

Fluorine Chemistry

Cobalt-Catalyzed Wagner–Meerwein Rearrangements with Concomitant Nucleophilic Hydrofluorination

Reece H. Hoogesteger, Nicola Murdoch, David B. Cordes, and Craig P. Johnston*

Abstract: We report a cobalt-catalyzed Wagner–Meerwein rearrangement of *gem*-disubstituted allylarenes that generates fluoroalkane products with isolated yields up to 84%. Modification of the counteranion of the *N*-fluoropyridinium oxidant suggests the substrates undergo nucleophilic fluorination during the reaction. Subjecting the substrates to other known metal-mediated hydrofluorination procedures did not lead to observable 1,2-aryl migration. Thus, indicating the unique ability of these cobalt-catalyzed conditions to generate a sufficiently reactive electrophilic intermediate capable of promoting this Wagner–Meerwein rearrangement.

Introduction

Carbocations are synthetically useful reactive intermediates as they can enable structural modifications of a molecule's carbon framework.^[1] For example, the generation of a carbocation that triggers the [1,2]-shift of an adjacent C–H or C–C bond to create a more stable carbocation is known as the Wagner–Meerwein rearrangement (Figure 1A).^[2] The formation of these positively-charged reactive intermediates can be implemented from a variety of starting materials, but often involves harsh reagents.^[3] Moreover, the synthetic utility of the Wagner–Meerwein rearrangement is often hampered by the presence of competing migration pathways.^[2] Equally, rendering these processes stereoselective is also challenging due to the low energetic barriers associated with carbocation rearrangement steps,^[4] although reactions that generate oxocarbenium or iminium ions have successfully led to the development of catalytic enantioselective pinacol,^[5] semipinacol,^[6] α -ketol,^[7] and α -iminol rearrangements.^[8] Exerting control over bond migrations would be synthetically powerful as the resulting changes to the carbon skeleton can provide rapid and selective access to more complex molecules.^[9]

[*] R. H. Hoogesteger, N. Murdoch, Dr. D. B. Cordes, Dr. C. P. Johnston
EaStCHEM, School of Chemistry, University of St Andrews
St Andrews, Fife, KY16 9ST (UK)
E-mail: cpj3@st-andrews.ac.uk

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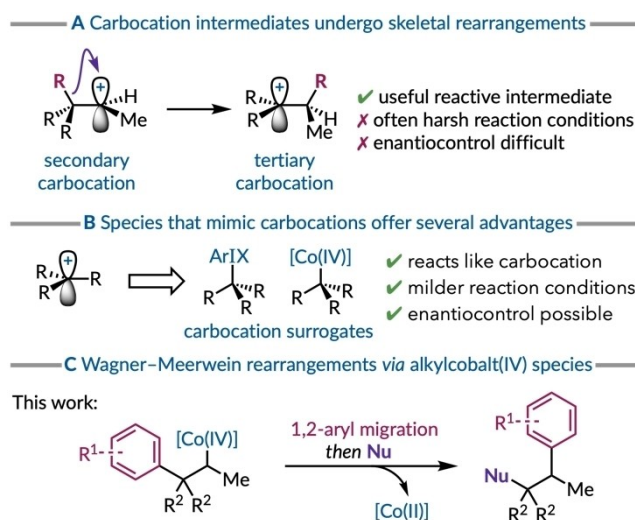


Figure 1. (a) The rearrangement of carbocations. (b) Intermediates that emulate carbocation behavior. (c) Co(IV) induced 1,2-aryl migration.

To overcome these challenges the application of carbocation surrogates that mimic the electrophilic reactivity of these intermediates has proven fruitful (Figure 1B). For example, arylidonium(III) ions have been described as hypernucleofuges due to their extraordinary leaving group aptitude.^[10] These species can be readily introduced into olefin-bearing substrates using hypervalent iodine reagents. Their ability to mimic carbocation reactivity has been demonstrated in several different reactions involving structural rearrangements and anchimeric assistance.^[11] The prominent electrophilicity of these intermediates has been illustrated by their ability to generate phenonium ions even with electron-poor aryl rings.^[12] Subsequent advances have shown that phenonium ions can also be created under catalytic conditions whereby iodoarenes are oxidised in situ.^[13–18] This approach presents further benefits as these catalytic processes can be rendered enantioselective as the arylidonium(III) entity is covalently bound to the substrate. Thus, it can function as a stereodefined carbocation surrogate as shown in a catalytic enantioselective Wagner–Meerwein rearrangement of β -substituted styrenes.^[19]

