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Asymmetric Electrophilic Fluorination Using an Anionic Chiral Phase-Transfer Catalyst

Vivek Rauniyar,* Aaron D. Lackner,* Gregory L. Hamilton, F. Dean Toste†

The discovery of distinct modes of asymmetric catalysis has the potential to rapidly advance chemists' ability to build enantioenriched molecules. As an example, the use of chiral cation salts as phase-transfer catalysts for anionic reagents has enabled a vast set of enantioselective transformations. Here, we present evidence that a largely overlooked analogous mechanism wherein a chiral anionic catalyst brings a cationic species into solution is itself a powerful method. The concept is applied to the enantioselective fluorocyclization of olefins with a cationic fluorinating agent and a chiral phosphate catalyst. The reactions proceed in high yield and stereoselectivity, especially considering the scarcity of alternative approaches. This technology can in principle be applied to the large portion of reaction space that uses positively charged reagents and reaction intermediates.

In the years since Knowles and co-workers demonstrated that synthetic catalysts could approach the levels of absolute stereocontrol achieved by enzymes (*1*), chemists have made remarkable progress on the synthesis of optically active molecules using catalytic chiral inputs. Despite the advances, the subset of reactions that can be performed with enantioselective methods still represents only a fraction of the pool of known organic transformations. One reason for this discrepancy is that, although new ligand designs and catalyst variants have been reported at a striking rate, a slower pace has been set for devising alternative underlying approaches to inducing asymmetry.

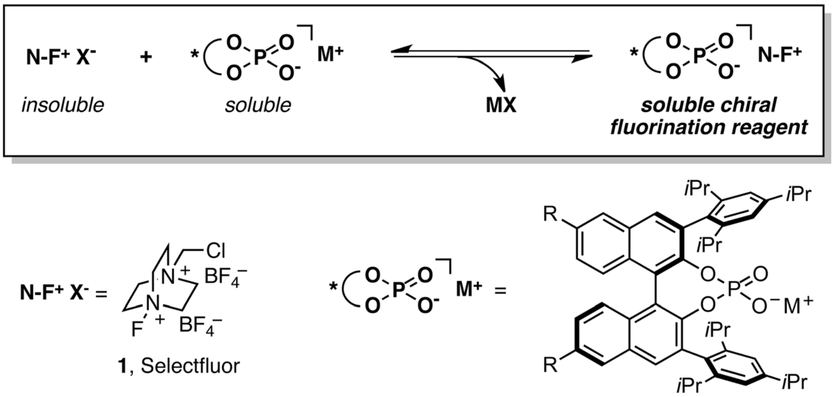
Among the distinct strategies that complement the traditional metal-chiral ligand methods, asymmetric phase-transfer catalysis has undoubtedly been one of the most successful. In this mode of catalysis, a lipophilic chiral cation salt mediates the reaction between a substrate in organic solution and an anionic reagent in a separate aqueous or solid phase. Ion pairing with the cation solubilizes the anionic reagent or reaction intermediate in the bulk organic phase, while also providing a chiral environment for the desired reaction with the substrate. Application of this simple logic has yielded a diverse array of operationally simple, highly enantioselective protocols (*2*–*5*).

However, almost no consideration has been given to an analogous charge-inverted strategy in which the salt of a chiral anion brings an insoluble cationic promoter into solution. Positively charged reagents and reaction intermediates are certainly quite common, so in principle this neglected other half of phase-transfer catalysis could be quite useful. Nelson and colleagues appreciated this possibility when they titled a 2003 publication "Towards phase-transfer catalysts with a chiral anion" (*6*). Although this report nicely demonstrated some asymmetric induction by a chiral borate anion in a ring opening of prochiral aziridinium intermediates, no catalysis (phase-transfer or otherwise) was investigated. The challenge of rendering this reaction catalytic and highly enantioselective seemed to us to be an excellent testing ground for the possibility of chiral anion phase-transfer catalysis. We realized this goal using a chiral phosphate anion catalyst and Ag^+ (in the form of silver carbonate) as the insoluble stoichiometric promoter (*7*). Essential to our success was the previous discovery that binaphthol-derived phosphates could convey asymmetry during reactions of cationic species (*8*–*10*) independent of their ability to act as chiral Brønsted acids and hydrogen-bond donors (*11*).

