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

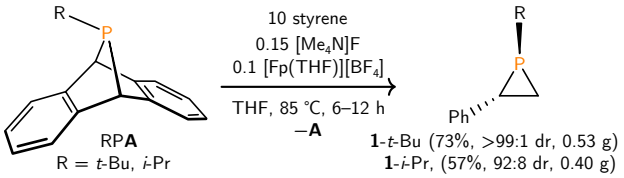
Michael B. Geeson, Wesley J. Transue, and Christopher C. Cummins*
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, USA
Received August 7, 2019; E-mail: ccummins@mit.edu

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 co-catalyst system requires tetramethylammonium fluoride (TMAF) and [Fp(THF)][BF_4] (Fp = Fe(η^5-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 — this 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 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*-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.



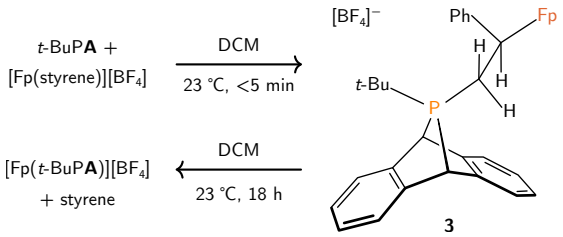
Scheme 1. Preparation of phosphiranes **1**-*t*-Bu and **1**-*i*-Pr from the corresponding RP**A** compounds.

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*-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

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 (Fig. 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



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

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 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 counter anion, 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 (10 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 (10 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*-butyl phosphinidene in place of *t*-BuP**A**, *t*-$BuPH_2$ and $(t\text{-BuP})_3$, did not lead to the formation of **1**-*t*-Bu.

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 ^{1}H 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 equivalents 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 (Fig. 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 49.26(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.

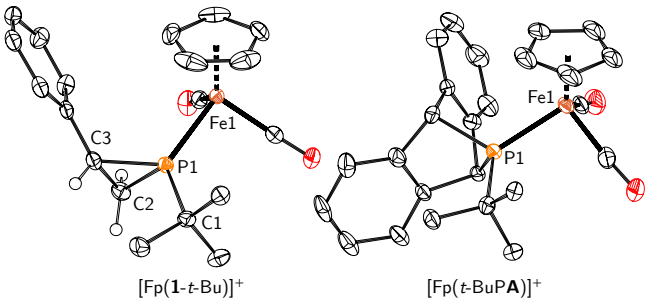


Figure 1. Molecular structures of [Fp(**1**-*t*-Bu)][BF_4] and [Fp(*t*-BuP**A**)][BF_4] with thermal ellipsoids set at the 50% probability level. Selected hydrogen atoms and the tetrafluoroborate anions have been omitted for clarity. Selected bond distances and angles (Å, °) [Fp(**1**-*t*-Bu)][BF_4]: 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).

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 (^{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 calc. = +391.2 ppm) and −202.6 ppm (DFT calc. = −226.0 ppm), respectively, along with a $^1J_{P-F}$ 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,[27] was observed by NMR spectroscopy under the standard reaction conditions at 85 °C in THF-d_8, 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

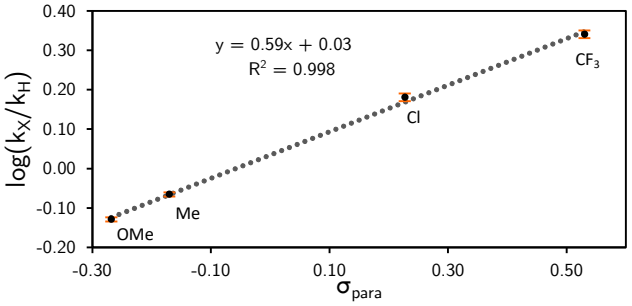


Figure 2. Hammett plot determined by competition experiments with *p*-substituted styrenes. Error bars correspond to the 95% confidence intervals.

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. This small positive value indicates build-up 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.