More recently, alkylcobalt(IV) intermediates have also been shown to demonstrate similarly high levels of electrophilicity. These organocobalt species are formed via hydrogen atom transfer from a metal hydride to an alkene and an oxidative radical–polar crossover event. Initial studies have focused on the intra- and intermolecular displacement of the cobalt complex with various nucleophilic functional

groups.^[20–31] The ability of alkylcobalt(IV) intermediates to act as carbocation surrogates has been demonstrated by catalyst-controlled product-selective reactions of tertiary allylic alcohol substrates.^[32] The stereodefined character of the carbon bound to the cobalt(IV) complex and the use of chiral non-racemic salen ligands has enabled catalytic enantioselective transformations involving alkylcobalt(IV) species.^[29,31,33,34] Although the electrophilic nature of alkylcobalt(IV) complexes has mostly been demonstrated in the context of nucleophilic displacements its utility as a carbocation surrogate to enable [1,2]-shifts has only been demonstrated in select semipinacol rearrangements.^[32,33] Herein, we show that carbon–cobalt(IV) bonds are sufficiently electrophilic to promote 1,2-aryl migration, likely via a phenonium ion intermediate,^[35] without heteroatom stabilization of the incipient carbocation. Subsequent regioselective ring opening with a nucleophile restores the aromaticity and affords the rearranged product. The reaction conditions are relatively mild and non-acidic offering improved chemoselectivity and functional group tolerance when compared to

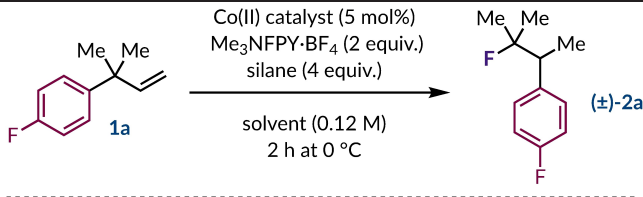
alternative methods for generating free carbocations from olefins.

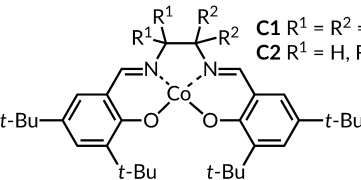
Results and Discussion

Determining the Optimal Reaction Conditions

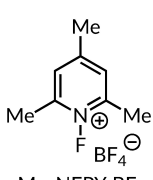
Alkene **1a** was chosen as the model substrate for the optimization phase as it enables straightforward quantification of the reaction components by ¹⁹F NMR spectroscopy (see Supporting Information for details). The preliminary conditions (Table 1, entry 1) of Co^{II} catalyst **C1** (5 mol%), *N*-fluoro-2,4,6-trimethylpyridinium tetrafluoroborate (Me₃NFPY·BF₄, 2 equiv.), 1,1,3,3-tetramethyldisiloxane (TMDSO, 4 equiv.) in PhCF₃ (0.12 M) afforded the desired rearranged fluoroalkane (±)-**2a** in a 38% yield. Evaluation of various cobalt catalysts uncovered the importance of reducing the level of substitution on the ethylenediamine backbone of the salen ligand, with catalyst **C2** proving

Table 1: Optimization of the Wagner–Meerwein rearrangement reaction.