Although this previous report hinted at the promise of the underlying concept, we hoped to find an area of chemistry with broader utility where charge-inverted phase-transfer catalysis could be uniquely advantageous. In this context, procedures for the construction of carbon-fluorine bonds are highly prized because of the scarcity of methods and the value of the products across applied chemistry (*12*–*15*). Electrophilic reagents have proven to be one of the most applicable vehicles for introducing fluorine into organic molecules (*16*–*21*). Unfortunately, the mechanism of these reactions offers little room for the addition of a chiral catalyst. Many of the most effective published enantioselective fluorination protocols require formation of a nucleophilic chiral enolate equivalent (*22*–*30*), including one report of formation through chiral cationic phase-transfer catalysis (*26*). On the other hand, the catalytic generation of a chiral electrophile has proven quite challenging; usually a stoichiometric amount of chiral promoter is necessary to suppress the racemic background reaction (*31*–*34*). With the current limitations in mind, we envisioned a chiral anion phase-transfer approach to electrophilic fluorination through the use of an insoluble cationic electrophilic fluorination reagent in conjunction with a chiral phosphate catalyst.

Specifically, we targeted Selectfluor (**1**, Fig. 1) as a versatile cationic fluorinating agent that would normally be insoluble in nonpolar media. We hypothesized that lipophilic, bulky chiral phosphate anions such as **2** (Fig. 1) could exchange with one or both of the tetrafluoroborate anions associated with Selectfluor to bring the reagent into solution. The resulting chiral ion pair could then mediate an asymmetric fluorination of an organic substrate in solution. Given its insolubility, no appreciable background reaction between Selectfluor and substrate would be anticipated.

To properly test our idea, it also seemed logical to investigate a previously unexplored reaction that would not be amenable to chiral nucleophile–based methods. We noted that fluorocyclizations, wherein a pendant nucleophile attacks a π-bond activated by an electrophilic fluorine source, are much less common than the analogous reactions of heavier halogens (*35*), and enantioselective var-



1, Selectfluor

2a, R = C_8H_{17}, $M^+ = Na^+$
2b, R = C_8H_{17}, $M^+ = H^+$
2c, R = H, $M^+ = H^+$

Fig. 1. Catalytic formation of a chiral fluorination reagent via chiral anion–mediated phase transfer in nonpolar solvents.

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iants are almost unknown (*34*). Based on precedent showing that enol ethers react efficiently with Selectfluor, we first focused on dihydropyran substrates tethered to various nucleophilic traps. Initial experimentation revealed that benzamide nucleophiles perform particularly well under the designed catalytic conditions (Fig. 2). These substrates display an interesting mode of reactivity wherein, upon fluorination of the enol ether, the amide carbonyl attacks the nascent oxocarbenium ion to form a spiro-fused oxazoline.

After brief optimization of the reaction parameters, the product from the model substrate **3a** could be obtained in 86% yield with exceptional enantio- and diastereoselectivity (92% ee, >20:1 diasteromer ratio) (Fig. 2). The inclusion of Proton Sponge [1,8-bis(dimethylamino)naphthalene] as a base served a dual purpose of generating the anionic phosphate catalyst in situ from its conjugate acid **2b** as well as neutralizing the equivalent of acid generated during the reaction. Consistent with our design plan, the hydrophobic alkyl chains attached to the backbone of the catalyst proved beneficial: Use of the unsubstituted catalyst (**2c**) reduced the enantioselectivity to 87%. Additionally, products with a variety of substituents on the benzamide ring—including halides, nitro, and alkyl groups—could be obtained in very good yields with enantioselectivities above 95% (products **4b** to **4f**). Substitutions at the 2- or 3-positions of the aryl ring gave rise to slightly more variability in terms of yield and stereoselectivity but were generally well tolerated (**4g** to **4i**). The absolute stereochemistry of product **4c** as shown in Fig. 2 was determined by single-crystal x-ray diffraction (see the supporting online material for crystallographic data), and all other products were assigned by analogy.

