

Three-Component Coupling of Acyl Fluorides, Silyl Enol Ethers, and Alkynes by P(III)/P(V)

Catalysis

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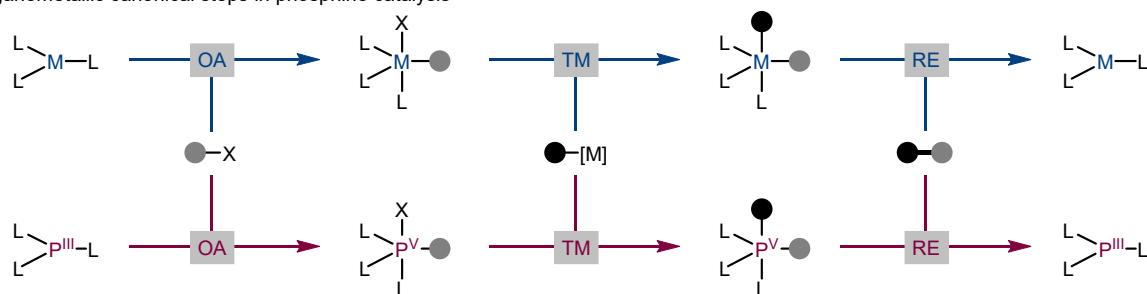
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Abstract (~200 words)

Catalysis by late transition metal complexes is enabled by their facile reversible redox reactivity based on their partially filled d-orbitals. The realization of such redox catalysis by p-block elements is a challenging but rewarding research subject for the advancement in both fundamental main group chemistry and sustainable catalytic technology.¹⁻⁶ In this context, a P(III)/P(V) redox cycle that involves pentacoordinate phosphorane is a competent manifold for applications to catalytic reactions via a formal oxidative addition/transmetalation/reductive elimination sequence. Despite the promising stoichiometric redox reactivity of pentacoordinate organophosphorus compounds,^{7,8} their use in catalytic processes have been primarily limited to oxygen transfer reactions that involve the interconversion between phosphines and phosphine oxides, except for relatively simple,

prototypical transformation, such as hydrogenation⁹ and reduction of allyl bromides.¹⁰ We report herein on the phosphine-catalyzed hydrovinylation reaction by three-component coupling of acyl fluorides, silyl enol ethers, and alkynoates. The key to the success of the reaction is the formal transmetalation between pentacoordinate P(V) species (i.e., fluorophosphorane) and a silyl enol ether, which allows for C–C bond formation between the polarity-mismatched sites. The bond formation that cannot be attained even by transition metal catalysis is accomplished by a P(III)/P(V) manifold.

a Organometallic canonical steps in phosphine catalysis



b Catalytic hydrovinylation of alkyne

Prior arts: via C–H activation by Rh, Ru

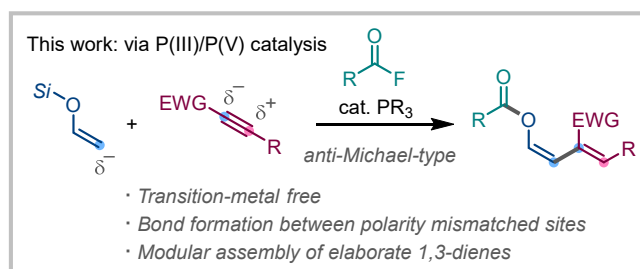
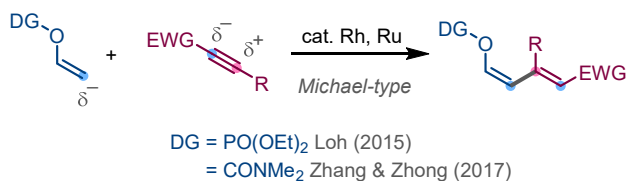


Fig. 1. Phosphorus mimics transition metal behavior. **a**, Comparison of well-established organometallic steps for transition metals and hypothetical steps mediated by phosphorus. OA = oxidative addition. TM = transmetalation. RE = reductive elimination. **b**, Catalytic hydrovinylation of alkynes using enol derivatives: prior arts and this work. DG = directing group. EWG = electron-withdrawing group.

The widespread use of transition metal complexes as catalysts stems from their facile reversible redox reactivity based on their partially filled d-orbitals. The use of p-block elements as surrogates for transition metal catalysts has also attracted considerable interest in terms of both the fundamental aspects of main group elements in uncommon oxidation states and concerns related to the shortage of some metallic elements.^{1–6} The P(III)/P(V) redox cycle is a competent main group-based manifold for applications in catalytic reactions (Fig. 1a). However, the reported examples of catalytic reactions based on the P(III)/P(V) couple are primarily limited to oxygen

