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Organoiron- and Fluoride-Catalyzed Phosphinidene Transfer to Styrenic Olefins in a Stereoselective Synthesis of Unprotected Phosphiranes

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Supporting Information

ABSTRACT: Catalytic phosphiranation has been achieved, allowing preparation of trans-1-R-2-phenylphosphiranes (R = t-Bu; 1-i-Pr; i-Pr) from the corresponding dibenzo-7-(R)-7-phospha-norbornadiene (RPA, \(A = C_9H_{18}\) anthracene) and styrene in 73% and 57% isolated yields, respectively. The catalytic system requires tetramethylammonium fluoride (TMAF) and \([\text{Fp(THF)}][\text{BF}_4]\) \((\text{Fp} = \text{Fe}(\eta^5-C_5H_5)(\text{CO})_2)\). In the case of the t-Bu derivative, the reaction mechanism was probed using stoichiometric reaction studies, a Hammett analysis, and a deuterium labeling experiment. Together, these suggest the intermediacy of iron-phosphido \(\text{FpP}(\text{F})(\text{THF})\) with TMAF. Two other plausible reaction intermediates, \([\text{Fp}(\text{t-Bu})][\text{BF}_4]\) and \([\text{Fp}(1-i-Pr)][\text{BF}_4]\), were prepared independently and structurally characterized.

Cyclopropanation, aziridination, and epoxidation reactions are widely used to construct strained three-membered rings desirable for further synthetic elaboration. Transition-metal catalysts have been widely used to facilitate these transformations under mild reaction conditions with good stereoselective and enantioselective control. In contrast, the phosphorus analog (‘phosphiranation’) remains in its infancy, despite the documented utility of phosphiranes as catalyst ligands, polymer precursors, and synthetic intermediates. Only a handful of transition metal-promoted phosphirane syntheses have been reported, and catalytic phosphiranation to give unprotected \(\lambda^2\)-phosphiranes remains unknown despite decades of interest.

Perhaps one reason for the underdevelopment of catalytic phosphinidene transfer reactions stems from the lack of availability of appropriate precursors, a limitation recently articulated by de Bruin and Schneider. Hallmarks of good substrates for group-transfer chemistry feature stable, neutral leaving groups, such as \(\text{N}_2\) or iodobenzene. In the case of phosphiranes, only a limited number of catalytic group transfer reactions are known, generally involving activation of \(\text{P}−\text{H}\) bonds of primary phosphines in reactions disclosed by the groups of Waterman and Layfield.

We have developed dibenzo-7-phosphanorbornadiene compounds (RPA, \(A = \text{anthracene}, C_9H_{18}\) Scheme 1), readily available from RPCl\(_3\) and MgA·3THF, as useful synthetic equivalents for phosphinidenes. When \(R\) is a \(\pi\)-donating substituent, such as a dimethylamino group, the \(\text{Me}_2\text{NPA}\) species can undergo a thermal unimolecular fragmentation to give anthracene and a free singlet \((\text{amu})\)phosphinidene \((\text{Me}_2\text{NP})\) that can add to unsaturated substrates such as 1,3-cyclohexadiene to give a 7-phosphanorbornene. In contrast, when \(R\) is an alkyl substituent (for example, t-BuPA), the corresponding triplet phosphinidene is not transferred to unsaturated substrates, instead leading to recovery of starting material and formation of some \((\text{t-BuP})_3\). Therefore, we sought to develop a process in which t-BuPA could be used as a reagent for catalytic tert-butyl phosphinidene transfer to alkenes, producing phosphirane products.