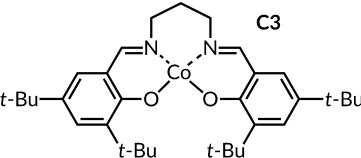




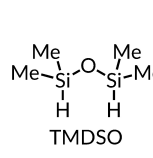
C1 R¹ = R² = Me



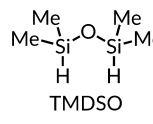
C2 R¹ = H, R² = Me



C3



Me₃NFPY·BF₄



TMDSO

Entry ^[a]	Co ^{II} Catalyst	Silane	Solvent	1a [%] ^[b]	2a [%] ^[b]
1	C1	TMDSO	PhCF ₃	33	38
2	C2	TMDSO	PhCF ₃	5	80
3	C3	TMDSO	PhCF ₃	48	3
4	C2	PhSiH ₃	PhCF ₃	6	68
5	C2	PhMeSiH ₂	PhCF ₃	4	73
6	C2	PhMe ₂ SiH	PhCF ₃	6	83
7	C2	PhMe ₂ SiH	MeCN	16	4
8	C2	PhMe ₂ SiH	CH ₂ Cl ₂	43	38
9	C2	PhMe ₂ SiH	THF	44	28
10	C2	PhMe ₂ SiH	PhCl	3	87
11 ^[c]	C2	PhMe ₂ SiH	PhCl	38	45
12 ^[d]	C2	PhMe ₂ SiH	PhCl	20	47
13 ^[e]	C2	PhMe ₂ SiH	PhCl	3	92
14 ^[e]	C2	TMDSO	PhCl	<1	90(76) ^[f]

[a] Unless otherwise stated optimization reactions were performed with **1a** (0.20 mmol), Me₃NFPY·BF₄ (2.0 equiv.), silane (4.0 equiv.) for 2 h at 0 °C. [b] Yield determined by ¹⁹F NMR analysis of the crude reaction with PhF (1.0 equiv.). [c] Reaction performed at -10 °C. [d] Reaction performed at RT. [e] 3 mol% of Co^{II} catalyst. [f] Isolated yield in brackets. See Supporting Information for further details on optimization.

optimal (Table 1, entry 2). Notably, the reaction performed very poorly if the chain length between the nitrogen atoms of the cobalt complex was increased by a methylene unit (Table 1, entry 3). Variation of the silane showed minor impact on product formation with PhMe_2SiH performing narrowly better than TMDSO (Table 1, entries 4–6). A survey of reaction media showed a strong preference for aromatic solvents such as PhCF_3 and PhCl , whereas other common solvents such as MeCN , CH_2Cl_2 , and THF performed poorly (Table 1, entries 7–10). Conducting the reaction at temperatures above and below 0°C showed a significant reduction in yield of the desired fluoroalkane (\pm)-**2a** (Table 1, entries 11–12). Lowering the catalyst loading of **C2** from 5 mol% to 3 mol% gave a minor boost in product yield (Table 1, entries 13–14). In the end, TMDSO was used in place of PhMe_2SiH , with only a slight cost in yield, as byproducts derived from PhMe_2SiH contaminated fluoroalkane (\pm)-**2a** after purification by column chromatography.

