN) δ 2.04 (s, 3H), 5.11 (s, 2H), 6.18 (s, 2H), 7.50 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 8.4 Hz, 2H), 8.43 (d, J = 9.1 Hz, 2H), 8.57 (d, J = 9.1 Hz, 2H), 9.65 (s, 2H), 9.73 (s, 2H). HRMS (ESI): $(M - PF_6)^+$ calcd for $C_{24}H_{19}N_2O_2$, 367.1447; found: 367.1464. Anal. Calcd for $C_{24}H_{19}BrN_2O_2 \cdot 1/2H_2O$: C, 63.17; H, 4.42; N, 6.14. Found: C, 63.43; H, 4.71; N, 6.15.

2-[4-(Acetoxymethyl)benzyl]-7-[4-(bromomethyl)benzyl]-2,7-diazapyrenium Bis(hexafluorophosphate) (12·2PF$_6$) was prepared by adding dropwise in 80 min, to a 15 mL solution of **6** (0.515 g, 1.95 mmol) in acetonitrile (HPLC grade) kept at 70 °C, 35 mL of an acetonitrile solution of **11·PF$_6$** (0.10 g, 0.195 mmol). The reaction mixture was kept at 70 °C for 42 h. The solution was cooled to room temperature, and to complete the precipitation of the salt as bromide, a saturated solution of Et_4NBr in acetonitrile was added to the reaction mixture until no further precipitation was observed. The yellow precipitate was filtered off and dissolved in 50 mL of water, and a saturated aqueous solution of NH_4PF_6 was added until no further precipitation was observed. After filtration, **12·2PF$_6$** was obtained as a yellow solid (0.156 g, yield 95%). ^{1}H NMR (300 MHz, CD_3CN) δ 2.05 (s, 3H), 4.62 (s, 2H), 5.13 (s, 2H), 6.26 (s, 4H), 7.50−7.68 (m, 8H), 8.83 (s, 4H), 9.95 (s, 4H); HRMS (ESI): $(M - PF_6)^+$ calcd for $C_{32}H_{27}BrN_2O_2PF_6$, 695.0898; found: 695.0915. Anal. Calcd for $C_{32}H_{27}Br_3N_2O_2$: C, 54.04; H, 3.83; N, 3.94. Found C, 53.82; H, 4.08; N, 4.02.

2-[4-(Acetoxymethyl)benzyl]-7-[4-(2,7-diazapyrenil)methylbenzyl]-2,7-diazapyrenium Tris(hexafluorophosphate) (13·3PF$_6$) was prepared by adding dropwise in 80 min, to a 61 mL solution of **10** (0.185 g, 0.825 mmol) in acetonitrile (HPLC grade) kept at 70 °C, 17.5 mL of an acetonitrile solution of **12·2PF$_6$** (0.149 g, 0.177 mmol). The reaction mixture was kept at 70 °C for 13 h. The solution was cooled to room temperature, and to complete the precipitation of the salt as bromide, a saturated solution of Et_4NBr in acetonitrile was added to the reaction mixture until no further precipitation was observed. The yellow precipitate was filtered off and dissolved in 50 mL of water, and a saturated aqueous solution of NH_4PF_6 was added until no further precipitation was observed. The precipitate was filtered off and purified by column chromatography (silica gel, CH_3CN/CH_3OH/2 N aqueous NH_4Cl solution 5:4:1). The fractions containing **13** were combined, and the solvent was removed in vacuo. The residue was dissolved in water, and a saturated aqueous solution of NH_4PF_6 was added until no further precipitation was observed. After filtration, **13·3PF$_6$** was obtained as a yellow solid (0.163 g, yield 83%). ^{1}H NMR (300 MHz, CD_3CN) δ 2.05 (s, 3H), 5.13 (s, 2H), 6.22 (s, 2H), 6.26 (s, 2H), 6.29 (s, 2H), 7.51 (d, J = 8.4 Hz, 2H), 7.65 (d, J = 8.4 Hz, 2H), 7.73 (s, 4H), 8.49 (d, J = 9.0 Hz, 2H), 8.68 (d, J = 9.0 Hz, 2H), 8.81 (s, 4H), 9.67 (s, 2H), 9.83 (s, 2H), 9.93 (s, 2H), 9.95 (s, 2H); ESI-MS (m/z) 965 $[M-PF_6]^+$. Anal. Calcd for $C_{46}H_{35}Br_3N_4O_2 \cdot 3H_2O$: C, 56.98; H, 4.26; N, 5.78. Found C, 57.15; H, 4.25; N, 5.70.