transfer reactions mediated by the reversible interconversion of phosphine/phosphine oxide (*i.e.*, P(III)/O=P(V) cycle).^{4,11} In a P(III)/O=P(V) cycle, the catalyst regeneration step (O=P(V) to P(III)) is irrelevant to the product formation, and a sacrificial reducing agent is essential. It would appear that the P(III)/P(V) manifold could be used for a wider range of catalytic reactions in view of a number of studies on the stoichiometric redox reactivity of organophosphorus compounds in mediating formal oxidative addition or reductive elimination processes through a pentacoordinate phosphorane intermediate as a P(V) species.^{1,7,8} However, examples reported thus far are limited to relatively simple, prototypical transformations, including hydrogenation,⁹ reduction of allyl bromides,¹⁰ and acylfluorination of alkynes.¹² Herein, we report on extending P(III)/P(V) catalyst system to a phosphine-catalyzed formal hydrovinylation reaction by the three-component coupling of acyl fluorides, silyl enol ethers, and alkynoates.

The 1,3-diene motif is frequently found in complex natural products and biologically active molecules,¹³ and also serve as a versatile synthetic precursor for a variety of important organic transformations.^{14,15} Consequently, intense efforts have been expended to development of efficient and practical methods for producing these valuable structural motifs.¹⁶ Among the methods reported to date, the catalytic hydrovinylation of alkynes is a straightforward approach and has been a subject of considerable research interest.^{17,18} The hydrovinylation of alkynes using enol derivatives is of particular interest because the resulting conjugate dienolate derivatives can be used in a variety of useful synthetic transformations.^{19,20} However, despite the potential synthetic impact, the

catalytic hydrovinylation of alkynes using enol derivatives has not been accomplished, except for the following two examples. Loh²¹ and Zhang²² independently reported that enol derivatives bearing a directing group on the oxygen atom can add across alkynes via transition metal-catalyzed vinylic C–H bond activation (Fig. 1b, left). In these reactions, a new C–C bond can be forged between the nucleophilic carbon of an enol and the electrophilic β -carbon of an alkyne when electron-deficient alkynes are used (Michael-type addition). The three component reaction reported herein involves the alkenylation of a vinylic C–H bond and the acylation of an Si–O bond of silyl enol ethers occur in one reaction sequence (Fig. 1b, right). Notably, the C–C bond formation involves umpolung, which allows for connection between polarity mismatched sites to afford an anti-Michael-type adduct. This regioselectivity is complementary to that observed in the transition metal-catalyzed hydrovinylation of alkynes using enol derivatives.^{21,22}