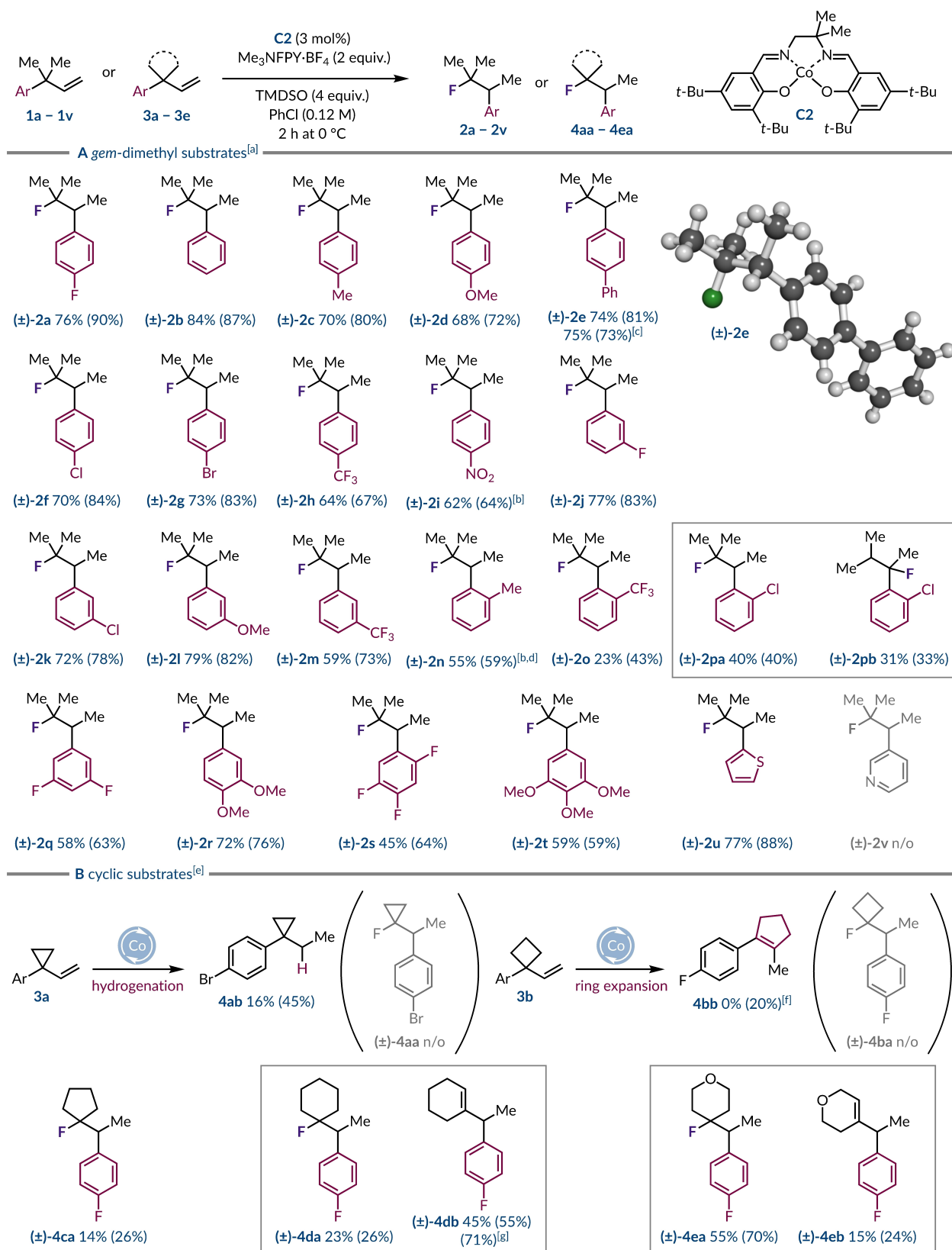
Scope and Limitations

With the optimal conditions in hand, we then explored the scope of *gem*-dimethyl substrates by varying the sterics, electronics, and position of the aryl ring substituents, **1a–1v** (Scheme 1). In general, *para*-substitution with electronically diverse functional groups was well tolerated ((\pm) -**2a–2i**). The simpler systems containing no substitution, or an alkyl fragment generated the desired rearranged fluoroalkanes (\pm)-**2b** and (\pm)-**2c** in great yield (70–84 %). The introduction of an electron-rich methoxy group was also well tolerated giving product (\pm)-**2d** in 68 % isolated yield. A biphenyl analogue gave 74 % yield of the rearranged fluoroalkane ((\pm) -**2e**) and when run on a 3.0 mmol scale, from a 0.20 mmol scale, the reaction saw no discernible drop in isolated yield. Importantly, single crystal X-ray diffraction of (\pm)-**2e** confirmed that 1,2-aryl migration had occurred.^[36] Halogen-containing substrates performed efficiently and chemoselectively in the presence of catalyst **C2** to deliver the desired rearranged products (\pm)-**2a**, (\pm)-**2f**, and (\pm)-**2g**. Remarkably, given the challenges associated with phenonium ion formation with electron-poor arenes the successful rearrangement of systems containing trifluoromethyl ((\pm) -**2h**) and nitro ((\pm) -**2i**) groups was surprising.^[37] This indicates that the (salen)cobalt(IV) complex can function as a hypernucleofuge akin to arylodonium(III) ions.^[12–18] When substituents were located at the *meta*-position of the arene the reaction still performed superbly with halogens ((\pm) -**2j** and (\pm)-**2k**), electron-rich ((\pm) -**2l**) and electron-deficient moieties ((\pm) -**2m**). In contrast, *ortho*-functionalized aryl groups led the reaction to become sluggish thus resulting in longer reaction times ((\pm) -**2n**) and lower yields of rearranged products ((\pm) -**2o**). Additionally, the presence of an *ortho*-chloro substituent led to a significant amount of a benzylic fluoride ((\pm) -**2pb**) byproduct, which was isolated independently from the desired fluoroalkane ((\pm) -**2pa**). Multi-substituted arenes bearing two or more fluorine atoms or methoxy groups also furnished the [1,2]-aryl migrated

