Electrostatic vs. inductive effects in phosphine ligand donor properties and reactivity††

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Enhanced rates and selectivity in enzymes are enabled in part by precisely tuned electric fields within active sites. Analogously, the use of charged groups to leverage electrostatics in molecular systems is a promising strategy to tune reactivity. However, separation of the through space and through bond effects of charged functional groups is a long standing challenge that limits the rational application of electric fields in molecular systems. To address this challenge we developed a method using the phosphorus selenium coupling value ($J_{p-Se}$) of anionic phosphine selenides to quantify the electrostatic contribution of the borate moiety to donor strength. In this analysis we report the synthesis of a novel anionic phosphine, PPh$_2$CH$_2$BF$_3$K, the corresponding tetraphenyl phosphonium and tetraethyl ammonium selenides [PPh$_4$][SePPh$_2$CH$_2$BF$_3$] and [TEA][SePPh$_2$CH$_2$BF$_3$], and the Rh carbonyl complex [PPh$_3$][Rh(acac)(CO)(PPh$_2$(CH$_2$BF$_3$)]. Solvent-dependent changes in $J_{p-Se}$ were fit using Coulomb’s law and support up to an 80% electrostatic contribution to the increase in donor strength of [PPh$_3$][SePPh$_2$CH$_2$BF$_3$] relative to SePPh$_2$Et, while controls with [TEA][SePPh$_2$CH$_2$BF$_3$] exclude convoluting ion pairing effects. Calculations using explicit solvation or point charges effectively replicate the experimental data. This $J_{p-Se}$ method was extended to [PPh$_3$][SePPh$_2$(2-BF$_3$Ph)] and likewise estimates up to a 70% electrostatic contribution to the increase in donor strength relative to SePPh$_2$. The use of PPh$_2$CH$_2$BF$_3$K also accelerates C–F oxidative addition reactivity with Ni(COD)$_2$ by an order of magnitude in comparison to the comparatively donating neutral phosphines PEt$_3$ and PCy$_3$. This enhanced reactivity prompted the investigation of catalytic fluoroarene C–F borylation, with improved yields observed for less fluorinated arenes. These results demonstrate that covalently bound charged functionalities can exert a significant electrostatic influence under common solution phase reaction conditions and experimentally validate theoretical predictions regarding electrostatic effects in reactivity.

Introduction

Spectroscopic and computational studies have cited oriented electric fields in active sites as key contributors to enzymatic reactivity.¹⁻⁷ Enzymes maintain and orient electric fields using polar and charged functional groups in the protein scaffold around the active site, a strategy that is appealing for synthetic molecular systems but difficult to mimic.⁸⁻¹² Multiple approaches have been proposed for incorporating similar electric fields into systems that lack an enzymatic superstructure. Electric fields can be directly applied to synthetic compounds through attachment to electrode surfaces or STM tips and these approaches have been shown to increase catalytic rates.¹³⁻²³ Another approach is to rationally append charged functional groups onto molecular scaffolds to offer control over the orientation and magnitude of electrostatic effects. Indeed, there has been enormous interest in modeling or leveraging electrostatic interactions in organic and inorganic molecules.²⁴⁻⁶¹ Computations predict that electrostatic effects can have a large impact on reactivity and catalysis.⁶²⁻⁶³ A detailed understanding of the relative magnitudes of inductive and electrostatic charged substituent effects would be valuable in rationally tuning molecular reactivity. In this context, inductive represents through bond polarization of the molecule, similar to effects observed with electron donating or withdrawing groups, while electrostatic indicates through space polarization of a bond consistent with Coulomb’s law. Experimentally parsing out the relative inductive and electrostatic contributions to reactivity and electronic structure from charged functional groups is challenging even in simple systems. A prime example of this is in classic Hammett literature where inductive through-bond and electrostatic through-space influences from substituents were predominantly treated as one lump effect, sometimes referred to as $\sigma^i$. However, in a subset of this literature, there has been
considerable debate on whether electrostatics or through-bond electron density factors are dominant in \( \sigma_e \). Hammett originally considered the influence of substituents to be entirely electrostatic in nature, a view supported by Ri, Eyring, and Westheimer.\(^{53-64} \) Conversely, Jaffe considered substituent effects primarily through electron density, foreshadowing modern computational analyses.\(^{65-66} \) The efficacy of both methods in rationalizing reactivity trends supports that both electrostatic and inductive interactions are active, and methods to distinguish between them are still being pursued to this day.\(^{67-69} \) A more thorough understanding of the inductive and electrostatic factors influencing the electronic structure and reactivity of distally charged ligands and complexes would be instructive, particularly as leveraging through-space interactions can serve as a strategy to break free-energy relationships.\(^{70-76} \)

Phosphines are ideal scaffolds for quantifying the influence of electrostatics as these ligands feature prominently in catalysis and have well defined parameters for rationalizing reactivity trends, such as the Tolman Electronic Parameter (TEP) and cone angle.\(^{77} \) Indeed, cationic and anionic moieties have previously been incorporated into phosphines, frequently leading to distinct properties or reactivity in comparison to neutral analogues.\(^{78-81} \) Phosphine borate ligands specifically have been prepared through the incorporation of triaryl- and trifluoroborate and carbonyl functional groups, and have shown enhanced reactivity in polymerization,\(^{82-93} \) cross coupling,\(^{84-96} \) and hydrofunctionalization\(^{97,98} \) reactions. These phosphines are uniformly considered to be stronger donors than their neutral isostructural analogues. However, the origin of this increase (electrostatic or inductive) has remained elusive, and has largely been considered inductive by default.\(^{98,99,100-103} \) The ambiguity regarding through space effects of covalently bound distal anions limits the rational design of ligand scaffolds that leverage electric fields to enhance reactivity. For instance, a recent computational study predicts accelerated oxidative addition (OA) reactivity at a PMe3 supported Pd complex in the presence of either an externally applied electric field or a correctly positioned chloride ion.\(^{53} \) This study suggests that similar effects may be replicated using distally charged anionic phosphines if a suitably thorough understanding of electrostatic effects in covalently bound anions can be obtained.

