

Influence of Ion Pairing on Styrene Hydrogenation Using a Cationic η^6 -Arene β -Diketiminato-Ruthenium Complex

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A series of salts composed of the coordinatively unsaturated ruthenium β -diketiminato cation $[(\eta^6 - C_6H_6)Ru((ArNCMe)_2CH)]^+$ (Ar = 2,6-dimethylphenyl) and different anions, i.e., OTf⁻ (1), BF₄⁻ (2), PF₆⁻ (3), BPh₄⁻ (4), and BArF⁻ (B((3,5-CF_3)_2C_6H_3)_4⁻) (5), have been prepared and characterized. The solid state structures of 1, 2, and 5 have also been established using single-crystal X-ray diffraction. Both solution and solid state data reveal the presence of anion–cation interactions, the extent of which depends on the nature of the anion, which have been further rationalized via computed charge density profiles using DFT energy optimized models. The catalytic activity of 1–5 in the hydrogenation of styrene was found to be highly dependent on the nature of the counteranion, as inferred from investigations based on high-pressure solution NMR, pulsed gradient spin–echo (PGSE) NMR diffusion, and Overhauser NMR spectroscopy. A good correlation between catalytic activity and the extent and nature of ion pairing was found, and the structure of the active catalytic species is proposed.

Introduction

Since the pioneering and paradigm-changing discovery of the catalytic properties of Wilkinson's catalyst, RhCl-(PPh₃)₃, irrespective of the metal employed, phosphine ligands overwhelmingly dominate ligand choice in homogeneous hydrogenation catalysis. Tolmann elegantly classified the electronic and steric properties of monophosphine ligands in his seminal review article, which ultimately led to rational ligand design in the field of homogeneous catalysis.¹ In addition, bisphosphine ligands have received considerable attention, in regard to parameters such as bite angles and chirality, leading to new design concepts.

Catalysts based on newer hybrid bidentate ligands such as phosphino-amino and carbene-amino systems also demonstrate high activity and good selectivity in hydrogenation reactions. However, very few hydrogenation catalysts are known where the supporting ligand chelates through two or more nitrogen centers,² with notable examples including the application of 2-aminomethyl-1-ethylpyrrolidine and 1,2-diphenyl-ethylenediamine ligands.³ Chelating diamino ligands find widespread use in catalytic transfer hydrogenation reactions whereby both the metal and ligand assist in the transfer of a hydride and proton from an appropriate hydrogen donor to the substrate.

 β -Diketiminates as supporting ligands for hydrogenation catalysts have received only minor attention despite their attractiveness in stabilizing electronically unsaturated metal centers.⁴ Budzelaar and co-workers found that 14-electron olefin-substituted β -diketiminato-rhodium complexes can hydrogenate a variety of alkene-based substrates at low H₂ pressures, albeit with very low turnover numbers.⁵ Further studies with rhodium and iridium β -diketiminato complexes revealed that di- and multihydride^{6,7}-containing species are formed readily in the presence of hydrogen and appear to be important intermediates in hydrogenation and dehydrogenation processes. We recently reported ruthenium complexes with 2,6-dimethylphenyl- α , α -dimethyl-substituted β -diketiminato ligands (Chart 1).⁸ The compounds exist in either the neutral form (type a), with a Ru-coordinated chloride ligand, or the cationic form (type **b**), prepared via the removal of the chloride ligand.

Notably, the cationic type **b** complex, as its triflate salt, undergoes thermoreversible addition reactions across the metal center and the β -carbon of the β -diketiminato ligand

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Chart 1



Scheme 1. General Synthesis of Cationic β -Diketiminato-Ruthenium Complexes with Different Anions^{*a*}



^a Ar corresponds to 2,6-dimethylphenyl. A single-pot synthesis is possible only in the case of the triflate salt, 1.

with reagents containing unsaturated carbon–carbon bonds. Adducts with both ethylene, **c**, and acetylene, **d**, have been isolated and characterized. Moreover, it has been shown that coordinatively unsaturated cationic complexes of type **b** are highly active toward heterolytic cleavage of H₂, forming a species containing a coordinated monohydride species **e**, supported by a β -diimine ligand,⁸ which readily reverts back to the β -diketiminato complex when the H₂ atmosphere is removed.

The observation of such cooperative reactivity indicates that the cationic type **b** complexes could be effective hydrogenation catalysts.⁸ We therefore prepared a series of cationic ruthenium β -diketiminato complexes with different anions, ranging from the strongly coordinating triflate anion to the weakly interacting trifluoromethylated tetrakis-phenyl borate (BArF⁻) anion, and compared their activity in the hydrogenation of styrene. Herein we report on the outcome of these studies.

Results and Discussion

As previously reported,⁸ the cationic ruthenium η^6 benzene- β -diketiminato species, **1**, with a triflate counterion is conveniently prepared in a one-step reaction from the η^6 -C₆H₆-dichlororuthenium dimer, β -diketiminato-lithium conjugate, and sodium or potassium triflate. However, the direct exchange of the chloride group with other anions, i.e., BF₄⁻, PF₆⁻, BPh₄⁻, and BArF⁻, cannot be performed as a single-pot reaction due to the strong basicity of the β diketiminato-lithium conjugates. In the case of PF₆⁻, for example, the above-mentioned procedure yielded significant quantities of PF₃. It is known that β -diketiminato-lithium complexes react readily with PCl₃ to form a variety of phosphorus-centered heterocycles.⁹ However, clean quantitative yielding reactions are observed when the corresponding Cl-ligated precursor is combined with the sodium salt of the desired anion, and the resulting complexes 2-5 are removed from the insoluble NaCl byproduct (Scheme 1).

The ¹H NMR spectra of 1–5 in CD₂Cl₂ confirm the $C_{2\nu}$ symmetry of the ruthenium cations, as only one single resonance for the *ortho* methyl groups attached to the flanking aryl groups of the β -diketiminato ligand is observed. The ¹H NMR spectra also indicate that the counterions interact to some extent with the cations, as some modest chemical shift variations among the different salts are observed. In particular, an increased amount of shielding for the arene protons is observed in complexes 4 and 5 that contain the BPh₄⁻ and BArF⁻ anions. Moreover, slight variations of the β -diketiminato ligand are observed. However, these minor differences still indicate that specific and well-defined cation—anion interactions are present in solution.

Characterization in the Solid State. All of the complexes were isolated as fine microcrystalline powders, and using liquid-vapor diffusion methods (see Experimental Section) 1, 2, and 5 were crystallized with dimensions suitable for structural determination using X-ray diffraction analysis. Data treatment and relevant parameters are given in the Experimental Section and Supporting Information.