We were naturally eager to extend the methodology to less electron-rich alkenes. However, this represented quite a challenge, as previously reported catalytic asymmetric electrophilic fluorination methods have largely relied on enol, enolate, or other strongly activated nucleophiles. Thus, it was encouraging to find that our technology enabled the efficient fluorocyclization of dihydronaphthalene and chromene substrates (Fig. 3A). Excellent enantioselectivities were obtained even at room temperature (92 to 96% ee), although in this case a slightly higher catalyst loading gave optimal results. Even more remarkably, an unactivated olefin with only alkyl substituents also delivered a good yield of fluorinated product, albeit with modestly reduced enantioselectivity (Fig. 3B). Fluorination of these less-reactive substrates was accomplished most effectively using inorganic bases such as sodium carbonate.

An unanticipated benefit of the phase-transfer protocol is an improved tolerance toward sensitive functionality. When treated with Selectfluor under homogeneous conditions, benzothiophene substrates **10a** and **10b** were converted to a complex mixture of products with only trace conversion to desired product (Fig. 3C). However, when the chiral anion–mediated phase-transfer

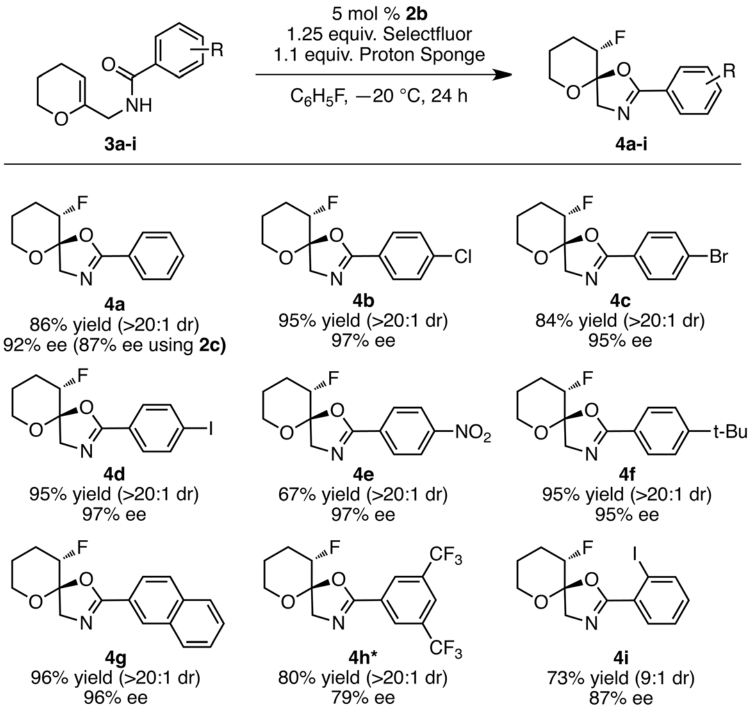
5 mol % **2b**
1.25 equiv. Selectfluor
1.1 equiv. Proton Sponge
C_6H_5F, −20 °C, 24 h
R
O
NH
F
N
3a-i
4a-i
4a
86% yield (>20:1 dr)
92% ee (87% ee using **2c**)
Cl
4b
95% yield (>20:1 dr)
97% ee
Br
4c
84% yield (>20:1 dr)
95% ee
I
4d
95% yield (>20:1 dr)
97% ee
NO_2
4e
67% yield (>20:1 dr)
97% ee
t-Bu
4f
95% yield (>20:1 dr)
95% ee
4g
96% yield (>20:1 dr)
96% ee
CF_3
CF_3
4h*
80% yield (>20:1 dr)
79% ee
I
4i
73% yield (9:1 dr)
87% ee

Fig. 2. Enantioselective synthesis of fluorinated heterocycles from dihydropyran-derived substrates. *Reaction run at −5°C.