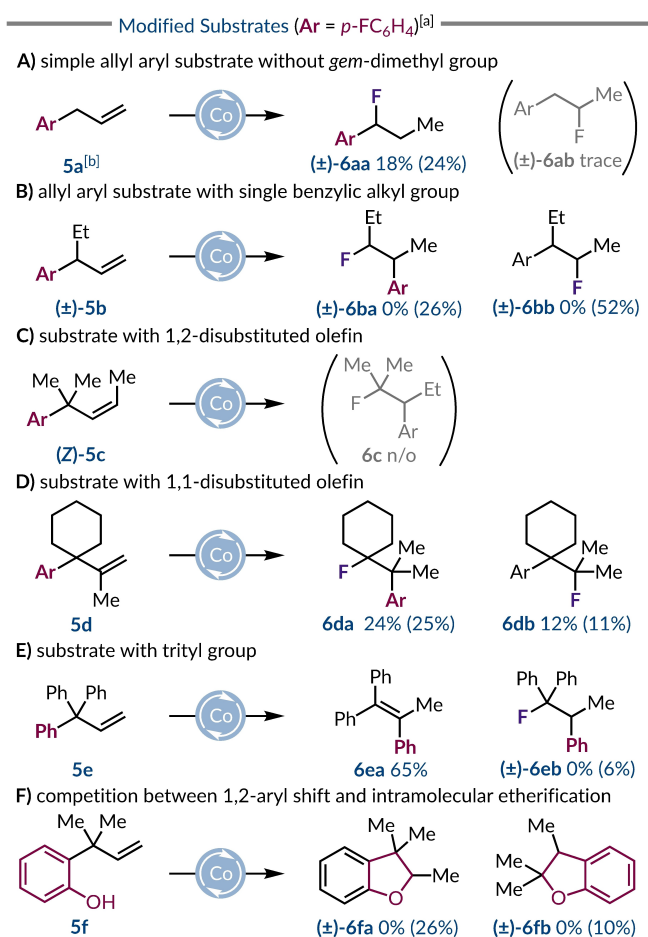
products in 45–72 % isolated yields ((\pm) -**2q–2t**). Exchanging the phenyl ring for a heterocyclic thiophene afforded product (\pm)-**2u** in 77 % yield. Unfortunately, the introduction of a Lewis basic pyridine ring ((\pm) -**2v**) appeared to shut down the reaction with only starting material returned.

Next, our attention turned towards cyclic substrates where the *gem*-dialkyl group was constrained in various ring systems (**3a–3e**). When subjected to the reaction conditions cyclopropyl substrate **3a** did not afford the rearranged fluoroalkane (\pm)-**4aa**, but instead generated a notable quantity of alkane **4ab** through olefin hydrogenation. This was unexpected as this was not a significant byproduct with the *gem*-dimethyl substrates and alkene hydrogenation has shown to be a minor pathway in closely related Co(salen) catalyzed systems.^[38] Likewise, cyclobutane analogue **3b** did not undergo a 1,2-aryl shift to form fluoroalkane (\pm)-**4ba**, but generated ring-expanded cyclopentene **4bb** as the major product.^[39,40] Increasing the ring size further restored selective migration of the arene albeit in poor yield for the cyclopentane product (\pm)-**4ca**. The incorporation of six-membered rings better facilitated the rearrangement process but the yields of the fluorinated products (\pm)-**4da** and (\pm)-**4ea** were moderate to poor. This can be attributed to the formation of alkenes (\pm)-**4db** and (\pm)-**4eb**, resulting from E1 elimination post-migration, which hampers product isolation. Attempts to hydrofluorinate these olefin products (**4db** and **4eb**) by introducing additional reagents post-reaction or resubjecting the pure material to the standard conditions were unsuccessful. However, performing the reaction with $\text{Me}_3\text{NFPY}\cdot\text{OTf}$ instead of $\text{Me}_3\text{NFPY}\cdot\text{BF}_4$ gave alkene (\pm)-**4db** as the sole product in 71 % NMR yield.