Herein we report a method to assign the electrostatic and inductive contributions of anionic functional groups to phosphine donor strength using the solvent dependence of phosphorus selenium coupling values \( (J_{P-Se}) \). This method is initially developed using the novel phosphine PPh\(_2\)CH\(_2\)BF\(_3\) (1) (Scheme 1). The R–BF\(_3\) functional group is ideal for this analysis as it provides a more compact charge in comparison to commonly used aryl borates.\(^{96} \) Additionally, trifluoroborate groups are reatively inert in comparison to aryl borates, which can engage in aryl-group transfer decomposition pathways\(^{87} \) and intramolecular C–H oxidative addition reactivity.\(^{99} \) The methylene linker to the phosphine precludes convolting resonance influences that may be present in aryl linkers. We report the synthesis of the potassium salt of this phosphine, K1, and assess the electrostatic impact of the R–BF\(_3\) moiety \( \textit{via} \) both the solvent dependent NMR coupling constants of its phosphine selenide SePPh\(_2\)CH\(_2\)BF\(_3\)\(^–\) (1\(^{Se}\)) and its complexation to Rh carbonyls to give [PPh\(_4\)][Rh(acac)(CO)(PPh\(_2\)CH\(_2\)BF\(_3\))] (2). The possibility of competing contributions to \( J_{P-Se} \) from ion pairing is excluded through controls with two different counterions, [PPh\(_4\)]\(^{104} \) and [TEA]\(^{105} \). The solvent dependence of [PPh\(_4\)]\(^{104} \) shows a 1/4\( \pi \) dependence, consistent with Coulomb's law, and fits suggest that up to 80% of the increase in donor strength relative to PPh\(_3\)Et is attributable to electrostatic effects, a conclusion which we replicate using calculations. This study is then extended to an additional anionic phosphine selenide with a longer and more rigid aryl linker, SePPh\(_2\)(2-BF\(_3\)Ph)\(^–\) (3\(^{Se}\)),\(^{96,101} \) and the 1/4\( \pi \) fit similarly suggests that up to 70% of the increase in donor strength relative to PPh\(_3\) results from electrostatic contributions.

Finally, an order of magnitude acceleration in the OA of aryl fluorides mediated by K1 and Ni(COD)\(_2\) is observed relative to neutral phosphines of comparable donor strengths, PPh\(_3\) and PCy\(_3\). This finding suggests a unique impact of electrostatic effects beyond that expected from increased donor strength. This accelerated reactivity is applied to the catalytic defluoroborylation of fluoroarenes, with improved reactivity observed with comparatively unactivated substrates. In summary, this work illustrates how electrostatic interactions from charged functional groups are a substantial contributor to phosphine donor strength in common organic solvents and that these electrostatic effects can be leveraged for increased reactivity and catalysis.

**Results and discussion**

**Synthesis and characterization of PPh\(_2\)CH\(_2\)BF\(_3\)K (K1)**

Synthesis of the phosphine proceeds readily \( \textit{via} \) deprotonation of PPh\(_2\)PH with KHMD (KHMD = potassium hexamethyldisilazide), followed by dropwise addition to a stirring THF solution of potassium iodomethyltrifluoroborate, and yields K1 as a white powder following workup (Scheme 1). We note that a related zwitterionic triphenyl phosphonium methyl trifluoroborate has been previously synthesized.\(^{102-104} \) The \(^1\)H NMR of K1 shows the expected aromatic signals for the phenyl groups, and a doublet of quartets at 0.8 ppm from coupling of the CH\(_2\) linker to phosphorus, boron, and fluoride (Fig. S1†). The \(^{31}\)P\(^{\text{1H}}\) NMR spectrum shows a quartet at \( –15 \) ppm due to

![Scheme 1](image-url)
fluorine coupling with an identical chemical shift to that observed for PPh₂Et (Fig. S2†). This observation is consistent with previous reports that charged phosphines have similar shifts as their neutral analogues.⁹⁰ Analysis by ¹³F{¹H} and ¹¹B{¹H} NMR indicates the expected shifts and coupling for a R–BF₃⁻/C group, supporting the presence of this anionic unit (Fig. S3 and S5†). Compound K1 was structurally characterized via single-crystal X-ray diffraction (SXRD, Fig. 1). The SXRD structure shows the expected connectivity with an average B···P distance of 2.858(3) Å and a close association between K and B (∼3 Å, Fig. S89†). While it is unclear if this association is preserved in solution, larger cations were chosen to limit ion pairing in further analyses (see below).

**Tolman electronic parameter and Jₚ₋₆e determination**

To assay the donor strength of phosphine 1, its Tolman Electronic Parameter (TEP) was determined using a Rh carbonyl complex of the form Rh(acac)(CO)L (L = phosphine). While the limitations of TEP in reflecting M–L bond strengths has been noted previously,¹⁰⁶ it remains a standard in the literature for the comparison of phosphine donor strength.¹⁰⁷ The TEP is a measure of the donation of electron density from a phosphine to a metal complex through the combined effects of σ donation (P → M) and π back-bonding (M → P) interactions.³¹,¹⁰⁷ TEP is traditionally determined from the A₂-symmetrical rCO stretching frequency in Ni(CO)₄L complexes, where a higher rCO indicates a less electron-rich metal center resulting from weaker phosphine donors. However, the toxicity of the Ni(CO)₄ starting material has motivated the development of other model complexes to determine TEP. One such complex which displays a robust linear correlation between rCO and TEP is Rh(acac)(CO)L (see Fig. S67† for equation), and accordingly the complex with L = K1 was synthesized.¹⁰⁸