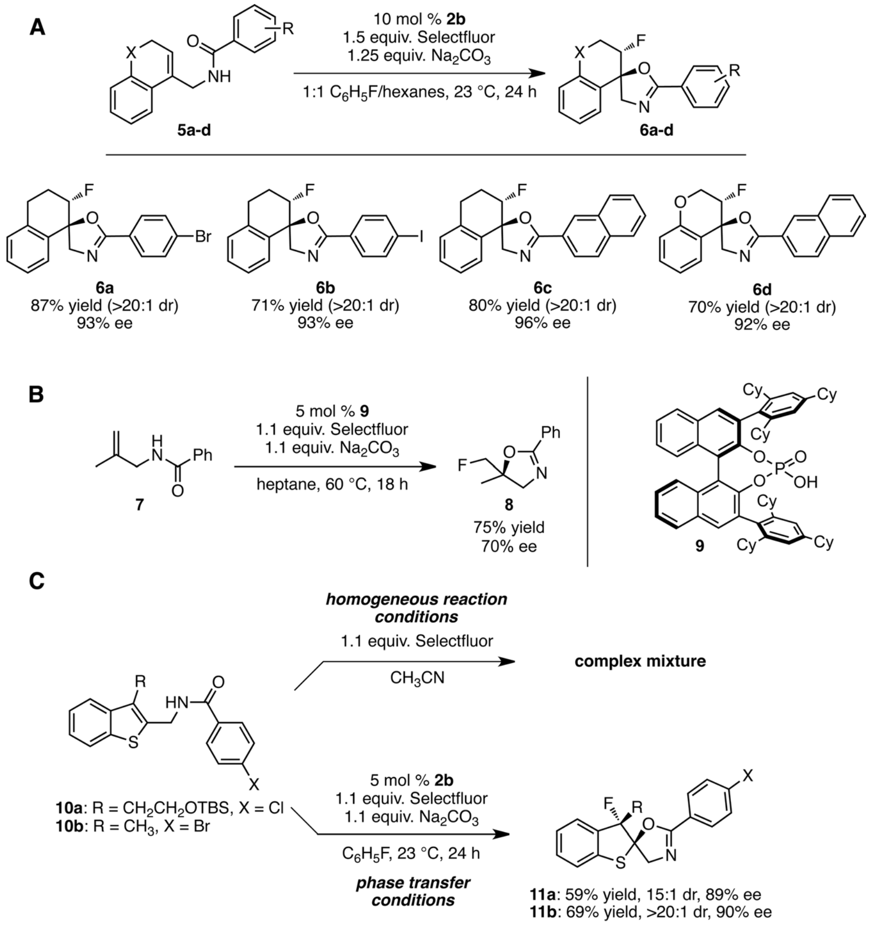
A
10 mol % **2b**
1.5 equiv. Selectfluor
1.25 equiv. Na_2CO_3
1:1 C_6H_5F/hexanes, 23 °C, 24 h
X
R
NH
F
5a-d
6a-d
Br
6a
87% yield (>20:1 dr)
93% ee
I
6b
71% yield (>20:1 dr)
93% ee
6c
80% yield (>20:1 dr)
96% ee
6d
70% yield (>20:1 dr)
92% ee
B
5 mol % **9**
1.1 equiv. Selectfluor
1.1 equiv. Na_2CO_3
heptane, 60 °C, 18 h
Ph
7
8
75% yield
70% ee
Cy
OH
9
C
homogeneous reaction conditions
1.1 equiv. Selectfluor
CH_3CN
complex mixture
R
HN
S
X
10a: R = CH_2CH_2OTBS, X = Cl
10b: R = CH_3, X = Br
5 mol % **2b**
1.1 equiv. Selectfluor
1.1 equiv. Na_2CO_3
C_6H_5F, 23 °C, 24 h
phase transfer conditions
11a: 59% yield, 15:1 dr, 89% ee
11b: 69% yield, >20:1 dr, 90% ee

Fig. 3. (**A**) Fluorocyclization of dihydronaphthalenes and chromenes. (**B**) Successful extension to an unactivated alkene. (**C**) The phase-transfer procedure displays improved chemoselectivity over homogeneous conditions.