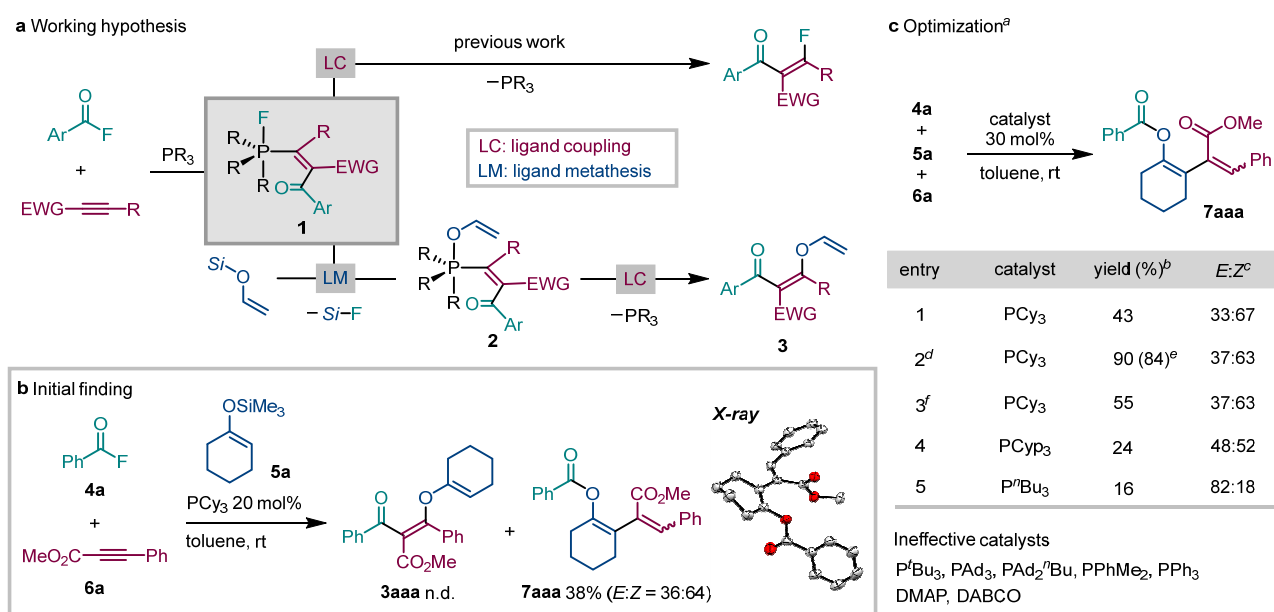


Fig. 2. Working hypothesis and experimental observations. **a**, Our previous work and our working hypothesis. LC = ligand coupling. LM = ligand metathesis. **b**, Experimental observation of the PCy₃-catalyzed three-component coupling of acyl fluorides, silyl enol ethers, and alkynes. Reaction conditions: **4a** (0.30 mmol), **5a** (0.30 mmol), **6a** (0.20 mmol), catalyst (0.04 mmol), and toluene (1.0 mL) in a sealed tube at room temperature for 20 h. **c**, Optimization of the phosphine-catalyzed hydrovinylation of alkynes ^aReaction conditions: **4a** (0.30 mmol), **5a** (0.30 mmol), **6a** (0.20 mmol), catalyst (0.06 mmol), and toluene (1.0 mL) in a sealed tube at room temperature for 20 h. ^bDetermined by ¹H NMR. ^cDetermined by ¹H NMR analysis. ^dDropwise addition of **4a** (0.40 mmol) at 7 μL/h to the mixture of **5a** (0.40 mmol), **6a** (0.20 mmol), and PCy₃ (0.06 mmol) in toluene (1.0 mL), then at room temperature for 14 h. ^eYield of the isolated product. ^f**4a** (0.60 mmol), **5a** (0.60 mmol), **6a** (0.20 mmol), PCy₃ (0.06 mmol), and toluene (1.0 mL) in a sealed tube at room temperature for 20 h.

Quite recently, we reported on the phosphine-catalyzed intermolecular addition of acyl fluorides across triple bonds in electron-deficient alkynes (Fig. 2a).¹² In this reaction, a pentacoordinate fluorophosphorane **1** is involved as the key intermediate, and a C–F bond is formed via ligand coupling (LC) on **1**, an alternative to reductive elimination on transition metal complexes. We envisioned that a three-component coupling would be possible if ligand metathesis (LM) between a fluoride on the phosphorus center of **1** and an organometallic nucleophile were to take

place, in a manner similar to the transmetalation reaction on transition metal complexes (Fig. 2b).^{8,10} Silyl enol ethers were chosen as a feasible nucleophile because they can be readily prepared from a range of carbonyl compounds by reliable protocols and exhibit temperate reactivity as an enolate equivalent amenable to various catalysis manifolds. We anticipated that ligand metathesis would generate the phosphorane **2**, which would eventually lead to the formation of densely functionalized alkene **3** via ligand coupling. The three-component coupling of benzoyl fluoride (**4a**), silyl enol ether **5a**, and methyl phenylpropiolate (**6a**) was initially examined. Although, the expected three-component coupling product **3aaa** was not observed, the 1,3-diene **7aaa**, which can be viewed as a formal hydrovinylation product, was obtained in 38% yield (*E:Z* = 36:64). X-ray crystallographic analysis unambiguously determined that the alkenylation of a vinylic C–H bond and *O*-acylation of silyl enol ether simultaneously occurred with C–C bond formation between the polarity mismatched sites. Intrigued by the unusual bond connection mode and the rapid assembly of elaborate 1,3-dienes from simple building blocks, we embarked on a study of this synthetic transformation in more detail. Increasing the catalyst loading to 30 mol% improved the yield of **7aaa** to 43% (Fig. 2c, entry 1). Since we identified the 1,3-diketone **8aa** and the vinyl ester **9aa** as major byproducts (see Fig. 4a-(i) for the structure of **8aa** and **9aa**), which were formed by the direct addition of **5a** to **4a**, the slow addition of **4a** was examined. The dropwise addition of **4a** (7 μ L/h, 2.0 equiv) to a mixture of **5a** (2.0 equiv), **6a** and PCy₃ afforded the 1,3-diene **7aaa** in 84% isolated yield (*E:Z* = 37:63) (entry 2). Alternatively, increasing the amount of **4a** and **5a** (3.0 equiv each)

also improved the yield of 1,3-diene **7aaa** without the dropwise addition of **4a** (entry 3). Other phosphines, such as P^tBu₃, PPhMe₂ and PPh₃, and amines (DMAP and DABCO) failed to promote this three-component coupling.