Subsequently, we investigated a range of substrates with distinct substitution patterns to aid determination of the requirements for reactivity and selectivity (Scheme 2). A simple allylbenzene system (**5a**) did not favour 1,2-aryl migration, but surprisingly the major product observed was benzyl fluoride (\pm)-**6aa** with only trace amounts of fluoroalkane (\pm)-**6ab** produced (Scheme 2A).^[41] We believe that hydrofluorination of the styrene produced via an initial Co-mediated isomerization of **5a** gives rise to product (\pm)-**6aa**.^[38] Introducing a single ethyl substituent at the benzylic position restored the migratory behaviour as (\pm)-**5b** generated rearranged fluoroalkane (\pm)-**6ba**, which was isolated as an inseparable 1:2 mixture with the regioisomeric product (\pm)-**6bb** in a combined yield of 74 %. This likely reflects the lack of an electronic bias in the phenonium ion intermediate with sterics dictating the major regioisomer (Scheme 2B).^[42,43] We also investigated starting materials containing more substituted C=C bonds. For example, exposing alkene (*Z*)-**5c** to the standard reaction conditions generated no fluoroalkane products with the alkene undergoing partial isomerization (*E:Z*=97:3 \rightarrow 83:17), demonstrating that 1,2-dialkyl-substituted alkenes are not viable substrates under these conditions (Scheme 2C). Limited reactivity and regioselectivity was observed with 1,1-disubstituted alkene **5d** as it generated a 2:1 mixture of regioisomers (**6da** : **6db**) in a combined NMR yield of 36 % (Scheme 2D). In contrast, 3,3,3-triphenylpropene **5e** demonstrated excellent reactivity with the major product (**6ea**)



Scheme 1. Substrate scope for Wagner–Meerwein reaction with (a) *gem*-dimethyl and (b) cyclic substrates. [a] Reactions performed on a 0.20 mmol of alkene, **C2** (3 mol%), Me₃NFPY·BF₄ (2.0 equiv.), and TMSO (4.0 equiv.) in PhCl (0.12 M) for 2 h at 0 °C. Yields refer to isolated products while ¹⁹F NMR yields are given in parentheses (determined by ¹⁹F NMR analysis of the crude reaction mixture using PhF (1.0 equiv.) as an internal standard). [b] Reaction performed for 4 h. [c] Reaction performed with 3.0 mmol of alkene. [d] Reaction performed with 0.40 mmol of alkene. [e] Reaction performed with 0.50 mmol of alkene, 5 mol% of **C2**, and PhCl (0.10 M). [f] Reaction performed with 0.70 mmol of alkene. [g] Reaction performed with Me₃NFPY·OTf



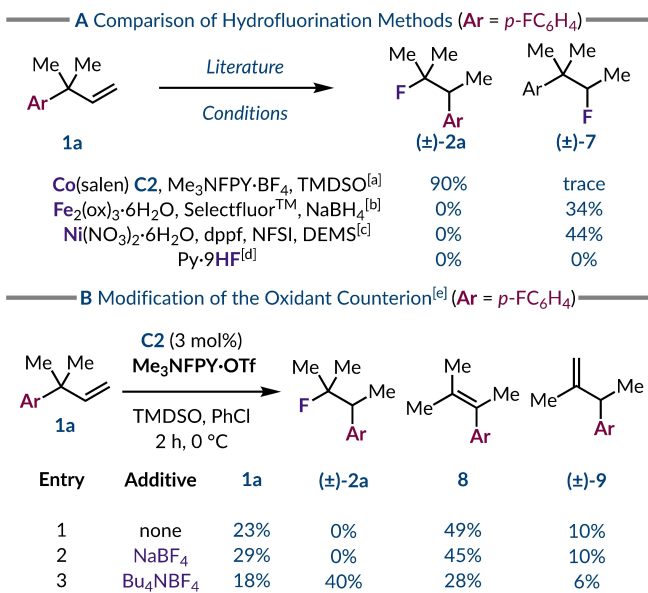
Scheme 2. Evaluating substrates with (a–b) a secondary or tertiary benzylic center, (c–d) 1,1- and 1,2-disubstituted alkenes, (e) a trityl group, and (f) *ortho*-phenol group. [a] Performed under standard conditions: 0.40 mmol of alkene, **C2** (3 mol%), Me₃NFPY·BF₄ (2.0 equiv.), and TMDSO (4.0 equiv.) in PhCl (0.12 M) for 2 h at 0 °C. Yields refer to isolated products while ¹⁹F NMR yields are given in parentheses (determined by ¹⁹F NMR analysis of the crude reaction mixture using PhF (1.0 equiv.) as an internal standard). [b] 0.60 mmol of alkene. [c] 0.20 mmol of alkene.