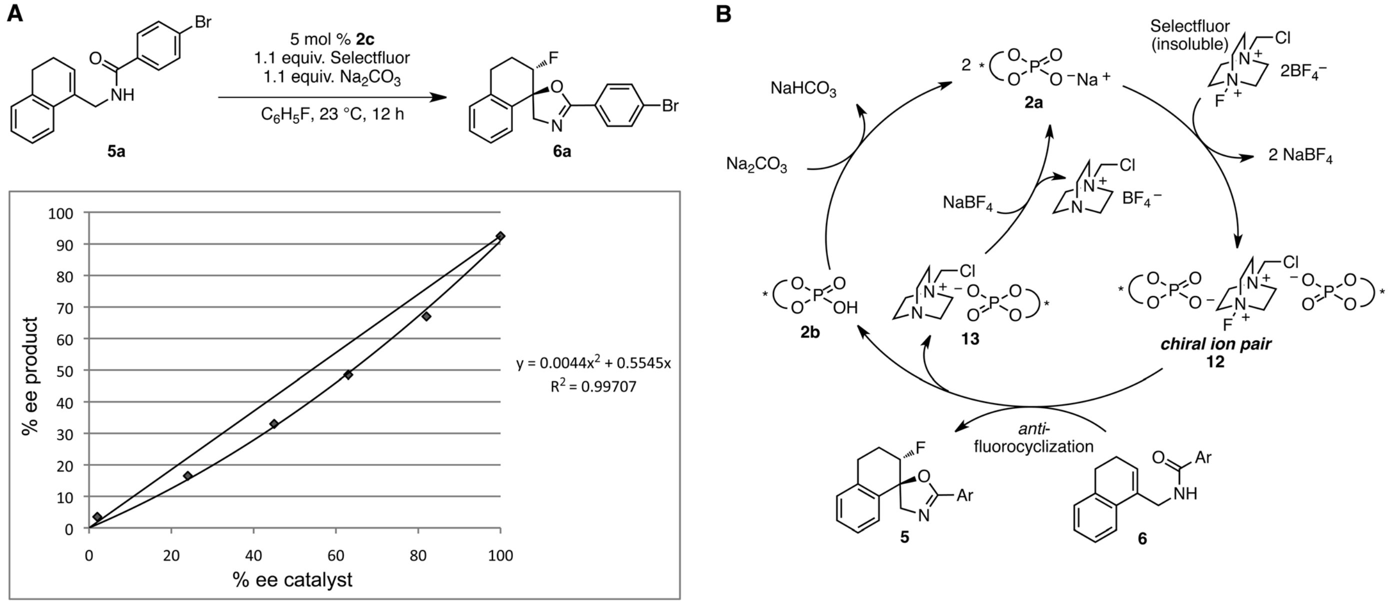

Fig. 4. (**A**) Nonlinear relationship between the optical activity of catalyst and product in the fluorocyclization reaction. (**B**) The proposed catalytic cycle supported by the observed nonlinear effect.

reaction conditions were applied, fluorocyclization products **11a** and **11b** were isolated in good yield and high optical purity. This improved chemoselectivity may be due to a combination of the slow introduction of the fluorinating agent into solution and possibly a reduction in reactivity in nonpolar solvent. This result is in contrast to a recent report from Lectka and co-workers, wherein increased reactivity of Selectfluor was observed through a postulated counterion exchange in acetonitrile (*36*).

In considering the mechanism of the reaction, we were interested in discerning the precise nature of the active fluorinating species: specifically, whether one or both of the tetrafluoroborate counteranions of Selectfluor are exchanged for chiral phosphate anions. The presence of multiple chiral components in a reaction transition state often results in a nonlinear relationship between the enantiopurity of catalyst and product (*37*). Such nonlinear effects thus offer a convenient tool for studying new catalyst formulations. To carry out the study, catalyst **2c** was prepared in six different levels of enantiopurity and used in the reaction of substrate **5a** (Fig. 4A) (see table S1 and accompanying text for further details). A nonlinear effect was observed, supporting a pathway in which both tetrafluoroborate anions are exchanged for chiral phosphates before the reaction with substrate.