Addition of K1 to Rh(acac)(CO)₂ with PPh₃Br affords [PPh₃] [Rh(acac)(CO)][PPh₃(CH₂BF₃)] (2) as a yellow solid. The SXRD structure of 2 shows a square planar geometry at Rh (Fig. 1). The BF₃⁻ unit is located significantly above the Rh square plane and close contacts (∼2.3 Å) are observed between the BF₃⁻ and protons on PPh₃, consistent with H-bonding interactions (Fig. S90†). No secondary interactions between PPh₃ and CO are observed. The B···C and B···O distances are 3.719(5) and 3.955(4) Å, notably shorter than the B···Rh distance of 4.150(4) Å, although the difference diminishes upon normalizing to van der Waals radii (see ES††). Compound 2 is readily identified in solution by the appearance of a doublet of quartets in the ³¹P{¹H} NMR spectrum arising from coupling of the phosphorus nucleus to ¹³¹Rh (J_P-Rh = 166 Hz) and ¹⁹F (J_P-F = 10 Hz), consistent with the solid-state structure (Fig. S7†). The solution IR spectrum of 2 in CH₂Cl₂ shows a rCO of 1965 cm⁻¹, which correlates to a TEP of 2061.7 cm⁻¹ (Fig. S67†). This TEP is identical to that of PEt₃ (2061.7 cm⁻¹), and is significantly more donating than the related alkyldiaryl phosphine PPh₂Et (2066.7 cm⁻¹) (Fig. 2).²⁷ This result is consistent with the commonly observed donation previously observed for phosphines with anionic borates.⁶⁸,⁶⁹,⁷⁰,⁹₂,⁹₅,₁₀₀,₁₀₁,₁₀₉–₁₁₂

In addition to metal carbonyl adducts, phosphine selenide compounds have also been used to quantify the donor strength and basicity of phosphines via their P–Se coupling constants (Jₚ₋₆e).¹¹³,¹¹⁴ The use of NMR coupling constants is advantageous
due to greater instrumental resolution and sensitivity in the coupling value as compared to vibrational spectroscopy.\textsuperscript{112} Changes in \( J_{P-Se} \) report on changes in the s character of the P–Se bond.\textsuperscript{116,117} The electron donating/withdrawing character of the substituents on P influences this s character through hybridization changes as predicted by Bent’s rule.\textsuperscript{118,119} Electron withdrawing R groups on PR\textsubscript{3} increase the s character in the P–Se bond and thereby \( J_{P-Se} \), while electron donating R groups effect the opposite.\textsuperscript{113}

The phosphine selenide, \([\text{PPh}_4]_2[\text{SePPh}_3\text{CH}_2\text{BF}_3]\) \( ([\text{PPh}_4]_2[\text{Se}]) \), was prepared by stirring K1 overnight in THF with an excess of elemental Se and PPh\textsubscript{3}Br. The facile oxidation is consistent with the increased donor strength of 1, as most preparations require heating of elemental Se or the use of soluble red selenium.\textsuperscript{118,120} The SXRD structure confirms the geometry of \([\text{PPh}_4][\text{Se}])\) and shows close contacts (\( \leq 2.7 \) Å) between the protons on PPh\textsubscript{3} and the BF\textsubscript{3} \( (\text{Fig. 1 and S9f}) \). The \( ^{31}\text{P}([\text{H}]) \) NMR spectrum of \([\text{PPh}_4][\text{Se}])\) shows full conversion to the selenide with a quartet peak at \( \sim 33 \) ppm and satellite quartets at \( \sim 31 \) and \( \sim 35 \) ppm from coupling to the \( ^{77}\text{Se} \) nucleus \( (\text{Fig. S12f}) \). In DMSO-d\textsubscript{6}, the \( J_{P-Se} \) of 687 Hz is nearly identical to the \( J_{P-Se} \) of SePPr\textsubscript{3} \( (686 \text{ Hz, CDCl}_3) \) and indicates an increase in donor strength relative to the neutral congeners SePPh\textsubscript{3}Et \( (722 \text{ Hz, CDCl}_3) \) \( (\text{Fig. S27 and S28f}) \).\textsuperscript{121}

We then sought to compare our two experimental assays of phosphine donor strength. While the use of \( J_{P-Se} \) to measure phosphine donor strength is well established, specific correlations between \( J_{P-Se} \) and TEP have not been clearly defined.\textsuperscript{118,122} Fitting of the reported \( J_{P-Se} \) and TEP values for a series of 18 alkyl and aryl phosphines resulted in a reasonable linear correlation \( (R^2 = 0.84, \text{ Fig. 2, S88 and Table S11f}) \).\textsuperscript{77,108,121} Using this analysis to extrapolate a value of \( J_{P-Se} \) from the experimentally determined TEP of 2 provides \( J_{P-Se} = 698 \) Hz, which is significantly larger than the experimentally determined value of 687 Hz for \([\text{PPh}_4][\text{Se}])\) in DMSO-d\textsubscript{6} \( (\text{Table S10f}) \). Surprisingly, measuring the \( J_{P-Se} \) of \([\text{PPh}_4][\text{Se}])\) in CDCl\textsubscript{3} results in a significant decrease in \( J_{P-Se} \) to 657 Hz (\( \Delta 30 \) Hz), suggesting that phosphine 1 is a stronger donor in CDCl\textsubscript{3} than DMSO. Overall, the TEP and \( J_{P-Se} \) values clearly indicate that the anionic charge promotes a large increase in the donor strength of phosphine 1. However, we wanted to further understand the origin of the large solvent dependence of this donor strength.