For 1, 2, and 5 no significant structural variation of the cation is observed to within experimental errors. Nevertheless, upon examination of the crystal packing for the salts, a

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Table 1. Selected ¹H and ¹³C NMR Data of the η^{6} -C₆H₆ and the 2,6-Dimethylphenyl, α, α' -Dimethyl β -Diketiminate Ligands in $1-5^{\alpha}$

	anion	$\frac{\delta(^{1}\mathrm{H})}{\beta\text{-}\mathrm{C}H}$	$\frac{\delta(^{13}\mathrm{C})}{\beta\text{-}C\mathrm{H}}$	$\frac{\delta(^{13}\text{C})}{\alpha\text{-}CC\text{H}_3}$	$\frac{\delta(^1\mathrm{H})}{\eta^6\text{-}\mathrm{C}_6\mathrm{H}_6}$	$\frac{\delta(^{13}\text{C})}{\eta^6\text{-}\text{C}_6\text{H}_6}$	
1 2 3 4 5	$\begin{array}{c} \text{OTf}^-\\ \text{BF}_4^-\\ \text{PF}_6^-\\ \text{BPh}_4^-\\ \text{BArF}^- \end{array}$	6.63 6.64 6.67 6.60 6.65	105.57 105.52 105.71 105.64 105.94	163.92 163.89 164.02 163.96 164.24	5.17 5.16 5.14 4.91 5.08	84.13 84.11 84.43 83.85 83.96	

^a Spectra recorded in CD₂Cl₂ at 25 °C.

Table 2. Comparison of Key Intermolecular Distances between theVarious Components of the Cation and Anion in Complexes 1, 2,
and 5^{a}

	anion	cation component	anion component	interaction distance (Å)
1	OTf ⁻	η^6 -C ₆ H ₆	O ₃ SCF ₃	2.397, 2.684
1	OTf^{-}	α -CH ₃	O ₃ SCF ₃	2.659
1	OTf^{-}	o-CH ₃	O ₃ SCF ₃	2.653
2	BF_4^-	η^6 -C ₆ H ₆	BF_4	2.404, 2.485, 2.580, 2.607
2	BF_4^-	α -CH ₃	BF_4	2.428, 2.439, 2.657, 2.713
2	BF_4^-	o-CH ₃	BF_4	2.633
2	BF_4^-	m-CH	BF_4	2.603
2	BF_4^-	p-CH	BF_4	2.485
5	$BArF^{-}$	η^6 -C ₆ H ₆	CF ₃	2.520, 2.619
5	$BArF^{-}$	α -CH ₃	CF_3	2.645, 2.655, 2.666

^{*a*} The interacting atoms are highlighted in bold.

clear distinction between the two classes of anions is apparent. The OTf⁻ and BF₄⁻ containing salts pack in a preferential arrangement that favors the formation of a maximum number of van der Waals type interactions between the fluorine and oxygen atoms of the anions and hydrogen atoms of the η^6 -C₆H₆ ring; see Table 2 and Figure 1. In the case of complex 2, the fluorine atoms of the BF_4^- anion form short interactions with the hydrogen atoms of the η^6 -C₆H₆ ligand. The anions in the crystal packing of 1 and 2 appear to help orientate the cations into a position in which the η^{6} benzene rings form $\pi - \pi$ stacking interactions, albeit at long distances (Figure 1). The interaction between an oxygen center of a triflate group and a hydrogen atom associated with an η^6 -benzene is quite common.¹⁰ Another series of cation-anion interactions is observed between the fluorine atoms of OTf⁻ and the 2,6-dimethyl hydrogens of the flanking aryl group, and interactions between the α -CH₃ of the β -diketiminato ligand and the trifluoromethyl group of the triflate moiety are also observed. In the case of BF_4^- , the closest interactions are between the η^6 -C₆H₆ ring and the fluorine atoms; however, benzene-benzene stacking is not as pronounced as for 1. The most important anion-cation interactions are summarized in Table 2.

In the structure containing the larger and weaker coordinating BArF⁻ counterion, a different packing arrangement is observed, whereby the backbone of the β -diketiminate ligand slots between two 3,5-(CF₃)₂C₆H₃ aryl groups (Figure 2). Accordingly, hydrogen bonding between the α -CH₃ and CF₃ group is present. A similar packing arrangement has been reported previously.¹¹ In order to maximize cation-anion packing, the four aryl groups of BArF⁻



Figure 1. ORTEP packing diagram of 1 showing the interactions between the benzene group of the cation and the oxygen and fluorine atoms of the triflate OTf^- anion. The thermal ellipsoids of non-hydrogen atoms were drawn at the 50% probability level. The chloroform solvate is omitted for clarity.

arrange to form an overall D_{2d} molecular symmetry instead of S_4 . However, the latter is calculated to be lower in energy by a very small amount, only 0.52 kcal mol⁻¹, and in the case of BPh₄⁻, 0.78 kcal mol⁻¹. Analogous with the OTf⁻ and BF₄⁻ anions, another set of interactions is formed with the hydrogen atoms of the η^6 -C₆H₆ ring, which are also relativity short (Table 2), although somewhat less extensive than those formed with the OTf⁻ and BF₄⁻ anions.

A computed charge density profile of the cationic component of 2 (Figure 3), obtained through a DFT energy optimized model with a constrained $C_{2\nu}$ symmetry, indicates that the highest areas of positive charge on the molecule are primarily associated with the hydrogen atoms of the η^6 -C₆H₆ ring. Secondary sites include the methyl groups of the flanking aryls and associated α -CH₃ groups attached to the β -diketaminato ligand. For OTf⁻, BF₄⁻, and PF₆⁻ all of the outer atoms are highly electronegative. In the case of BArF⁻, the fluorine atoms of the CF₃ groups represent the highest regions of electronegativity, but for BPh₄⁻, the outer edges of the phenyl groups are significantly less electronegative than the other counterions. Therefore, this anion is expected to interact with the higher regions of electronegativity on the cation, i.e., the α -CH₃ and flanking aryl protons. The electrostatic maps reveal that OTf^- , BF_4^- , and PF_6^- are small charge-localized anions and therefore prefer to interact with specific electropositive areas of the cation, whereas the larger, charge-diffuse anions, BPh4⁻ and BArF⁻, interact with a larger region of the cation, i.e., flanking aryls and the α -CH₃ groups. The individual intermolecular interactions between the cation and BPh₄⁻ and BArF⁻ may be weaker than those of OTf⁻, BF₄⁻, and PF₆⁻, but a greater total of interactions in the former results in stronger ion pairing for these types of anions. Thus, although the calculated cation and anion models represent isolated gas phase molecules, a good overall correlation with the crystal-packing arrangement is observed. Moreover, the anion-benzene interaction is also maintained in solution, as indicated by ¹H,¹⁹F HOESY data (see below).