We therefore propose the following catalytic mechanism (Fig. 4B): Two equivalents of phosphate **2a** undergo salt metathesis with dicationic Selectfluor to generate chiral ion pair **12**. Now soluble in the nonpolar reaction solvent, **12** is available to mediate the fluorocyclization of alkene substrate **5**. Upon reaction, one equivalent of phosphoric acid **2b** is generated along with one equivalent of the defluorinated monocationic ion pair **13**. The anionic phosphate **2a** can then be regenerated by deprotonation and ion exchange, respectively.

Like its chiral cation cousin, the anion-based phase-transfer procedure is appealing because it avoids the use of transition metals and the need to rigorously exclude air and moisture. More important, it offers a mechanism for robust catalyst turnover and suppression of the racemic background reaction. This makes it particularly advantageous for transformations like halocyclizations, where nucleophilic catalysis and other existing methods have often suffered from insufficient rate acceleration over the background reactivity.

The highly enantioselective fluorocyclizations demonstrated here exemplify the potential of the strategy. The method generates heterocyclic products with two stereogenic centers, including a carbon-fluorine stereocenter that would be very difficult to construct using alternative approaches. Furthermore, the reactivity of the present system allows less electron-rich olefins to be fluorinated relative to previous reports. The enhanced reactivity fortunately does not trade off with the stereoselectivity, which compares favorably with other chiral electrophile–based fluorination methods. Finally, the chiral anion phase-transfer catalysis scheme can be superimposed on any number of transformations involving cationic reagents or reaction intermediates. Its successful application to electrophilic asymmetric fluorination, which very few catalyst systems have achieved with consistently high enantioselectivities, suggests that it may find utility in other areas of chemistry as well.

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Supporting Online Material

www.sciencemag.org/cgi/content/full/334/6063/1681/DC1
Materials and Methods
SOM Text
Tables S1 to S6
References (*38*–*42*)

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Angular Momentum Conservation in Dipolar Energy Transfer

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Conservation of angular momentum is a familiar tenet in science but has seldom been invoked to understand (or predict) chemical processes. We have developed a general formalism based on Wigner's original ideas concerning angular momentum conservation to interpret the photo-induced reactivity of two molecular donor-acceptor assemblies with physical properties synthetically tailored to facilitate intramolecular energy transfer. Steady-state and time-resolved spectroscopic data establishing excited-state energy transfer from a rhenium(I)-based charge-transfer state to a chromium(III) acceptor can be fully accounted for by Förster theory, whereas the corresponding cobalt(III) adduct does not undergo an analogous reaction despite having a larger cross-section for dipolar coupling. Because this pronounced difference in reactivity is easily explained within the context of the angular momentum conservation model, this relatively simple construct may provide a means for systematizing a broad range of chemical reactions.

Conservation of angular momentum appears to be a fundamental property of nature (*1*). It is widely manifest in settings as varied as astrophysics, in which the idea of coupled momenta can be used to infer the presence of satellites, and figure skating, where skaters spin faster and faster as they draw their arms in. In chemistry, the principle figures prominently in the interpretation of optical spectra. For example, conservation of spin angular momentum (*2*) forms the basis of the so-called spin selection rule whereby radiative transitions between two states of differing spin multiplicity are forbidden (*3*). A familiar manifestation of this phenomenon is the (relatively) long lifetime of an electronic excited state with spin angular momentum different from that of the ground state. This condition leads to the observation of phosphorescence and has recently found application in the development of organic light-emitting diodes (OLEDs) (*4*) as well as the creation of charge-separated excited states that form the conceptual underpinning of many current approaches to solar energy conversion (*5*).