Analysis of donor strength solvent dependence

The presence of the charged borate in phosphine 1 and the discrepancy between TEP values determined \textit{via} different methods prompted us to investigate how electrostatic effects contribute to these measurements. “Through-space” interactions have been suggested previously to explain anomalous \( J_{P-Se} \) behavior in phosphines with 2-furyl and \( \alpha \)-methoxymethyl substituents, but a thorough analysis of this effect has not been undertaken.\textsuperscript{123} A dependence on solvent ionic strength was proposed as a means of separating electrostatic and inductive contributions of a R-NMe\textsubscript{3}\textsuperscript{+} substituent on the rate of acetate binding in iron porphyrins.\textsuperscript{124} We reasoned that a similar solvent variation approach would be useful for separating inductive and electrostatic contributions to the donor strength of 1. Specifically, the through-space electrostatic influence of the charged group should be modified by the solvent dielectric \( (\epsilon) \), a measure of a medium’s ability to shield a charge,\textsuperscript{125} while the through-bond interactions should remain constant.

IR spectra of 2 and the parent Rh(CO)\textsubscript{5}(acac) were initially acquired in MeCN, THF, and DCM. However, no variation of \( \epsilon_{CO} \) outside of instrumental error is observed \( (\text{Fig. S72 and S73f}) \). This is perhaps not surprising as the expected change in stretching frequency of \( \sim 10 \) cm\textsuperscript{-1} is not large compared to the instrumental resolution (4 cm\textsuperscript{-1}). Resolving dielectric induced shifts is further limited by spectral convolution or broadening, likely from Rh–P rotational isomers of 2 with different stretching frequencies as has been observed in other carbonyl systems.\textsuperscript{125} This manifests as substantially broader spectra for 2 than for Rh(CO)\textsubscript{5}(acac). These competing factors complicate the interpretation of donor strength in 2 and suggest that the higher sensitivity and resolution of \( J_{P-Se} \) may make it a more conducive method for examining electrostatic effects.

While the inductive donor effects in \([\text{PPh}_4][\text{Se}])\) should be insensitive to \( \epsilon \), the electrostatic stabilization of the formally cationic phosphonium in the dominant resonance structure \( \text{Se}^-\text{P}_3\text{R}_3 \) by the adjacent BF\textsubscript{3} \textsuperscript{−} anion should increase as \( \epsilon \) decreases.\textsuperscript{103,126} Lower \( \epsilon \) solvents will effectively screen the anion, resulting in greater stabilization of the positive formal charge and a lower \( J_{P-Se} \). Although it is difficult to predict solution structures, SXRD and DFT analysis \( (\text{see below}) \) of all phosphine selenides considered in this report show shorter distances between P and R than Se and B, supporting the feasibility of the anion stabilizing a formal positive charge on P \( (\text{Table S15f}) \). We note that previous literature studies demonstrate some solvent dependence to \( J_{P-Se} \), with one report suggesting variation between 2-3%.\textsuperscript{127,128} In our analysis, comparison of \( J_{P-Se} \) in the anionic phosphine to a neutral analogue and restricting solvent choice to aprotic solvents serve as controls for any incidental trends.

As mentioned, an overall decrease of 30 Hz in the \( J_{P-Se} \) of \([\text{PPh}_4][\text{Se}])\) is observed upon moving from CDCl\textsubscript{3} \( (\epsilon = 4.8) \) to DMSO \( (\epsilon = 46.7) \). Expanding the solvent selection to include CD\textsubscript{3}CN, acetone-d\textsubscript{6}, CDCl\textsubscript{3}, and mixtures thereof shows a consistent decrease in \( J_{P-Se} \) as \( \epsilon \) decreases \( (\text{Fig. 3, S27–S30 and S12f}) \). In comparison, only a slight change of 7 Hz is observed across the same \( \epsilon \) range for the neutral congener SePPh\textsubscript{3}Et \( (\text{Fig. 3, S37 and S12f}) \). Coulomb’s law suggests that a linear dependence on \( 1/4\pi\epsilon \) should be expected for a primarily electrostatic effect. Indeed, the observed solvent dependence of \( J_{P-Se} \) for \([\text{PPh}_4][\text{Se}])\) follows this trend. The variable solvent coupling for \([\text{PPh}_4][\text{Se}])\) was fit to the linear relationship \( J_{P-Se} = 693(1) - 2.12(12) \times 10^3 \times (1/4\pi\epsilon) \) \( (R^2 = 0.98) \). The neutral congener was also fit and shows a shallower slope of \( -5(6) \times 10^3 \) and a worse \( R^2 = 0.06 \) value \( (\text{Table S13f}) \).

While this solvent trend for \([\text{PPh}_4][\text{Se}])\) is well modeled by an electrostatic effect, we also wanted to account for any ion pairing interactions. Ion pairing can range from separated free ions to close contact ion pairs, with varying degrees of ion solvation and association in between. These solvent separated ion pairs may also exist in an equilibrium, and generally it is difficult to
precisely characterize the speciation of an ion pair in solution.\textsuperscript{139} Increased ion pairing in low $\epsilon$ solvents may influence the observed solvent dependence in the $J_{P_{-}Se}$ of [PPh$_4$]$_2$Se$^\text{2-}$ to exclude this possibility, [TEA][I$^\text{Se}$] (TEA$^+$ = NE$_4$)$^+$ was prepared as a control with comparatively stronger ion pairing due to the higher charge density of the TEA$^+$ cation. As H-bonding interactions between the cation and the BF$_3$ in solutions are observed in the crystal structures of [TEA][I$^\text{Se}$] and [PPh$_4$][I$^\text{Se}$], the CH$_3$ and BF$_3$ $^3$H and $^19$F resonances are used as reporters on ion pairing in solution (Fig. S91 and S93†). In DMSO-d$_6$, the methylene and fluorne resonances in [TEA][I$^\text{Se}$] and [PPh$_4$][I$^\text{Se}$] are superimposable, consistent with identical $^1$Se environments. In CD$_2$Cl$_2$ ($\epsilon = 9.1$), the methylene resonance in [TEA][I$^\text{Se}$] is shifted downfield by 0.4 ppm relative to [PPh$_4$][I$^\text{Se}$] and the F resonance is shifted downfield by 1.0 ppm (Fig. S39–S42†). The downfield shift is consistent with stronger H-bonding interactions in solution deshielding the methylene protons and fluorines of [TEA][I$^\text{Se}$] to a greater extent than in [PPh$_4$][I$^\text{Se}$]. Some degree of ion pairing in [PPh$_4$][I$^\text{Se}$] is likely present, as DOSY of [PPh$_4$][I$^\text{Se}$] in CD$_2$Cl$_2$ shows that the cation and anion diffuse at the same speed (Fig. S16†). However, the NMR experiments demonstrate that the extent of contact-ion pairing in solution appears to be greater in [TEA][I$^\text{Se}$] than in [PPh$_4$][I$^\text{Se}$], as is expected based on the differing size of the cations.