Following unproductive screening of a variety of catalysts \((\text{S1.2})\) selected for their ability to effect cyclopropanation or aziridination, we scored a hit by using sources of the \(\text{Fp}^+\) cation in conjunction with fluoride. In analogy to known reactivity of \([\text{Fp}(\text{alkene})][\text{BF}_4]\) compounds with phosphines, we sought to promote \(\text{P}−\text{C}\) bond formation by treatment with t-BuPA. Treatment of a slurry of \([\text{Fp}(\text{styrene})][\text{BF}_4]\) in dichloromethane with a stoichiometric amount of t-BuPA led to the rapid dissolution of all material. Analysis of this reaction mixture by electrospray ionization mass spectrometry (ESI-MS) and NMR spectroscopy \((\text{31P NMR:} +141.8 \text{ ppm})\) was consistent with the addition of t-BuPA to the iron-coordinated styrene complex to produce an addition product \((3)\) containing a phosphonium and iron-alkyl functionality within the same molecule (Scheme 2). Unfortunately, 3 could not be isolated in pure form. This was in part attributed to its relatively short lifetime in solution; after 24 h at 23 °C it had undergone complete conversion to \([\text{Fp}(\text{t-BuPA})][\text{BF}_4]\) and free styrene, suggesting that the formation of 3 is reversible \((\text{S1.8})\).

Having observed \(\text{P}−\text{C}\) bond formation, \([\text{Fp}(\text{styrene})][\text{BF}_4]\) and other sources of \(\text{Fp}^+\) were screened as catalysts for the phosphiranation reaction, leading to observation of the desired

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product by $^{31}$P NMR spectroscopy (−165.0 ppm). A complication was soon encountered as different sources of Fp$^+$ gave wide ranges of yield. The best performing reactions employed [BF$_4$]$^-$ as the counteranion, which was frequently observed to decompose at the reaction temperature (85 °C) as assayed by $^{19}$F NMR spectroscopy. This prompted an investigation of the possible catalytic role of fluoride, generated upon [BF$_4$]$^-$ decomposition. Addition of the fluoride source tetrabutylammonium fluoride (TMAF) in catalytic quantities (15 mol%) led to clean and reproducible formation of the desired phosphirane. The optimized reaction conditions comprise heating t-BuPA and styrene (10 equiv) with [Fp(THF)][BF$_4$] (10 mol%) and TMAF (15 mol%) in THF at 85 °C for 12 h (Scheme 1). Control experiments confirm the requirement of both catalysts for the formation of 1-t-Bu (Table 1). Using other potential sources of tert-butylphosphinidenyl (t-BuPH$_2$ or (t-BuP)$_3$) in place of t-BuPA did not lead to the formation of 1-t-Bu.

Table 1. Control Experiments

| deviation from standard conditions$^a$ | yield (%)$^b$ |
|--------------------------------------|-------------|
| none                                 | 90          |
| no [Fp(THF)][BF$_4$]                 | 5           |
| no TMAF                              | 5           |
| no [Fp(THF)][BF$_4$] or TMAF        | 0           |
| t-BuPH$_2$ instead of t-BuPA         | 0           |
| (t-BuP)$_3$ instead of t-BuPA        | 0           |

$^a$0.06 M t-BuPA in THF with reagent ratios shown in Scheme 1, 85 °C, 24 h. $^b$Yield of 1-t-Bu determined by integration of the product relative to a standard by $^{31}$P{1H} NMR spectroscopy.

The compound was produced exclusively as trans-1-t-BuPA-2-phenylphosphiranone (1-t-Bu) by comparison with previous literature reports$^{22,23}$ as well as characterization by multinuclear NMR spectroscopy, high-resolution mass spectrometry (HRMS), and elemental analysis. Evidence for the relative stereochemistry of the t-Bu and phenyl substituents on the phosphirane ring is provided by $^1$H NMR spectroscopy: the proton occupying the same face of the ring as the phosphorus lone pair is associated with a much larger $^3$J$_{P-H}$ coupling constant (18.8 Hz) than are the two on the opposing face (2.6 and 2.2 Hz, respectively).$^{24}$ No evidence for the cis isomer was observed by NMR spectroscopy. Use of i-PrPA in place of t-BuPA led to the new compound 1-i-Pr with only a small drop in diastereomeric ratio (Scheme 1).