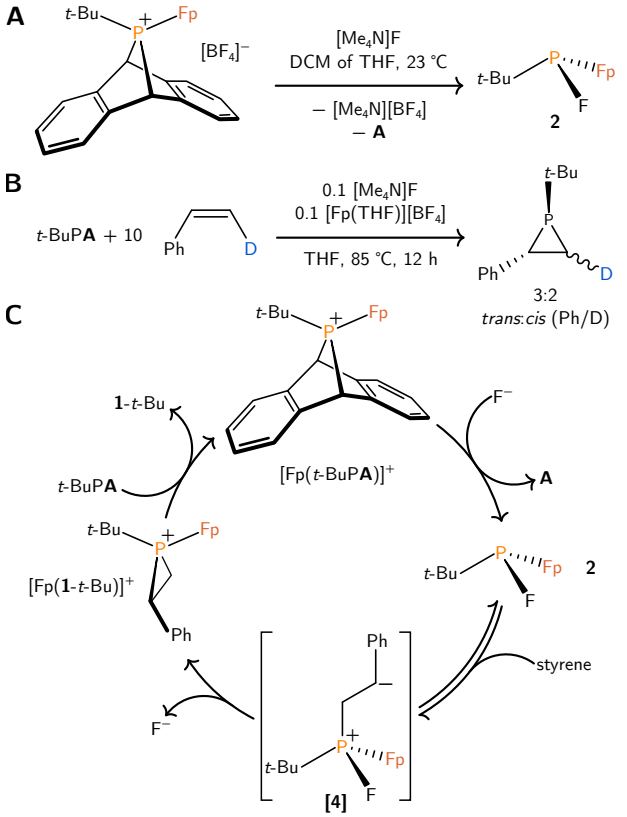


Figure 3. **A**: Stoichiometric reaction of [Fp(*t*-BuP**A**)][BF_4] with TMAF. **B**: Deuterium labeling study. **C**: Proposed catalytic cycle leading to the formation of **1**-*t*-Bu.

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 (Fig. 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**] (Fig. 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 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 forgoing mechanistic experiments, we put forward the working hypothesis shown in Fig. 3C. Initial ligand substitution of *t*-BuP**A** with $[Fp(THF)]^+$ results in $[Fp(t\text{-BuP}\mathbf{A})]^+$. 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 coworkers.[32] Next, addition of styrene to **2** furnishes intermediate [**4**] capable of rotation about the newly-formed C–C single bond, and which could plausibly go on to form $[Fp(\mathbf{1}\text{-}t\text{-Bu})]^+$ 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 phosphiranes products are chiral and the potential future use of a chiral catalyst raises the possibility of preparing *P*-chiral phosphiranes from RP**A** compounds using readily accessible organoiron and fluoride catalysts.

Acknowledgments

We thank the National Science Foundation (NSF-CHE-1664799) for financial support of this research and the MGH-PCC for computational resources.

Supplementary Information

Experimental and computational details are provided in the supporting information. This material is available free of charge via the internet at `http://pubs.acs.org`. Crystallographic data are available from the CSD under refcodes 1936231 and 1936232.

References

(1) (a) Lebel, H.; Marcoux, J.-F.; Molinaro, C.; Charette, A. B. Stereoselective Cyclopropanation Reactions. *Chem. Rev.* **2003**, *103*, 977–1050; (b) Müller, P.; Fruit, C. Enantioselective Catalytic Aziridinations and Asymmetric Nitrene Insertions into CH Bonds. *Chem. Rev.* **2003**, *103*, 2905–2920; (c) Lane, B. S.; Burgess, K. Metal-Catalyzed Epoxidations of Alkenes with Hydrogen Peroxide. *Chem. Rev.* **2003**, *103*, 2457–2474.