2-[4-(Bromomethyl)benzyl]-7-[4-(2,7-diazapyrenil)methylbenzyl]-2,7-diazapyrenium Tris(hexafluorophosphate) (3·3PF$_6$) The salt **13·3PF$_6$** (0.127 g, 0.114 mmol) in 12 mL of 48% HBr was heated at 85 °C for 6 days. The reaction mixture was diluted to 75 mL with water. The solid was filtered off and dissolved in H_2O-Me_2CO (1:1, 80 mL), and 1 mL of 60% HPF_6 was added. The precipitate was filtered to give **3H·4PF$_6$** (0.130 g, yield 89%). ^{1}H NMR (300 MHz, CD_3CN) δ 4.62 (s, 2H), 6.25 (s, 2H), 6.26 (s, 2H), 6.29 (s, 2H), 7.57 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 8.4 Hz, 2H), 7.75 (s, 4H), 8.69 (d, J = 9.1 Hz, 2H), 8.81 (s, 4H), 8.83 (d, J = 9.1 Hz, 2H), 9.83 (s, 2H), 9.89 (s, 2H), 9.93 (s, 2H), 9.95 (2s, 2H). **3H·4PF$_6$** was then converted to **3H·4Br** by anion exchange[11] with Et_4NBr in $MeNO_2$. Anal. Calcd for $C_{44}H_{33}Br_5N_4 \cdot 2H_2O$: C, 50.13; H, 3.51; N, 5.32. Found: C, 49.90; H, 3.41; N, 5.28. **3H·4Br** was dissolved in H_2O-Me_2CO (3:1, 90 mL) and deprotonated by adjusting the pH to 6 with $CaCO_3$ in powder. The excess $CaCO_3$ was removed by filtration, and a saturated aqueous solution of NH_4PF_6 was added until no further precipitation was observed. After filtration, **3·3PF$_6$** was obtained as a yellow solid (0.104 g, yield 90%). ^{1}H NMR (300 MHz, CD_3CN) δ 4.62 (s, 2H), 6.24 (s, 2H), 6.26 (s, 2H), 6.29 (s, 2H), 7.48−7.66 (m, 4H), 7.68−7.82 (m, 4H), 8.57 (d, J = 9.1 Hz, 2H), 8.74 (d, J = 9.1 Hz, 2H), 8.78−8.87 (m, 4H), 9.73 (s, 2H), 9.86 (s, 2H), 9.93 (s, 2H), 9.95 (s, 2H); HRMS (ESI): $(M - PF_6)^+$ calcd for $C_{44}H_{32}BrN_4P_2F_{12}$, 985.1094; found: 985.1117.

Kinetic Measurements. Kinetic measurements were carried out in acetonitrile, at 62 °C, in a 3 mL cuvette (optical path 1 cm) kept in the thermostatted cell compartment of the spectrophotometer. In a typical run, 100 μL of a 0.010 M solution of **3·3PF$_6$** was added to a 2.5 mL solution of either the template **14** or **15** at the appropriate concentration. The appearance of the charge-transfer band was followed at λ 502 and 520 nm. In all of the cases, a clean first-order behavior was observed. Relative kinetic constants (k_{obs}/k_0, where $k_0 = 2.1 \times 10^{-6}$ s^{-1}) at the various template concentrations (corrected for the volume increase at 62 °C and given in parentheses in M) were as follows: template **14**: 1 (0), 87.14 (1.54×10^{-2}), 116.67 (2.53×10^{-2}), 177.62 (3.99×10^{-2}), 241.42 (5.82×10^{-2}), 299.52 (7.70×10^{-2}). Data plotted in Figure 1. Template **15**: 1 (0), 200.95 (2.47×10^{-3}), 237.14 (3.42×10^{-3}), 323.33 (6.27×10^{-3}), 363.33 (7.77×10^{-3}), 439.05 (1.22×10^{-2}), 465.71 (1.54×10^{-2}). Data plotted in Figure 1.

Supporting Information Available: ^{1}H NMR spectrum of compound **3·3PF$_6$** (300 MHz, CD_3CN). This material is available free of charge via the Internet at http://pubs.acs.org.

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