Though previously observed by $^{31}$P NMR spectroscopy as one component of a mixture of several phosphorus-containing species, phosphirane 1-t-Bu evidently has not previously been isolated as a pure substance.$^{22,23}$ We found that 1-t-Bu could be purified by simple distillation at reduced pressure as a colorless liquid (73%, 0.53 g) that froze at −35 °C and could be stored for months at this temperature with no signs of decomposition. These observations are consistent with the properties reported for related phosphiranes.$^{25,26}$

The Fp$^+$-coordinated phosphirane complex [Fp(1-t-Bu)][BF$_4$] was prepared by independent synthesis in order to determine its spectroscopic properties and possible role as an observable reaction intermediate. Treatment of [Fp(THF)][BF$_4$] with 1.1 equiv of 1-t-Bu in dichloromethane gave rise to [Fp(1-t-Bu)][BF$_4$], isolated in 84% yield after precipitation by addition of pentane. Using the same synthetic procedure, [Fp(t-BuPA)][BF$_4$] could be prepared from [Fp(THF)][BF$_4$] and t-BuPA in 98% yield. Both [Fp(1-t-Bu)][BF$_4$] and [Fp(t-BuPA)][BF$_4$] were characterized by their $^{31}$P NMR shifts (+220.7 and −76.2 ppm, respectively), in addition to structural characterization by X-ray crystallography (Figure 1). The crystallographic study of [Fp(1-t-Bu)][BF$_4$] confirms the spectroscopically assigned trans arrangement of the phenyl and tert-butyl substituents of the phosphirane ring of 1-t-Bu. The bond angles comprising this ring were found to be 49.2(6)$^0$, 64.2(1)$^0$, and 66.6(1)$^0$ at P1, C3, and C2, respectively. With both Fp$^+$-coordinated phosphines characterized, the reaction was monitored at 85 °C by $^{31}$P NMR spectroscopy, confirming the presence of [Fp(t-BuPA)][BF$_4$] in the reaction mixture under conditions relevant to catalysis. In terms of its $^{31}$P{1H} NMR spectroscopy, the phosphoraphosphine 1-t-Bu was not observed under the same conditions, suggesting it either does not form or that 1-t-Bu is rapidly displaced by a different ligand.

In order to shed light on a plausible mechanism by which phosphirane 1-t-Bu forms under the reaction conditions, the stoichiometric reaction of [Fp(t-BuPA)][BF$_4$] with TMAF was studied. Treatment of [Fp(t-BuPA)][BF$_4$] with equimolar TMAF (CH$_2$Cl$_2$, 23 °C) resulted in a rapid color change from bright yellow to bright orange. Analysis by NMR spectroscopy ($^1$H, $^{31}$P, and $^{19}$F) indicates formation of iron-phosphido FpP(F)(t-Bu) (2) and anthracene, resulting from attack of fluoride at the phosphonium-like phosphorus center.$^{17}$ Iron-phosphido 2 was characterized by the chemical shift of the $^{31}$P and $^{19}$F nuclei, found at +370.2 ppm (DFT calcd = +391.2 ppm) and −202.6 ppm (DFT calcd = −226.0 ppm), respectively, along with a $^3$J$_{P-F}$ value of 823.3 Hz. $^1$H NMR data and HRMS were also consistent with the formulation of 2. In terms of its relevance to catalysis, iron-phosphido 2, which may be regarded as a phosphinidenoid,$^{17}$ was observed by NMR spectroscopy under the standard reaction conditions at 85 °C in THF–d$_2$.
along with \([\text{Fp}(\text{t-BuPA})][\text{BF}_4]\), \(\text{t-BuPA}\), and 1-t-Bu. So far, attempts to isolate 2 have been unsuccessful, in part due to its high solubility in organic solvents. Importantly, a closely related literature compound \((\text{Fp}^+\text{P}^-(\text{Cl})(\text{t-Bu})\), \(\text{Fp}^+ = \text{Fe}(\eta^3-\text{C}_5\text{Me}_3)(\text{CO})_2\)) is reported as being nucleophilic at phosphorus, reacting with the strong alkylating agent methyl iodide to give the phosphonium iodide \([\text{Fp}^+\text{P}^-(\text{Cl})(\text{t-Bu})(\text{Me})][\text{I}]\).