(2) (a) Kamer, P. C. J., van Leeuwen, P. W. N. M., Eds. *"Highly Strained Organophosphorus Compound" in Phosphorus(III) Ligands in Homogeneous Catalysis: Design and Synthesis*; John Wiley & Sons, Ltd: Chichester, UK, 2012; (b) Liedtke, J.; Loss, S.; Widauer, C.; Grützmacher, H. Phosphiranes as Ligands for Platinum Catalysed Hydrosilylations. *Tetrahedron* **2000**, *56*, 143–156; (c) Grützmacher, H.; Liedtke, J.; Frasca, G.; Läng, F.; Pé, N. Syntheses and Chemistry of Very Robust Phosphiranes. *Phosphorus, Sulfur Silicon Relat. Elem.* **2002**, *177*, 1771–1774; (d) Liedtke, J.; Rüegger, H.; Loss, S.; Grützmacher, H. BABAR-Phos Rhodium Complexes: Reversible Metal Insertion into a Three-Membered Ring and Catalytic Hydroborations. *Angew. Chem., Int. Ed.* **2000**, *39*, 2478–2481.

(3) (a) Kobayashi, S.; Kadokawa, J.-I. Ring-opening polymerization of 1-(2,4,6-tri-tert-butylphenyl)-phosphirane: direct synthesis of a polyphosphine derivative. *Macromol. Rapid Commun.* **1994**, *15*, 567–571; (b) Kadokawa, J.-I.; Kobayashi, S. New Ring-Opening Polymerization of Phosphorus-Containing Cyclic Monomers. *Phosphorus, Sulfur Silicon Relat. Elem.* **2002**, *177*, 1387–1390.

(4) Wit, J. B. M.; de Jong, G. B.; Schakel, M.; Lutz, M.; Ehlers, A. W.; Slootweg, J. C.; Lammertsma, K. iPr_2N–P=$Fe(CO)_4$ in Olefinic Solvents: A Reservoir of a Transient Phosphinidene Complex Capable of Substrate Hopping. *Organometallics* **2016**, *35*, 1170–1176.

(5) Marinetti, A.; Mathey, F. The carbene-like behavior of terminal phosphinidene complexes toward olefins. A new access to the phosphirane ring. *Organometallics* **1984**, *3*, 456–461.

(6) Breen, T. L.; Stephan, D. W. Phosphinidene Transfer Reactions of the Terminal Phosphinidene Complex $Cp_2Zr(PC_6H_2$-2,4,6-*t*-$Bu_3)(PMe_3)$. *J. Am. Chem. Soc.* **1995**, *117*, 11914–11921.

(7) Waterman, R.; Hillhouse, G. L. Group Transfer from Nickel Imido, Phosphinidene, and Carbene Complexes to Ethylene with Formation of Aziridine, Phosphirane, and Cyclopropane Products. *J. Am. Chem. Soc.* **2003**, *125*, 13350–13351.

(8) Vaheesar, K.; Kuntz, C. M.; Sterenberg, B. T. Formation of phosphorus heterocycles using a cationic electrophilic phosphinidene complex. *J. Organomet. Chem.* **2013**, *745-746*, 347–355.

(9) Goumans, T. P. M.; Ehlers, A. W.; Lammertsma, K. Toward the catalytic synthesis of phosphiranes. A computational study. *J. Organomet. Chem.* **2005**, *690*, 5517–5524.

(10) van Assema, S. G. A.; de Kanter, F. J. J.; Schakel, M.; Lammertsma, K. Decomplexation of Phosphirane and Phosphirene Complexes. *Organometallics* **2006**, *25*, 5286–5291.

(11) Amme, M. J.; Kazi, A. B.; Cundari, T. R. Copper-catalyzed phosphinidene transfer to ethylene, acetylene, and carbon monoxide: A computational study. *Int. J. Quantum Chem.* **2010**, *110*, 1702–1711.

(12) Abbenseth, J.; Delony, D.; Neben, M. C.; Würtele, C.; de Bruin, B.; Schneider, S. Interconversion of Phosphinyl Radical and Phosphinidene Complexes by Proton Coupled Electron Transfer. *Angew. Chem., Int. Ed.* **2019**, *58*, 6338–6341.