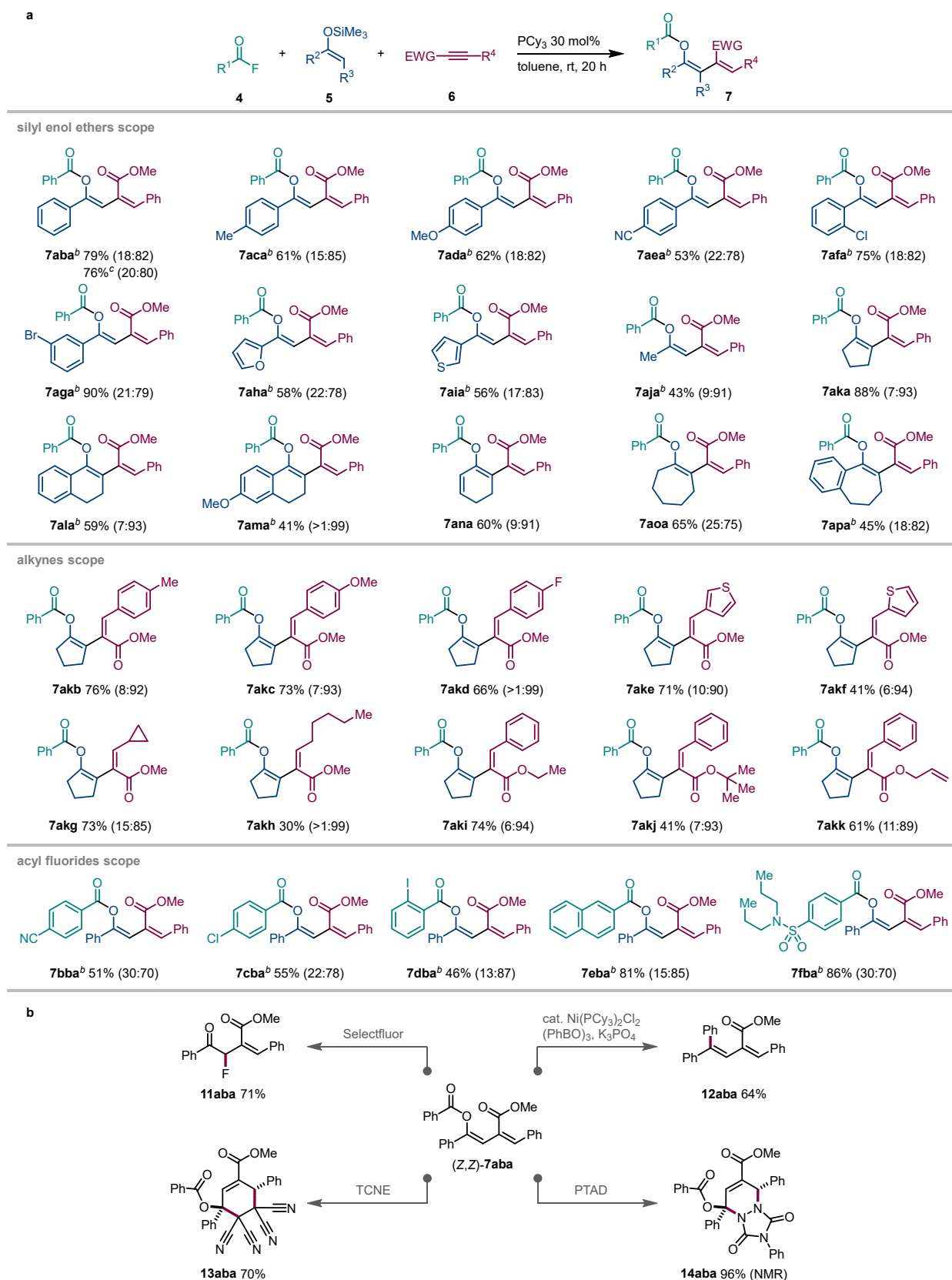


Fig. 3. Scope of the phosphine-catalyzed three-component coupling.

