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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

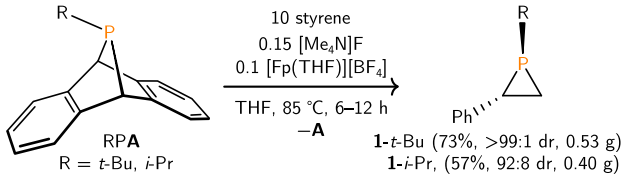
ABSTRACT: Catalytic phosphiranation has been achieved, allowing preparation of *trans*-1-R-2-phenylphosphiranes (R = *t*-Bu: **1**-*t*-Bu; *i*-Pr: **1**-*i*-Pr) from the corresponding dibenzo-7-(R)-7-phospha-norbornadiene (RP**A**, **A** = $C_{14}H_{10}$, anthracene) and styrene in 73% and 57% isolated yields, respectively. The cocatalyst system requires tetramethylammonium fluoride (TMAF) and $[Fp(THF)][BF_4]$ (Fp = $Fe(\eta^5\text{-}C_5H_5)(CO)_2$). 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 FpP(F)(*t*-Bu) (**2**), generated independently from the stoichiometric reaction of [Fp(*t*-BuP**A**)][BF_4] with TMAF. Two other plausible reaction intermediates, [Fp(*t*-BuP**A**)][BF_4] and [Fp(**1**-*t*-Bu)][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.[1] Transition-metal catalysts have been widely used to facilitate these transformations under mild reaction conditions with good stereoselective and enantioselective control.[1] In contrast, the phosphorus analog ("phosphiranation") remains in its infancy, despite the documented utility of phosphiranes as catalyst ligands,[2] polymer precursors,[3] and synthetic intermediates.[4] Only a handful of transition metal-promoted phosphirane syntheses have been reported,[5−8] and catalytic phosphiranation to give unprotected λ^3-phosphiranes remains unknown despite decades of interest.[6,7,9−11]

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.[12] Hallmarks of good substrates for group-transfer chemistry feature stable, neutral leaving groups, such as N_2 or iodobenzene.[1] In the case of phosphorus, only a limited number of catalytic group transfer reactions are known, generally involving activation of P−H bonds of primary phosphines in reactions disclosed by the groups of Waterman[13] and Layfield.[14]

We have developed dibenzo-7-phosphanorbornadiene compounds (RP**A**, **A** = anthracene, $C_{14}H_{10}$, Scheme 1), readily available from $RPCl_2$ and Mg**A**·3THF,[15] as useful synthetic equivalents for phosphinidenes.[16,17] When R is a π-donating

Scheme 1. Preparation of Phosphiranes 1-*t*-Bu and 1-*i*-Pr from the Corresponding RPA Compounds



substituent, such as a dimethylamino group, the Me_2NP**A** species can undergo a thermal unimolecular fragmentation to give anthracene and a free singlet (amino)phosphinidene (Me_2NP) that can add to unsaturated substrates such as 1,3-cyclohexadiene to give a 7-phosphanorbornene.[16] In contrast, when R is an alkyl substituent (for example, *t*-BuP**A**), the corresponding triplet phosphinidene is not transferred to unsaturated substrates, instead leading to recovery of starting material and formation of some $(t\text{-BuP})_3$.[16] Therefore, we sought to develop a process in which *t*-BuP**A** 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 (S1.2) selected for their ability to effect cyclopropanation or aziridination, we scored a hit by using sources of the Fp^+ cation in conjunction with fluoride. In analogy to known reactivity of [Fp(alkene)][BF_4] compounds with phosphines,[18−20] we sought to promote P−C bond formation by treatment with *t*-BuP**A**. Treatment of a slurry of [Fp(styrene)][BF_4][21] in dichloromethane with a stoichiometric amount of *t*-BuP**A** led to the rapid dissolution of all material. Analysis of this reaction mixture by electrospray ionization mass spectrometry (ESI-MS) and NMR spectroscopy (^{31}P NMR: +141.8 ppm) was consistent with the addition of *t*-BuP**A** 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 [Fp(*t*-BuP**A**)][BF_4] and free styrene, suggesting that the formation of **3** is reversible (S1.8).