Once it was established that TEA$^+$ ion pairs more strongly than PPh$_4^+$, the impact of cation identity on $J_{P_{-}Se}$ was investigated. The $J_{P_{-}Se}$ of [TEA][I$^\text{Se}$] in high $\epsilon$ solvents shows nearly identical $J_{P_{-}Se}$ values to that of [PPh$_4$][I$^\text{Se}$], consistent with isolated free ions. However, moving to lower $\epsilon$ solvents only results in a decrease of 9 Hz in the $J_{P_{-}Se}$ for [TEA][I$^\text{Se}$] (Fig. 2, S34, S35 and S12†). The magnitude of this change and the slope of the linear fit ($-7(2) \times 10^3, R^2 = 0.77$) resembles those of the neutral analogues (Table S13†). Intuitively, these results suggest that the enhanced ion pairing between TEA$^+$ and I$^\text{Se}$ results in shielding of the BF$_3$ charge, thus limiting the detection of electrostatic effects on $J_{P_{-}Se}$ in low $\epsilon$ solvents. In contrast, the large size and diffuse charge of PPh$_4^+$ less effectively shields the BF$_3$ and allows for the observation of solvent dependent through space effects. Similar effects have been observed in ion-pair catalysis, where a small compact SbF$_6$ anion stabilizes polar transition states and affords greater product selectivity in lower $\epsilon$ solvents, while a larger and more diffuse B(3,5-C$_6$F$_3$)$_2$ anion shows no improvement.\textsuperscript{7} The effect of alternative cations on the $J_{P_{-}Se}$ of [PPh$_4$][I$^\text{Se}$] in CDCl$_3$ was also explored. The addition of 20 equivalents of PPh$_4$Br or PPNCI (PPN$^+$ = bis(triphenylphosphine)iminium$^+$) results in minimal deviation (<4 Hz), while 20 equivalents of NBu$_4$Cl or TEABr result in significant increases in the coupling, as expected for the formation of tighter ion pairs and enhanced anion shielding (Table S14†). Overall, these controls with [TEA][I$^\text{Se}$] support the assignment of electrostatic effects instead of ion pairing in rationalizing the observed solvent dependence.

**Electrostatic contributions to donor strength**

Assigning the solvent dependence of $J_{P_{-}Se}$ as electrostatic in origin enables the separation of electrostatic and inductive contributions to donor strength (Table 1). The difference in $J_{P_{-}Se}$ between [PPh$_4$][I$^\text{Se}$] and the SePPh$_2$Et in high $\epsilon$ solvents, where the charge is effectively shielded, provides an estimate of the inductive contributions of the BF$_3$ group. The change in $J_{P_{-}Se}$

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![Fig. 3](image-url) (A) Solvent dependence of $J_{P_{-}Se}$ for anionic and neutral phosphines. The fit data for [PPh$_4$][I$^\text{Se}$] is provided in the text, and the fit data for [PPh$_4$][I$^\text{Se}$] (repeated from A for comparison), the fit data for [TEA][I$^\text{Se}$] in comparison to [PPh$_4$][I$^\text{Se}$] (repeated from A for comparison), the fit data for [TEA][I$^\text{Se}$] is provided in the ESI.† Different dielectrics ($\epsilon$) were generated with CDCl$_3$ ($\epsilon = 4.8$), CD$_2$Cl$_2$ ($\epsilon = 9.1$), acetone-$d_6$ ($\epsilon = 21$), CD$_3$CN ($\epsilon = 36.6$), DMSO-$d_6$ ($\epsilon = 46.7$), or mixtures thereof (Fig. S12†).
for [PPh₄][1³Se] upon moving to less shielding environments represents the introduction of electrostatic contributions, with the maximum contribution at the hypothetical vacuum limit. The high ε and vacuum limits of J_P-Se obtained from the linear fits to [PPh₄][1³Se] and SePP₄Et therefore provide the relative electrostatic and inductive contributions to donor strength. Simply shifting from the high ε limit (693 Hz) to the vacuum limit (524 Hz) of [PPh₄][1³Se] yields an overall change in J_P-Se of 169 Hz. Comparison of this electrostatic shift with the 207 Hz difference in coupling between the vacuum limit of [PPh₄][1³Se] (524 Hz) and the high ε limit of SePP₄Et (731 Hz) provides an estimated electrostatic contribution of 82% to the total increase in donor strength (Table 1). While this analysis uses the extrapolated limits, the experimental data from the accessible range of ε suggest that the electrostatic contribution is ~50% (Table S12†). These analyses show that electrostatic factors have a major, and even dominant, impact on the donor properties in these systems.