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Figure 2. ORTEP packing diagram of 5 showing the interactions between the η^6 -benzene ring and α -CH₃ groups of the cation with the fluorine atoms (shaded in gray) of the BArF⁻ anions. The thermal ellipsoids of non-hydrogen atoms are shown at the 50% probability level.



Figure 3. Visual representations of the electrostatic potential for the cation $[(\eta^6-C_6H_6)Ru((2,6-(CH_3)_2C_6H_3)NC(CH_3))_2CH]^+$ (top left) and the relevant anions, OTf⁻ (top right), BPh₄⁻ (bottom left), and BArF⁻ (bottom right). The areas of greatest electronegativity are represented in red, and the lowest electronegative areas are shown in blue.

Styrene Hydrogenation Studies Using 1–5. Complexes 1–5 were screened as (pre)catalysts for the hydrogenation of styrene under conditions similar to those reported for a related chelating bisphosphine complex.¹² All hydrogenation reactions were performed under an inert atmosphere, to avoid deactivation of the catalyst by reaction with O_2 , and the obtained results are listed in Table 3.

A comparison of the catalytic activity of salts 1-5 reveals a clear difference between the smaller potentially coordinating anions such as OTf⁻,¹³ BF₄⁻, and PF₆⁻ and the larger apparently weakly coordinating borates, BPh₄⁻ and BArF⁻.¹⁴ In most situations, BArF⁻ is employed to help accelerate catalytic-based reactions and has been shown to be particu-

Table 3. Turnover Frequencies for Styrene Hydrogenation for Complexes $1-5^a$

complex	anion	TOF (mol substrate $mol \text{ catalyst} \cdot h^{-1}$)
1	OTf ⁻	838
1^{b}	OTf^{-}	783
2	BF_4^-	759
3	PF_6^-	737
4	BPh_4^-	149
5	$BArF^-$	287

^{*a*} Complexes are listed in order of decreasing activity. Conditions: 40 atm of H₂, 80 °C, dry and degassed THF (2 mL), styrene (1 g, 9.60 mmol), 0.01% mmol catalyst. ^{*b*} Performed with the addition of 100 mg of Hg.

larly useful in hydrogenations performed by cationic Ir-PHOX complexes.¹⁵ For this ruthenium β -diketaminato complex, in contrast, the catalytic activity is dramatically reduced in the presence of these weakly coordinating anions.

Further control experiments were undertaken including a Hg poisoning experiment to establish the contribution from heterogeneous catalysts generated in situ under the reductive conditions of the hydrogenation reaction.¹⁶ Since only a small decrease in the conversion of styrene was observed in the presence of Hg, homogeneous catalysis presumably dominates. It is also worth noting that the postcatalysis solutions reveal no signs of decomposition. The choice of solvent for the hydrogenation reactions appears to be very critical. For all of the above-described hydrogenations, dry and degassed THF was used; however, when chloroform is used, TOFs for styrene hydrogenation by complex 1 are significantly reduced. Moreover, if 10% of THF is added to a solution 1 in chloroform, some activity is regained, suggesting a direct (coordination) role of the THF in the catalytic cycle; see complex 6 in Scheme 2.

High-pressure (sapphire) ¹H NMR spectroscopy¹⁷ was used to study the rate of styrene hydrogenation for $1 (X = OTf^{-})$ and $5 (X = BArF^{-})$ over 45 min. Conditions for the

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Figure 4. Graph of styrene hydrogenation by 1 and 5 established in situ using high-pressure ¹H NMR spectroscopy. Zero time corresponds to when the sample reached a temperature of 80 $^{\circ}$ C, typically within a 5 min period.

Scheme 2. Formation of the Hydride Species 1' from 1 and Subsequent Generation of the Proposed Active Catalytic Species 6 and Final Stable Species (7 and 8) at the End of the Reaction Following Release of the H₂ Pressure



catalytic hydrogenation of styrene were approximated as close as possible to those in the reactor; however, a higher pressure of 100 bar was used in place of 40 bar, to ensure effective mass transfer of H₂ into the solution due to less efficient mixing in the narrow sapphire NMR tube. The rate of conversion of styrene to ethylbenzene differs significantly for the two tested systems (Figure 4) and is consistent with the TOF numbers obtained in the batch reactor. Complex 1, with the triflate counterion, is significantly more active than 5, with the BArF⁻ anion, suggesting that the anion continues to exert an influence with respect to the active catalytic species. Interestingly, no induction period was observed from the time measurements started, although during the sample heating period of approximately 5 min, 1 undergoes conversion to the active catalytic species, which overall is relativity fast and tends to exclude the possibility of heterogeneous (nanoparticle) catalysts generated from the complexes.

A high-pressure ¹H NMR experiment was also performed using **1** in combination with D_2 and d_8 -styrene in d_8 -THF. Initially, prior to heating the sample, the formation of the deuterated monohydride β -diimide species was observed, i.e., complex **e** in Chart 1. Interestingly, a signal for HD was observed, suggesting the occurrence of a scrambling reaction involving the β -hydrogen position of the β -diimine ligand. As the temperature was raised to 80 °C over a 15 min period, the signal corresponding to the η^6 -C₆H₆ arene slowly disappears; however, there is no evidence for a resonance corresponding to free benzene or a deturated analogue. This observation suggests that the benzene ring is removed by (partial) hydrogenation, albeit in a stoichiometric fashion.

Moreover, the residual signals associated with the ${}^{1}H_{8}$ -THF solvent reveal a set of secondary peaks shifted to slightly higher field (+0.35 ppm) that are consistent with THF coordination to a metal center via the O atom. Therefore, it is proposed that the active catalytic species consists of a β -diimino ruthenium hydride species **6** supported by a THF ligand (Scheme 2). Electrospray ionization mass spectrometry (ESI-MS) was used to analyze the solution after depressurization, revealing the presence of species similar to the cation in 1, but in which the benzene has been replaced by styrene (7 in Scheme 2) or ethylbenzene (8 in Scheme 2). This observation suggests that the proposed THF-coordinated intermediate is unstable and reverts to a η^{6} -coordinated arene species in the absence of a pressurized hydrogen environment, which is as expected for a weakly coordinated ligand.