Having observed C−P bond formation, [Fp(styrene)][BF_4] and other sources of Fp^+ were screened as catalysts for the phosphiranation reaction, leading to observation of the desired

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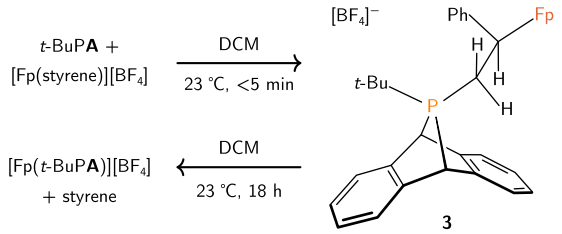
Scheme 2. Reaction of *t*-BuPA with [Fp(styrene)][BF_4]



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 tetramethylammonium fluoride (TMAF) in catalytic quantities (15 mol %) led to clean and reproducible formation of the desired phosphirane. The optimized reaction conditions comprise heating *t*-BuP**A** 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*-butylphosphinidene (*t*-$BuPH_2$ or $(t\text{-BuP})_3$) in place of *t*-BuP**A** 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*-BuP**A**	0
$(t\text{-BuP})_3$ instead of *t*-BuP**A**	0

[a]0.06 M *t*-BuP**A** 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 product was assigned exclusively as *trans*-1-*t*-Bu-2-phenylphosphirane (**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 ^1H NMR spectroscopy: the proton occupying the same face of the ring as the phosphorus lone pair is associated with a much larger $^2J_{P-H}$ 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*-PrP**A** in place of *t*-BuP**A** 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*-BuP**A**)][BF_4] could be prepared from [Fp(THF)][BF_4] and *t*-BuP**A** in 98% yield. Both [Fp(**1**-*t*-Bu)][BF_4] and [Fp(*t*-BuP**A**)][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

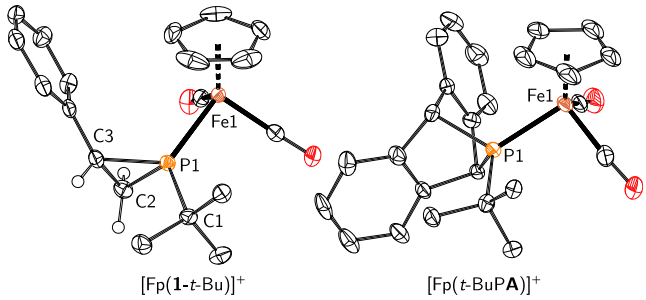


Figure 1. Molecular structures of [Fp(**1**-*t*-Bu)][BF_4] and [Fp(*t*-BuP**A**)][BF_4] with thermal ellipsoids set at the 50% probability level. Selected hydrogen atoms and the tetrafluoroborate anions have been omitted for clarity. Selected bond distances and angles (Å, °) [Fp(**1**-*t*-Bu)][BF_4]: P1−Fe1:2.2283(6); P1−C2:1.811(2); P1−C3:1.846(2); C2−C3:1.524(3). [Fp(*t*-BuP**A**)][BF_4]: Fe1−P1:2.258(2).

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 49.26(9)°, 64.2(1)°, and 66.6(1)° 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*-BuP**A**)][BF_4] in the reaction mixture under conditions relevant to catalysis. [Fp(**1**-*t*-Bu)][BF_4] 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*-BuP**A**)][BF_4] with TMAF was studied. Treatment of [Fp(*t*-BuP**A**)][BF_4] with equimolar TMAF (CH_2Cl_2, 23 °C) resulted in a rapid color change from bright yellow to bright orange. Analysis by NMR spectroscopy (^1H, ^{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 $^1J_{P-F}$ value of 823.3 Hz. ^1H 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,[27] was observed by NMR spectroscopy under the standard reaction conditions at 85 °C in THF-d_8,

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along with [Fp(*t*-BuP**A**)][BF_4], *t*-BuP**A**, and **1**-*t*-Bu. So far, attempts to isolate **2** have been unsuccessful, in part due to its high solubility in organic solvents. Interestingly, a closely related literature compound (Fp*P(Cl)(*t*-Bu), Fp* = Fe(η^5-C_5Me_5)-$(CO)_2$) is reported as being nucleophilic at phosphorus, reacting with the strong alkylating agent methyl iodide to give the phosphonium iodide [Fp*P(Cl)(*t*-Bu)(Me)][I].[28]

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.[29] The analysis showed that electron-poor styrenes react more rapidly than electron-rich styrenes, resulting in a Hammett parameter (ρ) of +0.59 (Figure 2). This small positive