In 1927, Wigner introduced the notion of spin conservation in chemical reactions (*6*) whereby a process would be designated "spin-allowed" if the spin angular momentum space spanned by the reactants intersects the spin angular momentum space spanned by the products. Although not explicitly stated in Wigner's original presentation, the relative energies of the spin-coupled reactant-product states must also be considered in order to define the thermodynamic viability of the reaction in question. A straightforward way to illustrate this idea is to envision a generic energy transfer reaction between an electronically excited donor species (D*) and an energy acceptor (A):

$$\mathrm{D} + \mathrm{A} \xrightarrow{h\nu} \mathrm{D}^* + \mathrm{A} \xrightarrow[\text{energy transfer}]{} \mathrm{D} + \mathrm{A}^* \qquad (1)$$

Focusing on the energy transfer step, the total spin angular momenta spanned by the coupled reactants ($\mathbf{S}_\mathrm{T}^\mathrm{R}$) and products ($\mathbf{S}_\mathrm{T}^\mathrm{P}$) can be described according to

$$|\mathbf{S}_\mathrm{T}^\mathrm{R}| = \mathbf{S}_{\mathrm{D}*} + \mathbf{S}_\mathrm{A} = |S_{\mathrm{D}*} + S_\mathrm{A}|, |S_{\mathrm{D}*} + S_\mathrm{A} - 1|, ..., |S_{\mathrm{D}*} - S_\mathrm{A}| \qquad (2)$$

$$|\mathbf{S}_\mathrm{T}^\mathrm{P}| = \mathbf{S}_\mathrm{D} + \mathbf{S}_{\mathrm{A}*} = |S_\mathrm{D} + S_{\mathrm{A}*}|, |S_\mathrm{D} + S_{\mathrm{A}*} - 1|, ..., |S_\mathrm{D} - S_{\mathrm{A}*}| \qquad (3)$$

where $|S_\mathrm{D}|$, $|S_{\mathrm{D}*}|$, $|S_\mathrm{A}|$, and $|S_{\mathrm{A}*}|$ represent the magnitudes of the spin angular momenta of the ground and excited states of the donor and acceptor, respectively. This formalism is identical to the vector coupling of spin angular momenta used to describe magnetic exchange interactions among weakly coupled paramagnetic species (*7*). In the present context, a spin-allowed reaction is possible if (i) there exists a value of S common to both the reactant and product manifolds (i.e., $\Delta S = 0$ for the reaction), and (ii) the energy of that common state is lower in the product manifold ($\Delta G < 0$). This concept has been invoked explicitly for the interpretation of collisional fragmentation reactions in the gas phase (*8*–*10*) and more implicitly in the context of spin effects in

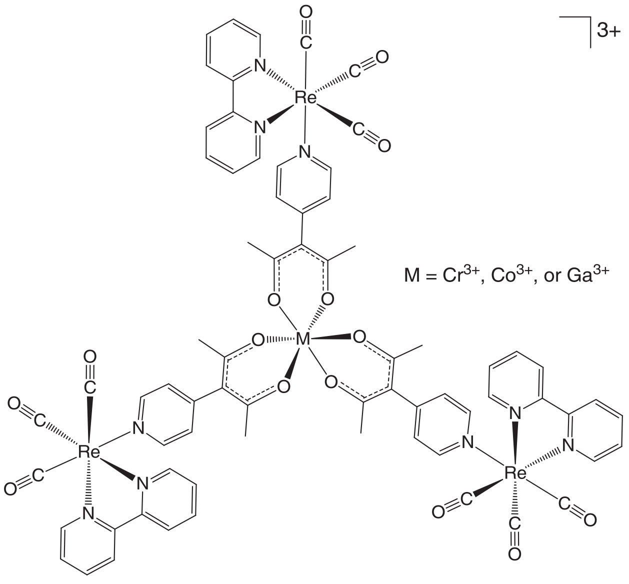

Fig. 1. Molecular structure of the cation of [M(pyacac)$_3${Re(bpy)(CO)$_3$}$_3$](OTf)$_3$ prepared for this study. **1**, M = Cr$^{\mathrm{III}}$; **2**, M = Co$^{\mathrm{III}}$; **3**, M = Ga$^{\mathrm{III}}$.

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