Table 4. $D (10^{-10} \text{ m}^2 \text{ s}^{-1})$ and $r_H (\text{\AA})$ Values^{*a*} for 1–5 in d_8 -THF

salt	anion	concn (mM)	fragment	D	$D_{ m c}/D_{ m a}$	$r_{\rm H}$	$r_{\rm H}^{\rm corr}$	TOF ^b
1	OTf ⁻	3.7	cation anion	8.21 8.97	0.92	5.8 5.3	6.5 6.1	788
2	$\mathrm{BF_4}^-$	2.3	cation anion	8.57 9.60	0.89	5.5 5.0	6.3 5.8	759
3	PF_6^-	2.8	cation anion	8.64 9.94	0.87	5.5 4.8	6.2 5.6	737
4	BPh_4^-	3.1	cation anion	7.52 7.55	1.00	6.3 6.3	6.9 6.9	149
5	$BArF^{-}$	6.4	cation	7.46 6.67	1.13	6.4 7.1	7.0 7.6	287

^{*a*} For the calculation of $r_{\rm H}$, the viscosity of the nondeuterated solvent at 299 K was used ($\eta(d_8\text{-THF}) = 0.46 \ 10^{-3} \ \text{kg s}^{-1} \ \text{m}^{-1}$). $r_{\rm H}$ was calculated using the Stokes–Einstein equation, while $r_{\rm H}^{\rm corr}$ was calculated using a semiempirical estimation of *c* ($r_{\rm vdW}$ of THF was estimated using Bondi's group increments²⁵).^{21,48 *b*} In units of moles of substrate per moles of catalyst per h⁻¹.

PGSE Diffusion and HOESY Studies. The recent literature^{15,18-20} suggests that, when salts are employed as catalysts, the choice of counterions can be important, not only in terms of determining the structure of the salt but in terms of its reactivity. While the anions may be "innocent", it has become clear that ion-pairing effects frequently play a significant role. Although measuring the extent of the ion pairing in solution is not a trivial matter, recent NMR studies, combining both pulsed gradient spin-echo (PGSE) NMR diffusion²¹ and Overhauser NMR spectroscopy, have begun to reveal how ions interact. Assuming that both of the charged species in question contain NMR-active spins, e.g., ¹H and ¹⁹F, inspection of the magnitudes of the NMR diffusion constants provides a direct estimate of the extent of the ion pairing. For 100% ion pairing (and in the absence of, for example, hydrogen-bonding or encapsulation effects), the diffusion constants (D-values) for the anion and cation will be identical within the experimental error.

In an effort to estimate the possible role of the anions in the catalysis described herein we have carried out PGSE and ¹H, ¹⁹F HOESY NMR studies on the ruthenium complexes **1–5**; see Table 4. In addition to the experimental *D*-values, we show a ratio, D(cation)/D(anion), as well as hydrodynamic radii, $r_{\rm H}$ (calculated from the Stokes–Einstein equation and its proposed modifications).²¹

For salts 1–5 there are considerable differences between the experimental *D*-values for the cations and the anions. For the OTf⁻, BF₄⁻, and the PF₆⁻ salts, the *D*(cation)/*D*(anion) ratio is <1, but quite substantial and indicative of a considerable amount of ion pairing. This result is also observed for a number of different salts in THF solution.^{22–24} For comparison it is worth noting that many BF₄⁻ and PF₆⁻

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Figure 5. ¹H,¹⁹F HOESY spectrum of **3** in d_8 -THF (14 mM). There are strong contacts to the 12 equivalent *ortho* methyl protons of the aryl rings and the protons of the η^6 -benzene ring. This is consistent with a selective position for the anion remote from the N,N-chelate ring, but close to the η^6 -benzene ring.

transition metal salts in methanol solution give much smaller $r_{\rm H}$ values (and thus faster translation due to less association) for these two anions.²⁴ For the BPh₄⁻ salt, the ratio D-(anion)/D(cation) is unity, suggesting 100% ion pairing for this salt. As a consequence of this ion pairing, this salt is effectively much larger and the calculated $r_{\rm H}$ value is ca. 6.9 Å. In the BArF⁻ analogue, the ratio is >1, which is certainly partially a reflection of the fact that this anion is quite large. The estimated corrected $r_{\rm H}$ value for this anion is about 6.6 Å; however the calculated $r_{\rm H}$ value of ca. 7.6 Å suggests more ion pairing than usually encountered for this anion in THF. The ¹H, ¹⁹F HOESY NMR spectra of 1-3share many similar features. There are strong contacts to (a) the 12 equivalent ortho methyl protons of the aryl rings (see the spectrum for 3 in Figure 5) and (b) the protons of the η^{6} complexed benzene ring. These features are consistent with a selective position for the anion in which it is somewhat remote from the N,N-chelate ring, but close to the benzene ring, in keeping with the computational study. The BPh₄⁻ salt 4 clearly reveals modest contacts from all three of its protons to the ortho methyl protons of the aryl rings. However, the BArF⁻ anion in 5 shows no significant contacts (from either the ¹⁹F or the ¹H spins) to the cation. If the BPh₄⁻ contacts are maintained during the catalytic cycle, they may reflect the observed TOF value for this salt

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either by (a) steric hindrance due to ion pairing or (b) the occupation of the coordination sites critical to catalytic activity. Given the ion pairing found for the BArF⁻ analogue, steric effects may be responsible for the reduced catalytic activity of this salt.

Concluding Remarks. The electronically unsaturated cationic ruthenium complexes 1-5, supported by the sterically demanding 2,6-dimethylphenyl α,α' -dimethyl β -diketaminate ligand, are good catalyst precursors for the hydrogenation of styrene to ethylbenzene. The active catalyst appears to be a homogeneous species, in which the benzene ring has been lost with the ruthenium center stabilized by weakly coordinating THF solvent molecules. The catalytic activity of the salts is additionally influenced to a significant extent by the nature of the counterion. A combination of structural, computational, and NMR studies suggest that the observed anion effects are due to ion-pairing phenomena and potentially, but probably to a much lesser extent, direct anion coordination. Indeed, the classic weakly coordinating anions (BPh₄⁻ and BArF⁻), often used to facilitate catalytic reactions,²⁶⁻²⁸ suppress activity more than the other anions included in this study (OTf⁻, BF₄⁻, and PF₆⁻). Thus, not only does this study demonstrate how careful the choice of the anion is required to optimize the catalytic activity, but at a molecular level, it also provides a rationalization for the observed anion effects.