(13) Pagano, J. K.; Ackley, B. J.; Waterman, R. Evidence for Iron-Catalyzed α-Phosphinidene Elimination with Phenylphosphine. *Chem. - Eur. J.* **2018**, *24*, 2554–2557.

(14) Pal, K.; Hemming, O. B.; Day, B. M.; Pugh, T.; Evans, D. J.; Layfield, R. A. Iron- and Cobalt-Catalyzed Synthesis of Carbene Phosphinidenes. *Angew. Chem., Int. Ed.* **2016**, *55*, 1690–1693.

(15) Freeman, P. K.; Hutchinson, L. L. Magnesium anthracene dianion. *J. Org. Chem.* **1983**, *48*, 879–881.

(16) (a) Velian, A.; Cummins, C. C. Facile Synthesis of Dibenzo-7λ^3-phosphanorbornadiene Derivatives Using Magnesium Anthracene. *J. Am. Chem. Soc.* **2012**, *134*, 13978–13981; (b) Transue, W. J.; Velian, A.; Nava, M.; García-Iriepa, C.; Temprado, M.; Cummins, C. C. Mechanism and Scope of Phosphinidene Transfer from Dibenzo-7-phosphanorbornadiene Compounds. *J. Am. Chem. Soc.* **2017**, *139*, 10822–10831; (c) Transue, W. J.; Yang, J.; Nava, M.; Sergeyev, I. V.; Barnum, T. J.; McCarthy, M. C.; Cummins, C. C. Synthetic and Spectroscopic Investigations Enabled by Modular Synthesis of Molecular Phosphaalkyne Precursors. *J. Am. Chem. Soc.* **2018**, *140*, 17985–17991.

(17) Szkop, K. M.; Geeson, M. B.; Stephan, D. W.; Cummins, C. Synthesis of acyl(chloro)phosphines enabled by phosphinidene transfer. *Chem. Sci.* **2019**, *10*, 3627–3631.

(18) Lennon, P.; Madhavarao, M.; Rosan, A.; Rosenblum, M. The addition of heteroatomic nucleophiles to dicarbonyl-η^5-cyclopentadienyl(olefin)iron cations. *J. Organomet. Chem.* **1976**, *108*, 93–109.

(19) Knoth, W. H. Reactions of ethylene coordinated to molybdenum, tungsten, and iron. *Inorg. Chem.* **1975**, *14*, 1566–1572.

(20) Bai, W.; Chen, J.; Jia, G. *"4.10 Reactions of Nucleophiles with Coordinated Alkynes, Alkenes, and Allenes" in Comprehensive Organic Synthesis II*; Elsevier, 2014; pp 580–647.

(21) Giering, W. P.; Rosenblum, M.; Tancrede, J. Stereospecific reduction of epoxides with sodium (cyclopentadienyl)dicarbonylferrate. New route to cationic iron-olefin complexes. *J. Am. Chem. Soc.* **1972**, *94*, 7170–7172.

(22) Muldoon, J. A.; Varga, B. R.; Deegan, M. M.; Chapp, T. W.; Eördögh, A. M.; Hughes, R. P.; Glueck, D. S.; Moore, C. E.; Rheingold, A. L. Inversion of Configuration at the Phosphorus Nucleophile in the Diastereoselective and Enantioselective Synthesis of P-Stereogenic syn-Phosphiranes from Chiral Epoxides. *Angew. Chem., Int. Ed.* **2018**, *57*, 5047–5051.

(23) Marinetti, A.; Mathey, F.; Ricard, L. Synthesis of optically active phosphiranes and their use as ligands in rhodium(I) complexes. *Organometallics* **1993**, *12*, 1207–1212.

(24) Li, X.; Robinson, K. D.; Gaspar, P. P. A New Stereoselective Synthesis of Phosphiranes. *J. Org. Chem.* **1996**, *61*, 7702–7710.