A Hammett study was carried out to illuminate the nature of the rate-determining step (RDS). Competition experiments were performed under the standard reaction conditions, using 5 equiv each of styrene and a para-substituted styrene as the substrates. The analysis showed that electron-poor styrenes react more rapidly than electron-rich styrenes, resulting in a Hammett parameter \((\rho)\) of +0.59 (Figure 2). This small positive value indicates buildup of negative charge in the RDS, consistent with attack of 2 toward styrene as the corresponding elementary step. A previous Hammett analysis of the addition of para-substituted styrenes to transient \((\text{CO})_2\text{W}-\text{coordinated phosphinidenes gave a negative value for} \rho \text{ of} \sim -0.60,\text{ highlighting the difference in mechanism between known reactions of electrophilic phosphinidenes with olefins versus our proposed pathway involving a nucleophilic iron-phosphido species.}

Finally, cis-β-deuterostyrene was tested as a substrate under the standard reaction conditions in order to differentiate between stepwise and concerted reaction mechanisms. The NMR spectra confirmed the formation of two isomers of deuterated phosphirane product in which the deuterium and phenyl substituents occupy cis and trans positions on the phosphirane ring, respectively (Figure 3B). This observation indicates a stepwise pathway (ionic or radical) in which a reaction intermediate has a sufficient lifetime for C-C bond rotation to occur. Nucleophilic attack on styrene by phosphido 2 to give intermediate 4 (Figure 3C), containing a C-C single bond, would fulfill this requirement. Under the reaction conditions, the bulk cis-β-deuterostyrene in solution was found to undergo scrambling to give a mixture of cis- and trans-β-deuterostyrene (3:1 ratio). However, this ratio is significantly less than that observed for the cis and trans isomers (with respect to the Ph and D substituents) of the product phosphiranes (1:1.5 ratio), suggesting that the observation of both the cis and trans isomers (with respect to Ph and D) in the product phosphiranes is not an artifact of bulk styrene isomerization (S1.13). Additionally, isomerization of the bulk styrene did not occur in a control experiment (standard conditions without \(\text{t-BuPA}\)) and is thus tentatively accounted for by reversible addition of iron-phosphido 2 to styrene. In this context, it is noteworthy that the related \(\text{Fp-phosphido species Fp}^-\text{P}(\text{Ph})_2\) catalyzes the isomerization of excess dimethyl maleate to dimethyl fumarate.

In light of the foregoing mechanistic experiments, we put forward the working hypothesis shown in Figure 3C. Initial ligand substitution of \(\text{t-BuPA with} \[\text{Fp}(\text{THF})\]^+ \text{ results in} \[\text{Fp}(\text{t-BuPA})]^+\). The addition of a fluoride anion to \([\text{Fp}(\text{t-BuPA})][\text{BF}_4],\) resulting in compound 2, is conceptually related to the ability of chloride to promote anthracene loss from a phosphonium derived from an RPA compound that we reported recently and was the subject of a more detailed computational study by Grimme and co-workers. Next, addition of styrene to 2 furnishes intermediate 4 capable of rotation about the newly formed C-C single bond, which could plausibly go on to form \([\text{Fp}(1-t-Bu)]^+\) with the ejection of fluoride. Closure of the phosphirane ring in this sequence presumably dictates the trans stereochemistry found in the product.

This work introduces a novel catalytic styrene phosphirane reaction. Phosphiranes are excellent target molecules for transition-metal catalyzed syntheses that do not suffer from product inhibition, as the phosphirane three-membered ring confers high s character on the included phosphorus lone pair with consequent diminished ligating ability and ease of dissociation relative to typical tertiary phosphines. Importantly, the reaction allows for facile preparation of two isomers (with respect to Ph and D) in the product phosphiranes in good yield, enabling their development as a ligands for transition metals and as potential phosphorus-containing polymer precursors. The phosphirane products are chiral, and the potential future use of a chiral catalyst raises the possibility of preparing \(P\)-chiral phosphiranes from RPA.
compounds using readily accessible organoiron and fluoride catalysts.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free on the ACS Publications website at DOI: 10.1021/jacs.9b07069.

Experimental and computational details (PDF)

Crystalographic data for CCDC 1936231 (PDF, CIF)

Crystallographic data for CCDC 1936232 (PDF, CIF)

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Notes

The authors declare no competing financial interest.

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