Experimental Section

General Procedures. Synthesis of the N-protonated 2,6-dimethylphenyl α, α' -dimethyl β -diketaminate was performed under conditions typical for organic synthesis, whereas other operations were carried out under a N2 atmosphere with standard Schlenk techniques. Synthesis and manipulations of all β -diketaminato-ruthenium complexes and reagents were performed in a drybox with a N2 atmosphere containing less than 1 ppm of O_2 and H_2O and equipped with a vacuum outlet. All glassware was predried, and the flasks underwent several purge/ refill cycles before the introduction of solvents or reagents. All solvents were dried by passage through aluminum oxide columns or, in some cases, degassed by passage through a copper column (Innovative Technologies) and then stored in Schlenk flasks equipped with Teflon stopcocks over 3 or 4 Å molecular sieves. Celite (545 grade, Merck Co.) was dried at 160 °C for two days. The ruthenium benzene precursor $[(\eta^6-C_6H_6)RuCl_2]_2$,²⁹ the unsolvated Li((2,6-CH₃)₂C₆H₃)NC(CH₃))₂CH complex,³⁰ and anhydrous Na[B(3,5-(CF₃)₂C₆H₃)₄)^{31,32} were prepared according to literature procedures. All other reagents and gases (technical grade) were purchased from commercial sources and used as received. NMR spectra were recorded using either a Bruker Avance 200 or 400 MHz instrument. ¹H (COSY, NOE) and ¹³C (HMBC and HSQC) one- and two-dimensional spectra were used to assign molecular connectivity and conformation in solution. High-purity CD_2Cl_2 was distilled over CaH_2 and

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stored over 4 Å molecular sieves. d8-THF was dried and distilled over 1:2 sodium-potassium alloy. Both solvents were degassed by repeated freeze-thaw cycles prior to sample preparation. Chemicals shifts for ¹H and ¹³C spectra were referenced to residual solvent peaks and external references for Et_2O-BF_3 for ¹¹B spectra, 85% H₃PO₄:H₂O for ³¹P spectra, and CF₃Cl for ¹⁹F spectra. Coupling constants were determined by iterative spectral simulation using the program gNMR.33 ATR FT-IR was performed with a Perkin-Elmer Spectrum One instrument, using freshly ground samples pressed on top of a diamond anvil window. Sample preparation and spectral recording (in air) were performed within 2 min. Elemental microanalyses were obtained using a CE Instruments EA-1110 or Exeter analytical CE-440 elemental analyzer. Mass spectra were recorded using either solution or nanoelectrospray ESI techniques using a ThermoFinnigan LCQ DECA XP Plus (quadrupole ion trap) with the following conditions: solvent THF; flow rate 5 μ L min⁻¹; spray voltage 5 kV; capillary temperature 100 °C; capillary voltage 20 V.

Synthesis of 1–5. To 0.125 g of μ^2 -((η^6 -C₆H₆)RuCl₂)₂ in a 50 mL round-bottom flask was added 10 mL of CH2Cl2, forming an orange suspension. While stirring, a solution of 2 equiv of β diketiminato-lithium complex, Li((2,6-CH₃)₂C₆H₃)NC(CH₃))₂, in 2 mL of CH₂Cl₂ was added slowly dropwise, and instantly the solution changed to a purple color then slowly after 10 to 20 min to orange-brown. The reaction flask was capped and the mixture was stirred for 14 h. Afterward the suspension was filtered through a frit containing at least 1 cm pad of Celite. The Celite was washed with CH₂Cl₂ until the filtrate was colorless. The volume of the filtrate was reduced, under vacuum, to 2 mL, and 25 mL of *n*-pentane was added to precipitate a purple-colored microcrystalline powder. The solution was decanted from the solid and dried under vacuum for several hours. The purple solid was dissolved with 25 mL of dry CH₂Cl₂ and transferred to a flask containing the sodium salt of the desired anion, i.e., NaO₃SCF₃(1), NaBF₄(2), NaPF₆(3), NaBPh₄(4), or NaBArF (5). After stirring for 1 h, the mixture was filtered through a 1 cm pad of Celite. The resulting orange-brown solution was reduced to a volume of approximately 2 mL, and n-pentane was added to precipitate a brown solid. The solid was washed several times with *n*-pentane and dried under vacuum overnight.

Complex 1. Yield: 0.278 g (88% based on $((\eta^{\circ}-C_{6}H_{6})RuCl_{2})_{2})$. Anal. Found [Calcd] C: 53.07 [52.98], H: 4.93 [4.78], N: 4.42 [4.30]. ¹H NMR (25 °C, 400.1 MHz, CD₂Cl₂): δ (ppm) 2.140 (s, 12H, Ar o-CH₃), 2.153 (s, 6H, α -CH₃), 5.165 (s, 6H, η^{6} -C₆H₆), 6.634 (s, 1H, β -CH), 7.362 (m, ${}^{3}J_{HH} = 1.86$ Hz, 2H, Ar *p*-CH), 7.422 (m, ${}^{3}J_{HH} = 1.86$ Hz, 4H, *m*-CH). 13 C NMR (25 °C, 100.1 MHz, CD₂Cl₂): δ (ppm) 19.08 (s, Ar *o*-CH₃), 23.28 (s, α-CH₃), 84.13 (s, η^{6} -C₆H₆), 105.57 (s, β-CH), 121.43 (q, ${}^{1}J_{CF}$ = 322 Hz, SO₃CF₃⁻), 128.03 (s, Ar *p*-CH), 129.56 (s, Ar *m*-CH), 129.98 (s, Ar *o*-C), 158.69 (s, Ar *i*-C), 163.92 (s, α -CCH₃). ¹⁹F NMR (25 °C, 188.1 MHz, CD₂Cl₂): δ (pp) –79.2 (s, ¹J_{FC} = 322 Hz, $CF_3SO_3^{-}$). UV-vis (25 °C, CH_2Cl_2), λ (nm) [ε (L mol⁻¹ cm⁻¹)]: 434 [5455], 291 [11 981]. ESI-MS (25 °C, CH₂Cl₂) (m/z): positive mode 485.200 [parent M⁺, 100%, calcd 485.153], negative mode 149.200 [parent M⁻, 100%, calcd 148.952]. FT-IR (25 °C, solid): ν (cm⁻¹) 1592.78(w); 1553.50(w); 1518.35(w); 1507.88(w); 1468.96(w); 1436.95(w); 1340.53(w); 1265.82(vs, S-O);¹³ 1221.21(m); 1178.10(w); 1147.33(s, C-F);¹³ 1087.72(w); 1097.08-(w, C-F);¹³ 1028.57(s); 981.17(w); 963.67(w); 867.34(w); 846.72-(m); 776.00(m); 752.27(w); 711.83(w); 667.72(w).