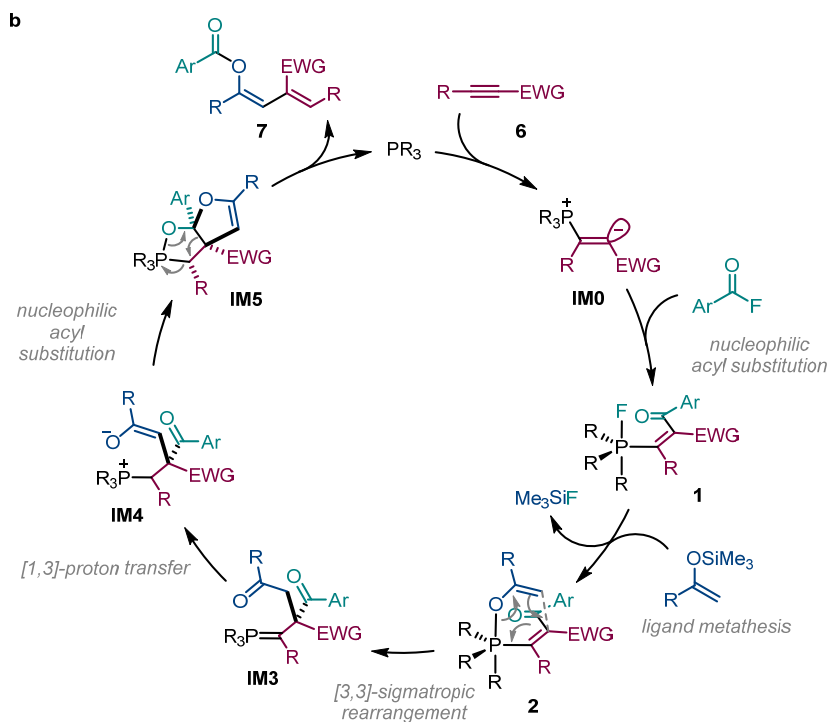
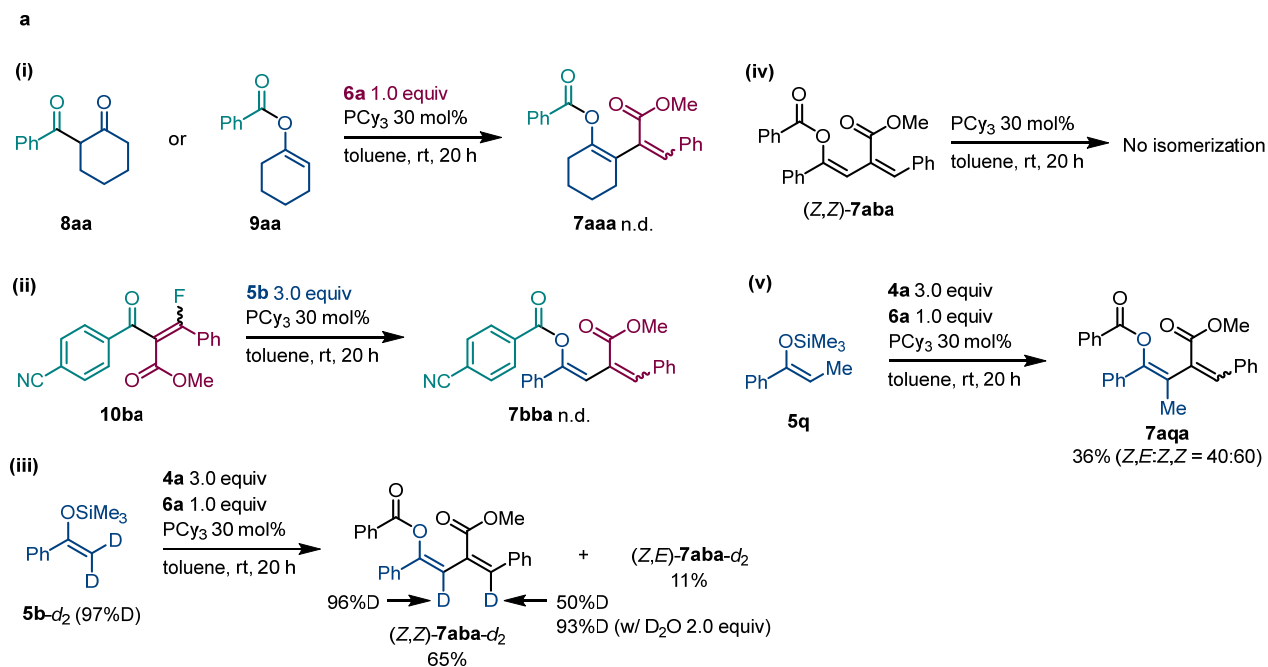
a, Scope of the phosphine-catalyzed three-component coupling. ^aReaction conditions: dropwise addition of **4a** (0.40 mmol) at 7 μ L/h to a mixture of **5a** (0.40 mmol), **6a** (0.20 mmol), and PCy₃ (0.06 mmol) in toluene (1.0 mL), then at room temperature for 14 h. Yields of isolated products are shown. The (Z,E):(Z,Z) ratios that were determined by ¹H NMR analysis are shown in parentheses. ^b**4a** (0.60 mmol), **5a** (0.60 mmol), **6a** (0.20 mmol), PCy₃ (0.06 mmol), and toluene (1.0 mL) at room temperature for 20 h. ^c**4a** (16.5 mmol), **5a** (16.5 mmol), **6a** (5.50 mmol), PCy₃ (1.65 mmol), and toluene (30 mL) at room temperature for 20 h. 1.62 g of product was obtained. **b**, Transformations of the three-component coupling product **7aba**. Selectfluor = 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate). TCNE = tetracyanoethylene. PTAD = 4-phenyl-1,2,4-triazoline-3,5-dione.

With the optimized reaction conditions in hand, we subsequently examined the scope of the three-component coupling (Fig. 3a). The silyl enol ether **5b**, which was prepared from acetophenone, participated in this reaction to produce **7aba**, in which the C–H bond *cis* to the siloxy group in **5b** was exclusively alkenylated. Regarding the stereochemistry of an alkene moiety derived from **6a**, the *E* configuration was dominated [(Z,E):(Z,Z) = 18:82]. The structure of (Z,Z)-**7aba** was confirmed by a single-crystal X-ray analysis. Silyl enol ethers bearing methyl (**5c**), methoxy (**5d**), and cyano (**5e**) groups readily participated in this reaction. Halogen groups such as chloro (**5f**) and bromo (**5g**) were compatible, allowing the resulting 1,3-diene to be amenable to