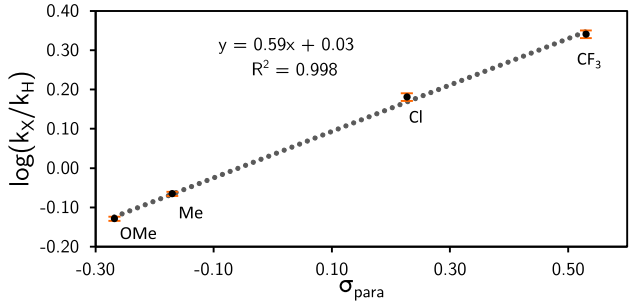

Figure 2. Hammett plot determined by competition experiments with *p*-substituted styrenes. Error bars correspond to the 95% confidence intervals.

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 $(CO)_5W$-coordinated phosphinidenes gave a *negative* value for ρ of −0.60,[30] highlighting the difference in mechanism between known reactions of electrophilic phosphinidene complexes 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. ^{2}H 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 *t*-BuP**A**) and is thus tentatively accounted for by *reversible* addition of iron-phosphido **2** to styrene. In this context, it is

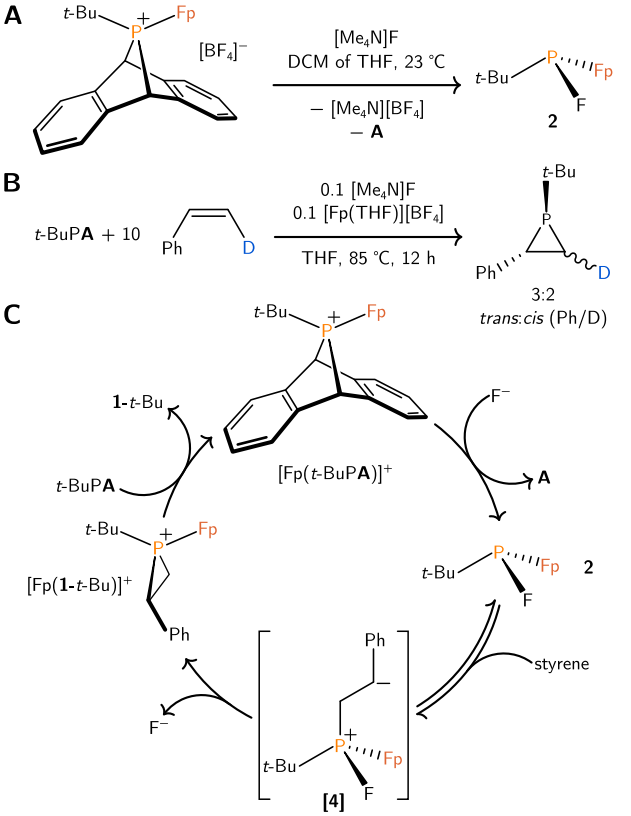

Figure 3. (A) Stoichiometric reaction of [Fp(*t*-BuP**A**)][BF_4] with TMAF. (B) Deuterium labeling study. (C) Proposed catalytic cycle leading to the formation of **1**-*t*-Bu.

noteworthy that the related Fp-phosphido species Fp−P(Ph)$_2$ catalyzes the isomerization of excess dimethyl maleate to dimethyl fumarate.[31]

In light of the foregoing mechanistic experiments, we put forward the working hypothesis shown in Figure 3C. Initial ligand substitution of *t*-BuP**A** with [Fp(THF)]$^+$ results in [Fp(*t*-BuP**A**)]$^+$. The addition of a fluoride anion to [Fp(*t*-BuP**A**)][BF_4], resulting in compound **2**, is conceptually related to the ability of chloride to promote anthracene loss from a phosphonium derived from an RP**A** compound that we reported recently[17] and was the subject of a more detailed computational study by Grimme and co-workers.[32] 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 [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 phosphiranation 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.[33] Importantly, the reaction allows for facile preparation of two phosphiranes in good yield, enabling their development as a ligands for transition metals and as potential phosphorus-containing polymer precursors.[3,34,35] The phosphirane products are chiral, and the potential future use of a chiral catalyst raises the possibility of preparing *P*-chiral phosphiranes from RP**A**

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compounds using readily accessible organoiron and fluoride catalysts.

■ ASSOCIATED CONTENT

Supporting Information

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Experimental and computational details (PDF)
Crystallographic 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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