Complex 2. Yield: 0.296 g (89% based on $((\eta^6-C_6H_6)RuCl_2)_2)$. Anal. Found [Calcd] C: 56.62 [56.75], H: 5.63 [5.47], N: 4.74 [4.90]. ¹H NMR (25 °C, 400.1 MHz, CD₂Cl₂): δ (ppm) 2.142 (s, 12H, Ar *o*-CH₃), 2.151 (s, 6H, α -CH₃), 5.162 (s, 6H, η^6 -C₆H₆), 6.627 (s, 1H, β -CH), 7.323 (m, ³J_{HH} = 1.83 Hz, 2H, Ar *p*-CH), 7.384 (m, ³J_{HH} = 1.83 Hz, 4H, *m*-CH). ¹³C NMR (25 °C,

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100.1 MHz, CD₂Cl₂): δ (ppm) 19.06 (s, Ar *o*-CH₃), 23.27 (s, α -CH₃), 84.11 (s, η^6 -C₆H₆ CH), 105.52 (s, β -CH), 128.00 (s, Ar *p*-CH), 129.55 (s, Ar *m*-CH), 130.01 (s, Ar *o*-C), 158.67 (s, Ar *i*-C), 163.89 (s, α -CCH₃). ¹⁹F NMR (25 °C, 188.2 MHz, CD₂Cl₂): δ (ppm) –153.42 (s, BF₄). ¹¹B NMR (25 °C, 128.4 MHz, CD₂-Cl₂): δ (ppm) –1.62 (s, BF₄). ESI-MS (25 °C, CH₂Cl₂) (*m*/*z*): positive mode 485.200 [parent M⁺, 100%, calcd 485.153], negative mode 87.267 [parent M⁻, 100%, calcd 87.003]. FT-IR (25 °C, solid): ν (cm⁻¹): 3055.16(w), 2983.25(w), 1643.49(w), 1579.13(w), 1553.60(w), 1508.22(w), 1478.69(w), 1468.40(w), 1438.18(w), 1426.37(w), 1377.60(w), 1342.56(w), 1298.53(w), 1262.79(w), 1239.94(w), 1203.58(w), 1178.67(w), 1147.57(w), 1132.70(w), 1096.27(w), 1065.33(w, B-F),³⁴ 1031.83(w), 999.36(w), 982.86(w), 912.44(w), 866.88(w), 839.21(w), 771.25-(w, B-F),³⁴ 748.26(w), 732.29(s), 703.19(s).

Complex 3. Yield: 0.290 g (92% based on ((η^6 -C₆H₆)RuCl₂)₂). Anal. Found [Calcd] C: 53.07 [51.51], H: 4.92 [4.96], N: 4.40 [4.45]. ¹H NMR (25 °C, 400.1 MHz, CD₂Cl₂): δ (ppm) 2.176 (s, 12H, Ar o-CH₃), 2.176 (s, 6H, α -CH₃), 5.178 (s, 6H, η^6 -C₆H₆), 6.668 (s, 1H, β -CH), 7.363 (m, ³J_{HH} = 1.83 Hz, 2H, Ar *p*-CH), 7.424 (m, ³J_{HH} = 1.83 Hz, 4H, *m*-CH). ¹³C NMR (25 °C, 100.1 MHz, CD₂Cl₂): δ (ppm) 19.17 (s, Ar *o*-CH₃), 23.23 (s, α -CH₃), 84.43 (s, η^6 -C₆H₆), 105.71 (s, β -CH), 127.69 (s, Ar *p*-CH), 129.34 (s, Ar *m*-CH), 130.14 (s, Ar *o*-C), 158.72 (s, Ar *i*-C), 164.02 (s, α -CCH₃). ¹⁹F NMR (25 °C, 188.2 MHz, CD₂Cl₂): δ (ppm) -73.62 (d, ¹J_{PF} = 711 Hz, PF₆). ³¹P NMR (25 °C, 161.9 MHz, CD₂Cl₂): δ (ppm) -144.4 (sept, ¹J_{PF} = 711 Hz, PF₆). ESI-MS (25 °C, CH₂Cl₂) (*m*/*z*): positive mode 485.200 [parent M⁺, 100%, calcd 144.964]. FT-IR (25 °C, solid): ν (cm⁻¹): 3095(w); 2921(w); 1554(m); 1516(w); 1506(w); 1469(m); 1437(m); 1382(m); 1351(m); 1299(m); 1265(w); 1265(w); 1241(w); 1205(w); 1178(w); 1097(w); 1088(w); 1025(w); 983(w); 831(s, P-F);³⁴ 769(s, P-F);³⁴ 740(m); 712(m); 667(w).