resulting from elimination after phenyl migration (Scheme 2E). Low quantities of the rearranged fluoroalkane (±)-**6eb** were detected by ¹⁹F NMR spectroscopy, but its poor stability reflects the preferential formation of **6ea** and precluded its isolation. We also probed the ionic nature of the reaction by using phenolic alkene **5f**, which generated dihydrobenzofuran products (±)-**6fa** and (±)-**6fb** in a 2.6:1.0 ratio via intramolecular etherification, which for the latter occurs after 1,2-aryl migration (Scheme 2F).^[44] This demonstrates that carbocation-like character is expressed at both the carbon atoms that form the new C–O bond during the course of the reaction.

To gain further insight into the nature of the migration pathway we used alternative metal-mediated hydrofluorination methods that have been proposed to only involve radical intermediates. For example, the treatment of alkene **1a** with stoichiometric iron(III) oxalate and SelectfluorTM led only to hydrofluorination of the olefin without 1,2-aryl

migration and provided fluoroalkane (±)-**7** in 34 % yield (Scheme 3A).^[45] Similarly, a nickel-catalyzed protocol that employs *N*-fluorobenzenesulfonimide (NFSI) did not generate the rearranged fluoroalkane (±)-**2a**, nor any another rearranged compounds previously observed under the cobalt-catalyzed conditions, but solely product (±)-**7**.^[46] Given the evidence for carbocation-like reactivity in cobalt-catalyzed processes that use *N*-fluoropyridinium salts,^[20,32,47] and the lack of aryl migrated products with the other hydrofluorination protocols tested suggests that the reaction proceeds via a phenonium ion intermediate.^[42] Thus, a neophyl-type radical rearrangement pathway for aryl migration seems less likely.^[48] Additionally, to test for ionic reactivity in the absence of any metals we treated neat **1a** with pyridine·9HF (10 equiv.), but no reactivity was observed with near full recovery of **1a** after 5 hours (96 %).^[49]

To determine the source of the fluorine in product (±)-**2a** we employed an *N*-fluoropyridinium oxidant with a triflate anion rather than tetrafluoroborate counterion. This led to a noticeable change in product composition as fluoroalkane (±)-**2a** was no longer observed, but instead alkenes **8** and (±)-**9** were obtained by elimination from the phenonium ion (Scheme 3B, Entry 1). Reintroducing tetrafluoroborate anions into the reaction partially restored the formation of the fluorinated product (±)-**2a**. The use of NaBF₄ as an additive with Me₃NFPY·OTf had minimal impact on the product distribution likely due to its low solubility in chlorobenzene (Scheme 3B, Entry 2). Switching to a more lipophilic tetrabutylammonium cation resolved



Scheme 3. (a) Evaluation of different hydrofluorination methods. (b) The role of the oxidant counterion. Yields determined by ¹⁹F NMR analysis of the crude reaction mixture using PhF (1.0 equiv.) [a] Reaction conditions as per Table 1, entry 14. [b] Iron-mediated radical hydrofluorination.^[45] [c] Nickel-catalyzed radical hydrofluorination.^[46] [d] pyridine·9HF (10 equiv.), neat, RT, 5 h. [e] Performed with 0.10 mmol of alkene **1a**, **C2** (3 mol%), Me₃NFPY·OTf (2.0 equiv.), additive (2.0 equiv.) and TMDSO (4.0 equiv.) in PhCl (0.12 M) for 2 h at 0 °C.

this issue and fluoroalkane (\pm)-**2a** was again the major product implying that the tetrafluoroborate anion is acting as a nucleophilic fluoride source (Scheme 3B, Entry 3).^[50]