further structural elaboration via common C–X bond functionalization reactions. Substrates containing heteroarenes such as furan (**5h**) and thiophene (**5i**) also successfully underwent the three-component coupling. The silyl enol ether **5j**, which was prepared from acetone, participated in this reaction to produce **7aja** with a high stereoselectivity [(*Z,E*):(*Z,Z*) = 9:91]. Five-membered (**5k**), six-membered (**5l**, **5m**, **5n**), and seven-membered (**5o**, **5p**) cyclic silyl enol ethers all reacted to afford the corresponding 1,3-diene derivative. Aromatic alkynoates bearing methyl (**6b**), methoxy (**6c**), fluoro (**6d**), and thienyl groups (**6e**, **6f**) were also viable substrates for this three-component coupling with high *Z*-selectivity. The three-component coupling can also be applied successfully to non-aromatic alkynoates bearing cyclopropyl (**6g**) and *n*-pentyl (**6h**) groups. This three-component coupling also proceeded when alkynoates bearing a different ester moiety such as ethyl (**6i**), *t*-butyl (**6j**), and allyl (**6k**) esters were used. It was also possible to use several acyl fluorides, such as those bearing cyano (**4b**), chloro (**4c**), iodo (**4d**), and π -extended aryl (**4e**) groups to afford the corresponding products **7bba**–**7eba**. The structural elaboration of pharmaceuticals containing a carboxylic acid functionality into the corresponding 1,3-dienes is possible through acid fluoride formation followed by the three-component coupling (*i.e.*, the conversion of probenecid into **7fba**).

Containing both vinyl ester and 1,3-diene moieties, the three-component coupling products can serve as valuable synthetic intermediates (Fig. 3b). For example, the vinyl ester moiety could be selectively converted into the corresponding fluorinated 1,4-dicarbonyl product **11aba** by treating (*Z,Z*)-**7aba** with Selectfluor.²³ The vinyl ester moiety in (*Z,Z*)-**7aba** could also be arylated by

Ni-catalyzed Suzuki–Miyaura coupling via C(sp²)–O activation.²⁴ The Diels–Alder reaction of (Z,Z)-**7aba** with the tetracyanoethylene (TCNE) and 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) afforded the densely functionalized cyclohexene **13aba** and **14aba**, respectively, with retention of the relative stereochemistry.