Complex 4. Yield: 0.290 g (83% based on $((\eta^6-C_6H_6)RuCl_2)_2)$. Anal. Found [Calcd] C: 76.09 [76.20], H: 6.46 [6.39], N: 3.71 [3.48]. ¹H NMR (25 °C, 400.1 MHz, CD₂Cl₂): δ (ppm) 2.100 (s, 12H, Ar *o*-CH₃), 2.131 (s, 6H, α -CH₃), 4.906 (s, 6H, η^6 -C₆H₆), 6.600 (s, 1H, β -CH), 6.872 (m, ³J_{HH} = 6.84 Hz, 4H, BPh₄ p-CH), 6.999 (m, ${}^{3}J_{HH} = 6.84$ Hz, 8H, BPh₄*m*-CH), 7.285 (br s, 8H, BPh₄*o*-CH), 7.369 (m, ${}^{3}J_{HH} = 1.81$ Hz, 2H, Ar *p*-CH), 7.366 (m, ${}^{3}J_{HH} = 1.81$ Hz, 4H, *m*-CH). 13 C NMR (25 °C, 1000 C) (2000 C) 100.1 MHz, CD₂Cl₂): δ (ppm) 19.12 (s, Ar *o*-CH₃), 23.29 (s, α -CH₃), 83.85 (s, η^{6} -C₆H₆), 105.64 (s, β -CH), 122.33 (s, BPh₄ *p*-CH), 126.17 (s, ³J_{BC} = 2.8 Hz, BPh₄ *m*-CH), 128.15 (s, Ar p-CH), 129.61 (s, Ar m-CH), 129.78 (s, Ar o-C), 136.46 (s, $J_{BC} = 1.4$ Hz, BPh₄, o-CH), 129.70 (S, AI i-C), 150.40 (S, $J_{BC} = 1.4$ Hz, BPh₄, o-CH), 158.59 (s, Ar i-C), 163.96 (s, α -CH₃), 164.50 (m, ${}^{1}J_{BC} = 49.9$ Hz, BPh₄i-C). ${}^{11}B$ NMR (25 °C, 128.4 MHz, CD₂Cl₂): δ (ppm) -6.62 (s, ${}^{1}J_{BC} = 49.9$ Hz, BPh₄⁻). ESI-MS (25 °C, CH₂Cl₂) (m/z): positive mode 485.467 [parent M⁺, 100%, calcd 485.153], negative mode 319.533 [parent M⁻, 100%, calcd 319.166]. FT-IR (25 °C, solid): 3055.16(m), 303.174(w), 2983.25(w), 2996.03(w), 2916.66(w), 1642.40(w), 1579.13(w), 1553.60(w), 1477.59(w), 1468.40(w), 1435.94(w), 1426.37(m), 1377.60(w), 1342.56(m), 1298.53(w), 1262.79(w), 1239.94(w), 1178.67(w), 1147.57(w), 1132.02(w), 1096.27(w), 1065.33(w), 1031.83(w), 982.86(w), 913.16(w), 866.88(w), 839.21(m), 771.25(m), 748.26(m), 732.29(s), 703.19(s).

Complex 5. Yield: 0.579 g (86% based on $((\eta^6-C_6H_6)RuCl_2)_2)$. Anal. Found [Calcd] C: 51.46 [52.58], H: 3.02 [3.22], N: 1.78 [2.08], *note*: residual traces of CH₂Cl₂ could not be removed under vacuum or washing with *n*-pentane. ¹H NMR (25 °C, 400.1 MHz, CD₂Cl₂): δ (ppm) 2.108 (s, 12H, Ar *o*-CH₃), 2.147 (s, 6H, α -CH₃), 5.080 (s, 6H, η^6 -C₆H₆), 6.651 (s, 1H, β -CH), 7.317 (m, ³J_{HH} = 1.73 Hz, 3H, Ar *p*-CH), 7.366 (m, ³J_{HH} = 1.73 Hz, 6H, Ar *m*-CH), 7.556 (br s, 4H, BArF *p*-CH), 7.718 (br s, 8H, BArF *o*-C*H*). ¹³C NMR (25 C, 100.1 MHz, CD₂Cl₂): δ (ppm) 19.02 (s, Ar *o*-CH₃), 23.28 (s, α -CH₃), 83.96 (s, η^6 -C₆H₆), 105.94 (s, β -CH), 118.04 (s, BArF, *p*-CH), 125.14 (m, ¹J_{CF} = 271 Hz, BArF *m*-CCF₃), 129.35 (q, ²J_{CF} = 79 Hz, BArF *m*-CCF₃), 128.28 (s, Ar *p*-CH), 129.65 (s, Ar *m*-CH), 129.74 (s, Ar *o*-C), 135.35 (s, BArF, *o*-CH), 158.69 (s, Ar *i*-C), 162.30 (m, ¹J_{BC} = 49.5 Hz, BArF *i*-C), 164.24 (s, α -CCH₃). ¹⁹F NMR (25 °C, 188.2 MHz, CD₂Cl₂): δ (ppm) –62.95 (s, ¹J_{FC} = 271 Hz, BArF *m*-CF₃). ¹¹B NMR (25 °C, 128.4 MHz, CD₂Cl₂): δ (ppm) –6.61 (s, ¹J_{BC} = 49.5 Hz, *B*(ArF)₄). ESI-MS (25 °C, CH₂Cl₂) (*m*/*z*): positive mode 485.317 [parent M⁺, 100%, calcd 485.153], negative mode 863.467 [parent M⁻, 100% calcd 863.068]. FT-IR (25 °C, solid): 1610.25(w), 1555.14(w), 1467.84(w), 1439.69(w), 1352.78(m), 1338.48(w, sh), 1276.81(s), 1157.84(m, sh), 1116.18(s), 887.09(m), 869.87(w), 838.25(m), 816.19(w), 781.97(w), 772.85(m), 744.12(w), 715.78(m), 710.11(m), 681.82(m), 669.04(m).

Crystallographic Details. Suitable single crystals were removed from the sample vial under a flow of N2 and manipulated in a perfluoropolyalkyl ether oil matrix (F06206K, ABCR Company) in a specially constructed Dewar partially filled with liquid nitrogen. The crystals were mounted to the end of a glass fiber (diameter at least 0.1 mm) attached to a metal pin fixed to a goniometer head, which was placed in the Euler cradle, while maintaining a cold blanket of N2 gas. For all structures, an Oxford-Kuma KM-4 diffractometer setup with a Sapphire CCD area detector was used as the collecting instrument. Both instruments utilize a graphite-monochromated Mo Ka radiation source with $\lambda = 0.71073$ Å. The crystals were kept under a 140 or 100 K gaseous flow of N₂ during the collection procedure. The unit cell and orientation matrix was determined by indexing reflections measured from the entire data set using CrysAlis RED.³⁵ All data sets are composed on collecting reflections using an optimized scanning strategy utilizing the program CrysAlis CCD.³⁶ After data integration with CrysAlis RED³⁵ a multiscan absorption correction based on a semiempirical method was applied using the SCALE3 ABSPACK scaling algorithm contained within the CrysAlis CCD suite.³⁶ Space group determination was performed with the XPREP program.³⁷ A structure solution based on the direct-method algorithm was employed with SHELXS-97.38 Afterward, anisotropic refinement of all non-hydrogen atoms was completed on the basis of a least-squares full-matrix method against F^2 data using SHELXL-97.³⁸ Hydrogen atoms were added through geometrically calculated positions and refined as a riding model whereby the thermal parameter is a scaled value of the connecting atom. In complexes 2 and 5, the counterion (BF_4^-) and BArF⁻) featured positional disorder of the fluorine atoms. The disorder was treated by splitting the affected atoms over two positions and allowing the total occupancy of the disordered groups to freely refine (details described in the CIFs). A small number of reflections in some cases were removed when $\Delta (F_o^2 F_{\rm c}^{2}$)/ σ exceeded 10.0. In the case of 5, the absolute structure was determined (a Flack parameter equal to 0.03(2)) by refinement against the inverted twin matrix. Important data for all structures are given in the Supporting Information, Table S1. Drawings in the paper were produced with the program XP,38 and CIF data formatting was performed using the program CIFTAB³⁸ and enCIFer.³⁹