Based on prior work and our own findings we tentatively present the following catalytic cycle for the generation of the phenonium ion intermediate (Figure 2). The combination of cobalt(II)-salen catalyst **A**, silane, and $\text{Me}_3\text{NFPy}\cdot\text{BF}_4$ is proposed to generate a transient $\text{Co}^{\text{III}}\text{-H}$ species **B** and a cationic Co^{III} complex **C**.^[51] Hydrogen atom transfer from the metal hydride (MHAT) to the olefin **1b** would generate a carbon-centred radical solvent-caged with the Co^{II} catalyst **A**.^[52] At this stage cage collapse would form organocobalt(III) complex **D**, which appears to resist rearrangement. Subsequent, single electron oxidation (SEO) of the alkylcobalt(III) species **D** could be effected by the cationic Co^{III} complex **C** or by the excess of oxidant.^[23,47] The produced alkylcobalt(IV) intermediate **E**, which acts as a carbocation surrogate, could incite formation of a phenonium ion and lead to regeneration of the Co^{II} catalyst **A**. Preferential 1,2-migration of the aryl group over the alkyl group is consistent with their migratory aptitude in carbocation instigated rearrangements.^[53] The tetrafluoroborate anion could then regioselectively fluorinate the phenonium ion to give the rearranged product (\pm)-**2b**.^[54]

Conclusion

In summary, we have developed a cobalt-catalyzed Wagner–Meerwein hydrofluorination protocol that utilizes a simple Co^{II} -salen catalyst and $\text{Me}_3\text{NFPy}\cdot\text{BF}_4$ as a bifunctional

reagent that acts as an oxidizing agent and fluoride source. This mild, general, and scalable procedure allows for synthesis of fluoroalkanes in good to excellent yield and with high functional group tolerance. Our experimental evidence supports a cationic reaction pathway whereby a phenonium ion intermediate is generated, which is regioselectively fluorinated, to give products resulting from 1,2-migration of the aryl ring.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The research data underpinning this publication can be accessed at <https://doi.org/10.17630/5944443f-21ce-4570-95c4-ee55c518f9c1>.

Keywords: Cations · Cobalt Catalysis · Hydrofluorination · Phenonium Ion · Wagner–Meerwein

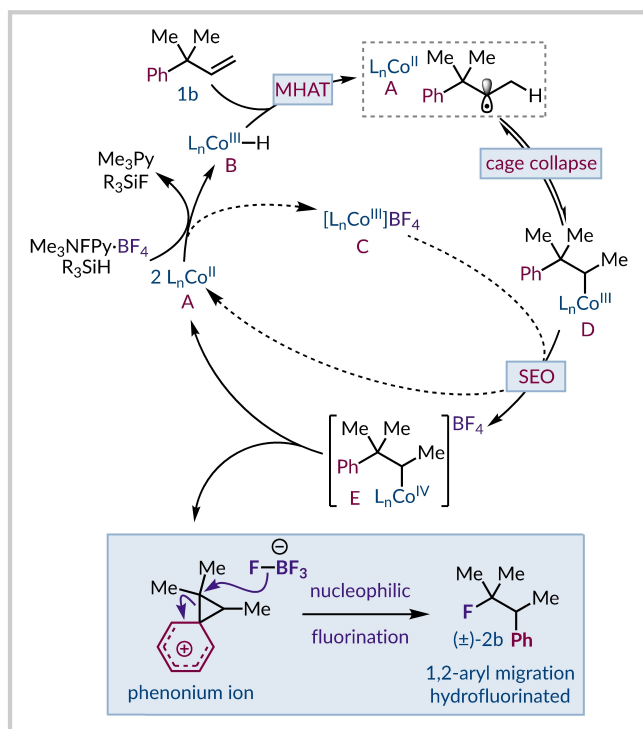


Figure 2. Proposed catalytic cycle for the reaction.

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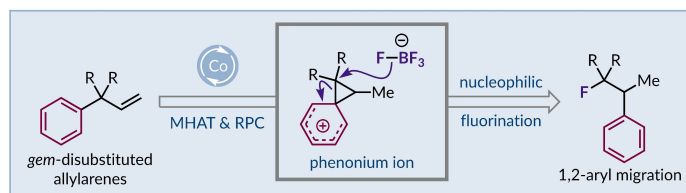
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Research Articles

Fluorine Chemistry

R. H. Hoogesteger, N. Murdoch,
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Cobalt-Catalyzed Wagner–Meerwein Rearrangements with Concomitant Nucleophilic Hydrofluorination



A cobalt-catalyzed reaction has been developed, which proceeds via hydrogen atom transfer and radical-polar cross-over steps, to form a phenonium ion under non-acidic conditions. This cationic intermediate can be regioselectively

fluorinated by a tetrafluoroborate anion to give 1,2-aryl migrated products. Evaluation of distinctly substituted phenonium ion intermediates demonstrated the constraints for good reactivity and high selectivity.