To further investigate the relative contribution of through-space and through-bond effects, Density Functional Theory (DFT) calculations were performed to estimate J_P-Se and compare with experimentally determined values (Table 1). For simplicity, two local geometries of the phosphine 1³Se were considered to capture limiting rotamers that may be present in solution: one transoid rotamer with a Se–P–C–B dihedral of 158° and one cis rotamer with a Se–P–C–B dihedral of 74° (Fig. S80 and S81†). A Boltzmann weighted average of these two extremes predicts a nearly 100% population of the transoid isomer at room temperature, with a calculated gas phase J_P-Se of 792 Hz. We then performed optimizations of the transoid rotamer with explicit solvation to see if the observed experimental trends were reproduced computationally. Optimizations in CHCl₃, DCM, and MeCN predict J_P-Se values of 648, 675, and 684 Hz respectively (Fig. S84–S86 and S12†). These values are in remarkably good agreement with both the experimentally determined J_P-Se as well as the observed trend with solvent dielectric.

To computationally deconvolute electrostatic contributions to J_P-Se, we analyzed the effect of including point charges in the gas phase. Coulomb's law was used to estimate the electric field at P generated by a negative point charge located at B in the transoid rotamer of 1³Se. This analysis gives an electric field parallel to the P–Se bond (defined as the z-axis) of ~−1.07 V Å⁻¹ (Table S4†). The electrostatic contribution to J_P-Se was then determined by calculating the J_P-Se for SePP₄Et with a negative point charge at ~3.7 Å from P in the z direction, resulting in an applied field of comparable magnitude. The inclusion of this point charge lowers J_P-Se to 809 Hz from 872 Hz in the neutral analogue, suggesting that the purely electrostatic contribution to J_P-Se is 63 Hz. This electrostatic contribution is 79% of the total computed difference in J_P-Se between 1³Se and SePP₄Et (80 Hz, Table 1), which is identical within error to that determined experimentally. Thus, DFT calculations support the experimental data demonstrating that electrostatic effects play a significant role in the donor properties of 1.

### Extension and comparison to other phosphines

The selenide of an anionic phosphine previously investigated for Pd catalyzed olefin polymerization/oligomerization, [PPh₄][SePP₄(2-BF₃Ph)] ([PPh₄][3³Se]), was synthesized analogously to [PPh₄][1³Se]. This phosphine was targeted to test the generality of this solvent-dependence analysis of electrostatic contributions to donor properties, particularly in the presence of increased rigidity and possible convoluting resonance effects from an aryl linker.⁹⁰,⁹¹ The SXRD structure of [PPh₄][3³Se] confirms the expected connectivity and also shows that the B of the BF₃⁻ group is farther from the phosphine than in [PPh₄][1³Se] (Fig. 1, 3.562(2) and 3.029(6) Å respectively). The P of the PPh₄⁺ cation is located at 5.895(2) Å from the B, however H-bonding interactions between the PPh₄⁺ aryl protons and the BF₃⁻ fluorines are observed (Fig. S95†).

The solvent dependence of J_P-Se for [PPh₄][3³Se] was measured with the related assumption that inductive and resonance contributions along the covalent linkage would be predominantly independent of solvent ε screening. The J_P-Se of [PPh₄][3³Se] decreases by 18 Hz upon moving from DMSO-d₆ to CDCl₃, a smaller change than the 30 Hz shift observed for [PPh₄][1³Se] (Fig. 3, S36 and S12†). Furthermore, the magnitude of the slope of the linear fit to the solvent dependence for [PPh₄][3³Se] is ~70% of that for [PPh₄][1³Se]. This is consistent with the ratio predicted from a 1/(r²) dependence from Coulomb's law based on the relative B…P distances in the anionic fragments of [PPh₄][3³Se] and [PPh₄][1³Se] from SXRD (3.562(2) and 3.029(6) Å respectively, 72%, see ESIF†).

The neutral congener of [PPh₄][3³Se], SePP₄, was also prepared and the J_P-Se changes by 5 Hz upon switching from

### Table 1 Experimental and computational determination of electrostatic and inductive contributions to J_P-Se coupling constants

| Experimental | R = Et; X = 1 | R = Ph; X = 3 | DFT |
|--------------|---------------|---------------|-----|
| SePP₄Et (ε = ∞, J_neutral) | 731 Hz | 741 Hz | 872 Hz |
| [PPh₄][X³Se] (ε = ∞, J_max) | 693 Hz | 700 Hz | 809 Hz |
| [PPh₄][1³Se] (ε = 1, J_neutral) | 524 Hz | 591 Hz | 792 Hz |
| Δ-electrostatic = J_neutral – J_max | −38 Hz | −41 Hz | −17 Hz |
| Δ-electrostatic = J_neutral – J_max | −169 Hz | −109 Hz | −63 Hz |
| Δ-electrostatic = J_neutral – J_max | −207 Hz | −150 Hz | −80 Hz |
| Δ-electrostatic/Δtot | 0.82 | 0.73 | 0.79 |
| Δ-electrostatic/Δtot | 0.18 | 0.27 | 0.21 |

For SePP₄Et (point charge, ε = 1, J_point) | 524 Hz | 591 Hz | 792 Hz |
CDCl₃ to DMSO-d₆ (Fig. 3, S38 and S12†). Using the Jᵢ–X values from the high ε and vacuum limits determined from the linear fit of [PPh₄][X] and an identical comparison method to that described above suggests an electrostatic contribution to the overall shift of 73%, which is slightly smaller than that for [PPh₄][I] (82%). In sum, all the experimental data acquired on both [PPh₄][Se] and [PPh₄][Se] support a significant and potentially major role that through-space electrostatic interactions have in the donor properties of these phosphines, and furthermore illustrate that Jᵢ–X is a useful probe for deconvoluting electrostatic from inductive or resonance effects.