In Silico Studies. Computational modeling of the cations and anion described in this paper were performed using the Gaussian

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03 program⁴⁰ on a SGI Altix ICE 8200EX cluster, employing density functional theory with the three-parameter hybrid method developed by Becke (B3LYP).⁴¹ For all nonmetal atoms, the contracted 6-31G(d,p)⁴² basis set was selected, which included diffuse functions. For the ruthenium center, the double- ζ basis set Lanl2dz was used in conjunction with a pseudopotential representing the core set of electrons.⁴³ All structures were geometrically optimized to an energy minimum. The position on the local potential energy surface was confirmed through vibration analysis using second derivatives, where no imaginary frequencies were observed. The electrostatic potential maps, as shown in Figure 3, were generated from the calculated electron density and potential using Gaussview.⁴⁴

Catalytic Evaluation Studies. The experiments were conducted in a custom in-house built multicell steel autoclave reactor. For each cell, a 10 mL volume glass liner was inserted into an autoclave block, along with a Teflon-coated stir bar. A stock solution (4.8 \times 10^{-3} mol $mL^{-1})$ of each catalyst was prepared using dry and degassed tetrahydrofuran. The catalytic reaction mixture consisted of 2.00 mL of stock solution (9.6 \times 10^{-3} mmol) with 1.00 mL of styrene (9.602 mmol) (Acros, stabilized, degassed and dried with molecular sieves) and 0.10 mL of degassed and dried *n*-octane (8.7 \times 10⁻¹ mmol). All preparations and autoclave loading were performed in a N2filled drybox. After sealing the autoclave, the cells were purged with high-purity H₂ for at least three cycles. The autoclave was then heated to 80 °C under 10 bar of H₂. The reactor was pressurized and stirred at 40 bar of H₂, which continued for 1 h at 80 °C. The reaction was quenched by depressurizing and rapid cooling to ambient temperature. The autoclave was opened in air, small aliquots from each cell were taken, and the sample was diluted with toluene. The reaction mixture was analyzed with GC with the following conditions. A Varian CP-3380 gas chromatographic analyzer was used with a CP-Sil 5CB normal phase (low polarity) 25 m \times 0.25 mm column. The reported TON values are averages from three separate runs. Highpressure NMR studies were performed by preparing solutions identical to those used in the autoclave experiments, except for the use of d_8 -THF. The solution was added to a 10 mm mediumpressure sapphire NMR tube equipped with a stainless steel head with lockable gas-inlet valve, under a N2-filled atmosphere. Subsequently, the NMR was pressurized with 100 atm of H₂, causing in all cases an instant color change.

Warning: Sapphire NMR tubes when filled with pressurized gas represent a potential explosion hazard; moreover, hydrogen gas is highly flammable. Protective Plexiglas shields were placed around the samples at times when not residing inside in the NMR magnet. The NMR tube was weighed to ensure gas transfer and to verify that the tube was sealed. The progression of the catalytic reaction

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was monitored by ¹H NMR spectroscopy, and recording of the spectra was initiated when the probehead had reached a temperature of 80 °C, which typically occurred within a period of 5 min.

PGSE NMR Studies. The PGSE measurements were carried out without spinning and in the absence of external airflow. The sample was dissolved in 0.7 mL of d_8 -THF, with a concentration range of 2.0-6.4 mM. The sample temperature was calibrated, before the PGSE measurements, by introducing a thermocouple inside the bore of the magnet. All the PGSE diffusion measurements were performed using the standard stimulated echo pulse sequence on a 400 MHz Bruker Avance spectrometer equipped with a microprocessor-controlled gradient unit and an inverse multinuclear probe with an actively shielded Z-gradient coil. The shape of the gradient pulse was rectangular, its duration δ was 1.75 ms, and its strength varied automatically in the course of the experiments. The calibration of the gradients was carried out via a diffusion measurement of HDO in D₂O, which afforded a slope of 1.976×10^{-3} . The data obtained were used to calculate the D values of the samples, according to the literature.^{22,45–47}

In the ¹H-PGSE experiments, the diffusion delay, Δ , was set to 117.75 and 167.75 ms, respectively. The number of scans was 16 per increment with a recovery delay of 10 to 30 s. Typical experimental times were 2–4 h. For 19 F, Δ was set to 117.75 and 167.75 ms, respectively. Sixteen scans were taken with a recovery delay of 10 to 25 s and a total experimental time of ca. 2-4 h. All the spectra were acquired using 32K points and processed with a line broadening of 1 Hz (¹H) and 2 Hz (¹⁹F). The slopes of the lines, m, were obtained by plotting their decrease in signal intensity vs G^2 using a standard linear regression algorithm. Normally, 15-20 points were used for regression analysis, and all of the data leading to the reported D-values afforded lines whose correlation coefficients were > 0.999. The gradient strength was incremented in 3–4% steps from 3 to 72%. A measurement of 1 H and 19 F T_1 was carried out before each diffusion experiment, and the recovery delay set to 5 times T_1 . We estimate the experimental error in *D*-values at $\pm 2\%$. The hydrodynamic radii, $r_{\rm H}$, were estimated using the Stokes-Einstein equation (c = 6) or by introducing the semiempirical estimation of the c factor, which can be derived from the microfriction theory proposed by Wirtz and co-workers,⁴⁸ in which c is expressed as a function of the solute to solvent ratio of radii.

The ${}^{1}\text{H}-{}^{19}\text{F}$ HOESY NMR measurements were acquired using the standard four-pulse sequence on a 400 MHz Bruker Avance spectrometer equipped with a doubly tuned (${}^{1}\text{H}$, ${}^{19}\text{F}$) TXI probe. A mixing time of 800 ms was used. The number of scans was 8-16, and the number of increments in the F1 dimension is 512. The delay between the increments was set to 2.5-4.5 s. The concentrations of the samples were 10-14.1 mM.

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Supporting Information Available: A table of single-crystal X-ray diffraction data for complexes 1, 2, and 5 is given, and

additional data are found in the included CIFs. An ORTEP plot of **2** and atomic coordinates for the computational models are also included as well as ESP maps for the BF_4^- and PF_6^- anions. This material is available free of charge via the Internet at http:// pubs.acs.org.