(25) Baudler, M.; Germeshausen, J. Beiträge zur Chemie des Phosphors, 154. 1-tert-Butyl-2-methylphosphiran – ein thermisch beständiges Monophosphiran. *Chem. Ber.* **1985**, *118*, 4285–4287.

(26) Ficks, A.; Martinez-Botella, I.; Stewart, B.; Harrington, R. W.; Clegg, W.; Higham, L. J. Taming functionality: easy-to-handle chiral phosphiranes. *Chem. Commun.* **2011**, *47*, 8274.

(27) (a) Nesterov, V.; Schnakenburg, G.; Espinosa, A.; Streubel, R. Synthesis and Reactions of the First Room Temperature Stable Li/Cl Phosphinidenoid Complex. *Inorg. Chem.* **2012**, *51*, 12343–12349; (b) Nesterov, V.; Özbolat Schön, A.; Schnakenburg, G.; Shi, L.; Cangönül, A.; van Gastel, M.; Neese, F.; Streubel, R. An Unusual Case of Facile Non-Degenerate P–C Bond Making and Breaking. *Chem. Asian J.* **2012**, *7*, 1708–1712; (c) Fassbender, J.; Schnakenburg, G.; Ferao, A. E.; Streubel, R. Effects of diminished steric protection at phosphorus on stability and reactivity of oxaphosphirane complexes. *Dalton Trans.* **2018**, *47*, 9347–9354; (d) Schmer, A.; Volk, N.; Espinosa Ferao, A.; Streubel, R. Access and unprecedented reaction pathways of Li/Cl phosphinidenoid iron(0) complexes. *Dalton Trans.* **2019**, *48*, 339–345.

(28) Malish, W.; Angerer, W.; Cowley, A. H.; Norman, N. C. Dicarbonyl(η^5-pentamethylcyclopentadienyl)ferrio(t-butyl)-chlorophosphine: a metallo-phosphine exhibiting multifaceted reactivity. *J. Chem. Soc., Chem. Commun.* **1985**, *0*, 1811–1812.

(29) Mullins, R. J.; Vedernikov, A.; Viswanathan, R. Competition Experiments as a Means of Evaluating Linear Free Energy Relationships. An Experiment for the Advanced Undergraduate Organic Chemistry Lab. *J. Chem. Educ.* **2004**, *81*, 1357.

(30) Hung, J. T.; Lammertsma, K. Hammett reaction constant for a terminal methylphosphinidene complex. *Organometallics* **1992**, *11*, 4365–4366.

(31) Ashby, M. T.; Enemark, J. H. Cycloaddition of alkenes and alkynes to $CpFe(CO)_2PR_2$ to give $Cp(CO)FePR_2C{=}CC{=}O$ heterometallacycles. *Organometallics* **1987**, *6*, 1323–1327.

(32) Qu, Z.-W.; Zhu, H.; Grimme, S. Acylation Reactions of Dibenzo-7-phosphanorbornadiene: DFT Mechanistic Insights. *ChemistryOpen* **2019**, *8*, 807–810.

(33) Mézailles, N.; Fanwick, P. E.; Kubiak, C. P. Synthesis and Reactivity of Phosphirane Ligands and the Structural Characterization of Cp^*IrCl_2(tert-butylphosphirane). *Organometallics* **1997**, *16*, 1526–1530.

(34) Dück, K.; Rawe, B. W.; Scott, M. R.; Gates, D. P. Polymerization of 1-Phosphaisoprene: Synthesis and Characterization of a Chemically Functional Phosphorus Version of Natural Rubber. *Angew. Chem., Int. Ed.* **2017**, *56*, 9507–9511.

(35) Priegert, A. M.; Rawe, B. W.; Serin, S. C.; Gates, D. P. Polymers and the p-block elements. *Chem. Soc. Rev.* **2016**, *45*, 922–953.

Graphical TOC Entry