Comparing the overall shifts in Jᵢ–X from [PPh₄][I] and [PPh₄][Se] from their respective neutral congeners to other anionic phosphine systems is instructive, even in the absence of comparable solvent dependence studies. In one example a triptycene borate phosphine with a P–B distance of 3.03 Å was compared to a silicon based neutral analogue. The shift in Jᵢ–X observed in CDCl₃ upon switching from the neutral to anionic version approached 90 Hz. The magnitude of this shift is larger than the 63 Hz shift between [PPh₄][I] and SePPh₂Et and the 54 Hz difference between [PPh₄][Se] and SePPh₃ in CDCl₃. The greater magnitude of the shift can be rationalized by the orientation of the anionic functional group, which is constrained to align with the P–Se bond in the triptycene case. The significant change in Jᵢ–X coupling observed in the triptycene case contrasts with another example featuring an anionic BPh₃⁻ group, SePPh₂(p-BPh₃)Ph²⁻. The difference in coupling between this compound and the neutral congener SePPh₃ is only 30 Hz in CDCl₃, likely due to the larger distance between the charged group and the phosphine (6.49 Å from DFT) and delocalization of the anionic charge into the aryl rings on boron. These examples illustrate that the distance, orientation, and anion structure influence the magnitude of the impact on phosphine donor properties.

**C–F oxidative addition reactivity**

The comparatively strong donor properties of phosphine 1 prompted up to consider its application in challenging oxidative addition (OA) reactions. Indeed, anionic phosphines have previously shown enhanced coupling reactivity with aryl chlorides in comparison to neutral isostructural congeners. Uniquely, the Jᵢ–X analysis carried out above with [PPh₄][I] allows for comparison between the reactivity of K1 and phosphines of quantitatively similar donor strengths. Comparison with PEt₃ is instructive as the Jᵢ–X (684 Hz) closely matches that of [PPh₄][I] in DMSO (687 Hz) and the cone angles are similar (132° and 140° for PEt₃ and PPh₂Et)⁷⁷. The reactivity of PCy₃ was also investigated as the Jᵢ–X (675 Hz) closely matches that predicted for [PPh₄][Se] in THF using the 1/4πσ line fit (ε = 7.6, 671 Hz). While these comparisons do not perfectly account for enhanced ion pairing from K⁺ or imperfect matching of cone angles, they are nonetheless useful to reveal trends in reactivity as a function of electrostatic contributions to donor strength.

The OA of aryl fluoride bonds was chosen for this comparison due to a recent computational report suggesting that this reaction is accelerated in the presence of an electric field. Additionally, the OA of C₆F₆ by Ni(COD)₂ (COD = 1,5-cyclooctadiene) with PEt₃ has been previously reported to proceed very slowly, taking ~4 weeks in hexane for completion. Therefore, the rates of C₆F₆ OA by Ni(COD)₂ with K1, PEt₃ and PCy₃ in THF were determined along with the overall conversion.

The combination of Ni(COD)₂ and 2 equivalents of K1 in THF generates a red solution with an absorbance in the UV-vis spectrum at 464 nm (Fig. S79†). The ¹¹B NMR spectrum of the reaction shows the appearance of three new resonances with some unreacted K1, indicating a mixture of differentially ligated species (Fig. S43†). Addition of 10 equivalents of C₆F₆, as well as CFP₃ and OPPh₃ as internal standards, results in the disappearance of these resonances and the formation of a new doublet at 9.6 ppm consistent with coupling to a Ni-F (Fig. S48†). Similarly, the ¹⁹F NMR spectrum shows the appearance of resonances consistent with Ni–C₆F₆ (−117.5, −166.4, and −167.1 ppm) and Ni-F (−383.6 ppm) moieties (Fig. S44 and S45†). The product resonances grow in with an average observed rate of 1.6(2) × 10⁻⁴ s⁻¹, and level off after ~7 hours with an average yield of 25(3)% (Fig. S47, S49 and Table S1†). The reaction between Ni(COD)₂ and 2 equivalents of K₁ and 21 equivalents of C₆F₆ was also examined by monitoring the decay of the absorbance at 464 nm using UV-vis spectrocopry (Fig. S75†). The observed rate of decay is on the same order of magnitude as the rate of formation determined by NMR methods (5.6(4) × 10⁻⁴ s⁻¹). Reducing the amount of added K₁ to 1 equivalent decreases the observed rate (2.8 × 10⁻⁴ s⁻¹), which is inconsistent with a mechanism involving the dissociation of a ligand prior to OA (Fig. S74†). The rate is also reduced with the addition of 3, 4, or 8 equivalents of K₁, with the appearance of a new absorbance at 375 nm suggesting additional coordination of K₁ to Ni may be possible (Fig. S76–S78†). As a control, the absorbance at 464 nm was monitored in the absence of substrate and indicated minimal decay over the same time frame (Fig. S79†).

Carrying out the same reaction with PEt₃ and PCy₃ results in the growth of similar NMR signals as those observed with K₁, but with significantly slower rates of product formation (3.7(7) × 10⁻⁴ s⁻¹ and 2.0(1) × 10⁻⁵ s⁻¹, respectively) (Fig. S30–S38 and Table S1†). In contrast to K₁, the OA product growth continues throughout the time the reaction was monitored, reaching 24(2)% at 114 h for PEt₃, and 66(15)% at 53 h for PCy₃. The enhanced rate observed with K₁ not only supports previous observations that anionic groups enhance rates of OA reactions, but also demonstrates that the rate enhancement is greater than would be predicted on the basis of donor strength. This is perhaps most clearly illustrated by the one order of magnitude rate acceleration with K₁ over PCy₃, despite the nearly identical donor strengths predicted by our analysis. A distinct mechanism for electrostatic rate enhancement beyond an increase in donor strength has been suggested previously with an anionic carborane phosphine, wherein accelerated OA reactivity was attributed to ligand dissociation and transition state (TS) stabilization. The exact nature of the rate acceleration with K₁ is not yet clear. It is possible that the TS is lowered by the presence of an electric field generated by the BF₃⁻ ion, as is predicted computationally, but other factors, such as ion...
pairing with K⁺, may also be determinative. Regardless, these results emphasize that anionic charges enhance reactivity through mechanisms beyond simply increasing donor strength.