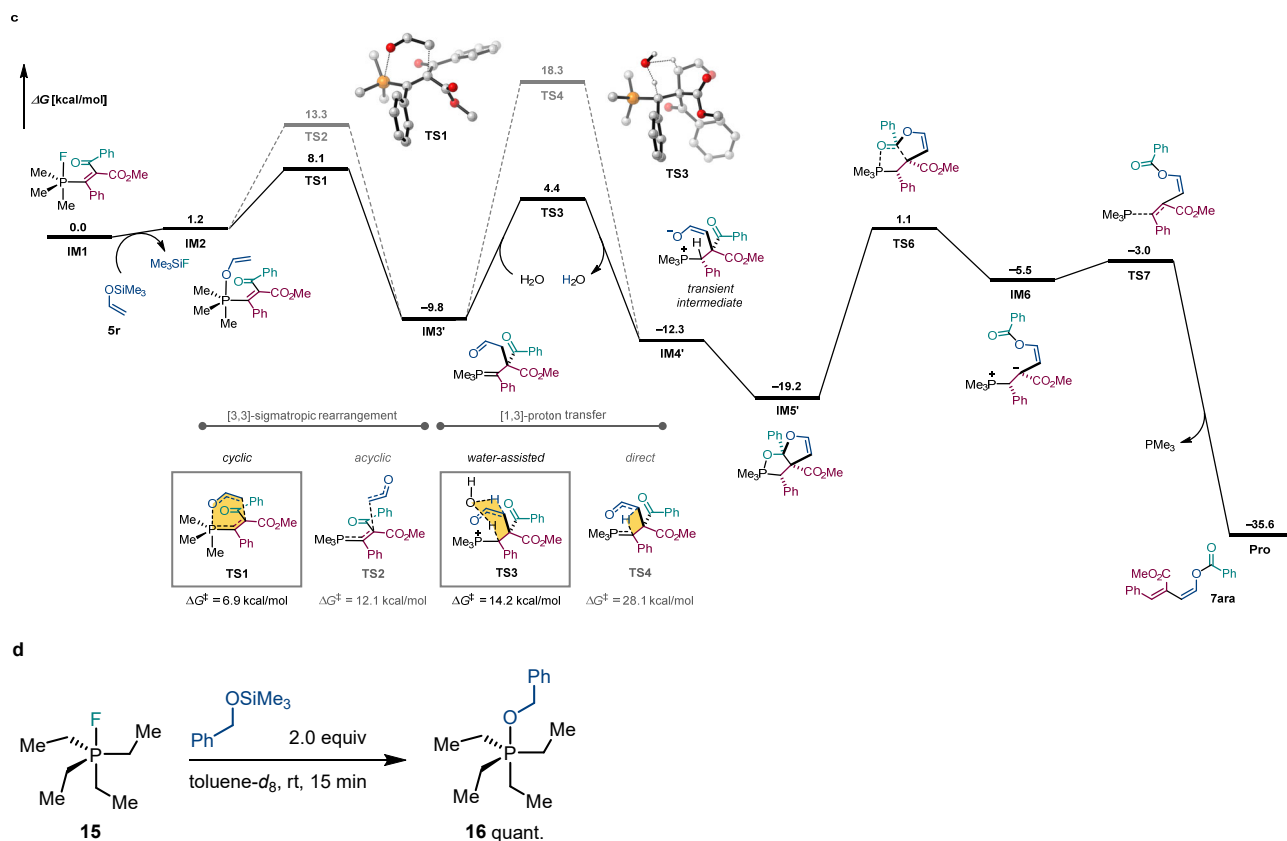


Fig 4. Mechanistic studies. **a**, Mechanistic studies involving control experiments, deuterium-labeled experiments and isomerization experiments. **b**, Proposed mechanism by P(III)/P(V) catalysis. **c**, Computed energy profile of the three-component coupling from a fluorophosphorane intermediate. Calculations were performed at the PCM (toluene)-M06-2X/6-31+G(d,p) level of theory. **d**, Experimental observation of ligand metathesis.

To gain insights into the reaction mechanism, several control experiments were performed (Fig. 4a). In this three-component coupling between **4a**, **5a**, and **6a**, 1,3-diketone **8aa** and vinyl ester **9aa** were observed as byproducts, which are likely formed by the direct reaction between **4a** and **5a**. To examine the involvement of **8aa** and **9aa** as a viable intermediate in this

three-component coupling, the PCy₃-catalyzed reaction of **8aa** (or **9aa**) with **6a** was conducted. However, the expected 1,3-diene **7aaa** was not formed, excluding the intermediacy of **8aa** and **9aa** (Fig. 4a-(i)). Monofluoroalkene **10ba**, which can also be formed by phosphine-catalyzed carbofluorination¹² between acyl fluoride **4b** and alkynoate **6a**, is a potential intermediate in this three-component coupling. However, the desired product **7bba** was not formed from **10ba** under these reaction conditions, ruling out the involvement of **10ba** (Fig. 4a-(ii)). Deuterium labeling experiments were performed to investigate the origin of the vinylic hydrogen atoms (Fig. 4a-(iii)). The three-component coupling of **4a**, **6a**, and the deuterium labeled silyl enol ether **5b-d₂** (97%D) afforded **7aba-d₂** under the standard reaction conditions, with deuterium atoms incorporated at the 4-position (50%D), in addition to the 2-position (96%D). Although the deuterium content at the 4-position was 50%, the majority of the cleaved deuterium atoms are incorporated into the product. When this labeling experiment was carried out in the presence of 2.0 equiv of deuterium oxide (D₂O), the deuterium content of **7aba-d₂** at the 4-position increased to 93%. This result indicates that the decrease in the deuterium content at the 4-position is due to exchange with trace amounts of water that are present in the system.^{25,26} Regarding the stereochemistry of the alkene moiety derived from the alkyne, (*Z*)-isomers were predominantly formed, even though the corresponding (*E*)-isomers were thermodynamically more stable (For example, (*Z,E*)-**7aba** is more stable than (*Z,Z*)-**7aba** by 1.8 kcal/mol). In fact, the exposure of the geometrically pure (*Z,Z*)-**7aba** to the catalytic conditions did not induce any isomerization, indicating that the (*Z,Z*)-isomer is a

kinetically favored product (Fig. 4a-(iv)). Regarding the stereochemistry of the alkene moiety derived from the silyl enol ethers, the vinylic C–H bond that is *cis* to the siloxy group is exclusively alkenylated. However, when the (*Z*)-silyl enol ether **5q** was used as a substrate, 1,3-dienes with a (*Z*)-geometry with respect to the enol moiety was formed exclusively. The structure of (*Z,Z*)-**7aqa** was confirmed by a single-crystal X-ray analysis. These results indicate that this three-component coupling involves a stereoconvergent process with respect to the geometry of the enol moiety (Fig. 4a-(v)).

A proposed reaction pathway is depicted in Fig. 4b. The catalytic reaction starts with the addition of PR_3 to an alkynoate to generate the carbanion **IM0**, which subsequently undergoes nucleophilic acyl substitution with an acyl fluoride to form the fluorophosphorane **1**.¹² Ligand metathesis between **1** and the silyl enol ether driven by the formation of a stable Si–F bond proceeds to afford alkoxyphosphorane **2**, in preference to the ligand coupling of **1**, to form a C–F bond. The [3,3]-sigmatropic rearrangement of **2** forges a new carbon–carbon bond between the α -carbon of the silyl enol ether and α -carbon of an electron-deficient alkyne to afford the phosphonium ylide **IM3**. The ylide moiety in **IM3** abstracts the α -hydrogen derived from the silyl enol ether to generate the enolate **IM4**. This [1,3]-proton transfer could be mediated by a trace amount of endogenous water in the system,^{25,26} which also explains the decrease in the deuterium content at the 4-position of the product in the labelling experiment (Fig. 4a-(iii)). The enolate moiety in **IM4** subsequently adds to the carbonyl group derived from the acyl fluoride, and the

resulting alkoxide anion attacks the phosphorus center to generate the bicyclic phosphorane intermediate **IM5**. The intermediate **IM5** then collapses to the final 1,3-diene **7** with the regeneration of PR_3 . The (*Z*)-geometry of the enolate moiety in **IM4** is essential for the cyclization to occur to form **IM5**, which is consistent with the fact that the both (*E*) and (*Z*)-enolates converge into 1,3-dienes with a (*Z*)-enol moiety.

Density functional theory (DFT) calculations were carried out using PMe_3 as a model catalyst in order to examine the feasibility of the proposed mechanism after the formation of **1**¹² (Fig. 4c).²⁷ Ligand metathesis between **IM1** and the silyl enol ether is endoergonic by 1.2 kcal/mol to generate phosphorane **IM2**, which undergoes the [3,3]-sigmatropic rearrangement to form the phosphonium ylide **IM3'** with a reasonable activation barrier ($\Delta G^\ddagger = 6.9$ kcal/mol). An alternative pathway involving the addition of enolate to vinylphosphonium²⁸ via an acyclic open transition state (*i.e.*, **TS2**) was found to be energetically less favored ($\Delta G^\ddagger = 12.1$ kcal/mol). The subsequent [1,3]-proton transfer step (*i.e.*, **IM3'** \rightarrow **IM4'**) requires a high energy transition state (**TS4**, $\Delta G^\ddagger = 28.1$ kcal/mol) when proton migrates directly. The activation barrier is significantly lowered when water is considered to be the proton shuttle (**TS3**, $\Delta G^\ddagger = 14.2$ kcal/mol), a finding that is consistent with the results of the labelling experiment (Fig. 4a-(iii)). DFT calculations revealed that the intermediate **IM4'** behaves as a short-lived transient intermediate and is converted to bicyclic phosphorane **IM5'** with no appreciable energetic barrier. The regeneration of the phosphine catalyst was found to proceed through two steps via **IM6** with an activation barrier of 20.3 kcal/mol, which

is reasonable for reactions that proceed at room temperature. The energy diagram also indicates that the process from **IM6** to the product is irreversible (ΔG^\ddagger for the product to **IM6**: 32.6 kcal/mol), which is consistent with the geometrical stability of (Z,Z)-**7aba** under the catalytic conditions (Fig. 4a-(iv)).

To further verify the intermediacy of alkoxyphosphorane, a stoichiometric reaction between isolable fluorophosphorane **15**²⁹ and silyl alkoxide was performed (Fig. 4d). The ligand metathesis proceeded immediately, quantitatively giving alkoxyphosphorane **16**, which has a pentacoordinate geometry³⁰ determined by VT-NMR experiments (Fig. S3).

In conclusion, we report on the phosphine-catalyzed three-component coupling of acyl fluorides, silyl enol ethers, and alkynes, which provides straightforward access to a variety of densely functionalized 1,3-dienes. This reaction operates under mild conditions and in the absence of transition metals, therefore permitting a wide functional group tolerance. The key feature of this reaction is ligand metathesis on the fluorophosphorane platform, which allows for the bond formation between polarity mismatched sites to form anti-Michael-type adducts. This study demonstrates the potential utility of a P(III)/P(V) manifold as a viable alternative to transition metal-mediated catalytic cycles consisting of oxidative addition, transmetalation and reductive elimination. Further studies directed at the development of new reactions using the fluorophosphorane platform are currently underway in our laboratory.

Author contribution

H.F., M.K., and T.K. performed and analysed the experiments. H.F., M.K., and M.T. designed the experiments. H.F. and M.T. prepared the manuscript.

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Data Availability

Crystallographic data for the structures reported in this Article have been deposited at the Cambridge Crystallographic Data Centre, under deposition numbers CCDC 2049459 ((Z,Z)-**7aaa**), 2049460 ((Z,Z)-**7aba**), 2051832 ((Z,Z)-**7aqa**). Copies of the data can be obtained free of charge via <https://www.ccdc.cam.ac.uk/structures/>. All other data is available in the main text or the Supplementary Information.

Code Availability

Calculations were performed with the Gaussian 09 (G09RevD.01) program.³¹ Geometry optimizations and frequency calculations for all reported structures were performed using M06-2X density functional with the 6-31+G(d,p) basis set. PCM solvent effects were incorporated for all calculations with toluene as the solvent.

Competing interests

The authors declare no competing interests.

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