Catalytic defluoroborylation reactivity

The significant rate acceleration observed in stoichiometric reactivity led us to investigate catalytic C–F borylation with K1 and Ni(COD)₂. Defluoroborylation of fluorinated arenes with Ni has been reported previously with N-heterocyclic carbene (NHC) and PCy₃ ligands.¹³¹–¹³³ The use of strongly donating ligands is consistent with the difficulty of the OA step, as C–F bonds have the highest BDE among carbon–halogen bonds.¹³¹ Likewise, high catalyst loadings (10%), reaction temperatures (110 °C), and long reaction times (≥12 h) highlight the difficulty of these transformations.

Optimization reactions were carried out using K1 and Ni(COD)₂ for the defluoroborylation of 1,3-difluorobenzene using B₂pin₂ (bis[pinacolato]diboron) as the test substrate. Ultimately, a 50% yield of 1-Bpin-3-C₆H₄F₂ was realized with the following conditions: 9% catalyst loading with 1.8 equivalents of CsOH, 0.72–0.75 equivalents of CsOH–xH₂O (15–20% H₂O), and 1.9 equivalents of methanol in THF heated at 50 °C for 4 hours (Tables S17–S24† contain information on optimization trials). Notably, substituting K1 with PEt₃, PCy₃, or PPh₂Et under identical reaction conditions results in no conversion to the borylated product (Table S21†). NMR monitoring over time indicates that the reaction is complete after 2 hours (Table S21†). Increasing the temperature to 100 °C for 2 hours or stirring at room temperature for 22 hours only slightly affects the yield (48% and 44%, respectively, Table S22†). Switching B₂pin₂ for B₂neop₂ (bis[neopentyl glycolato]diboron) or B₂cat₂ (bis[chatecolato]diboron) to test alternative transmetallating agents significantly reduces the yield (32% and 0%, Table S22†), in contrast to previous studies with PCy₃.¹³⁴ Both MeOH and CsOH are required for catalysis, with alternative alcohols or metal salts reducing the yield. Exchanging the K⁺ counterion on 1 for more solubilizing counterions does not improve the yield (Table S23†), and no trend is observed with solvent ε across a limited series of etheral solvents (Table S24†).

This method was extended to other fluoroarenes to examine the scope of reactivity (Fig. 4). The highest yield observed is for 1,3 difluorobenzene (50%), followed by fluorobenzene (42%), with lower yields for more highly fluorinated substrates. The trend of decreasing yields with higher levels of fluorination contrasts with the trend observed with an NHC, where more highly fluorinated substrates are more easily defluoroborylated.¹³³ Additionally, homocoupling is competitive in substrates with adjacent fluorine atoms in our system. The fluorobenzene borylation with K1 is higher than that with an NHC ligand (20%),¹³¹ but in general other systems perform defluoroborylation of more diverse fluoroarenes with higher yields than the current system.¹³¹,¹³²

Based on the observed formation of a C–F OA product with C₆F₆, it is likely that defluoroborylation proceeds through a traditional OA, transmetalation, and reductive elimination mechanism. The differing reactivity trend with arené fluorination implies that the enhanced OA rate in the present system makes transmetalation the turnover limiting step. This hypothesis is consistent with increased yields with an excess of B₂pin₂ as well as the need for more nucleophilic hydroxide or alkoxide additives over fluoride sources. We speculate that in situ generated methoxide may facilitate transmetalation of B₂pin₂ by exchanging with Ni–F intermediates, as a similar σ-bond metathesis of B₂pin₂ with Ni alkoxide complexes has been reported.¹³⁵ However, the specific role played by Cs⁺ and MeOH remains unclear. Faster rates and unique reaction conditions for this system (i.e., lower temperature, base, water and alcohol) suggest that it may offer complementary reactivity to the established neutral phosphine systems and motivates further investigation. Regardless of specific methodological applications, the fact that the inclusion of a BF₃ group enables a dialkylalky phosphine to perform comparably with an NHC in C–F borylation highlights how electrostatic effects can both dramatically enhance stoichiometric OA reactivity as well as catalytic processes.

Conclusions

In conclusion, a new anionic phosphine ligand has been synthesized and demonstrates that the inclusion of an anionic trifluoroborate group dramatically increases the donor properties relative to neutral analogues. Furthermore, a series of experiments and calculations have demonstrated that a significant portion of the increase in donor strength arises from electrostatic as opposed to inductive effects. The electrostatic interactions in this ligand accelerate OA rates by an order of magnitude compared to ligands of similar donor strength, consistent with theoretical predictions. This enhanced OA reactivity can be leveraged for the catalytic defluoroborylation of
C–F bonds with reactivity trends that differ from previously reported examples. While there are several reports on the influence of appended anionic groups on mono- or polydentate phosphine ligands, this work is the first case where the relative contributions from inductive versus electrostatic donation have been disentangled. The ability of charged groups to stabilize specific resonance structures, such as the zwitterionic Se–P′R3 structure, offers tremendous potential in tuning catalytic systems as we demonstrate here. The fact that a major portion of the increase in donor strength arises from electrostatic effects in common organic solvents with charge-diffuse counterions has important implications for ligand design as the directionality of electric fields provides a unique variable for influencing reactivity and breaking classic free–energy relationships.

Data availability
Detailed experimental and computational data can be found in the ESI.†

Author contributions
The project was planned out and the manuscript was written by M. L. K., A. J. M., and J. S. A. The experiments were carried out by M. L. K. and A. J. M. The crystallographic characterization was carried out by A. J. M. and A. S. F. The optimization of NMR parameters for reaction kinetics was carried out my M. L. K. and J. W. K.

Conflicts of interest
There are no conflicts to declare.

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