Azide-Free Synthesis of *N*-Alkyliminophosphoranes from Phosphines and Hydroxylamine Derivatives

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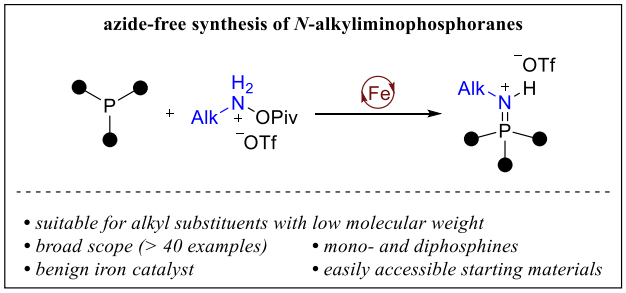


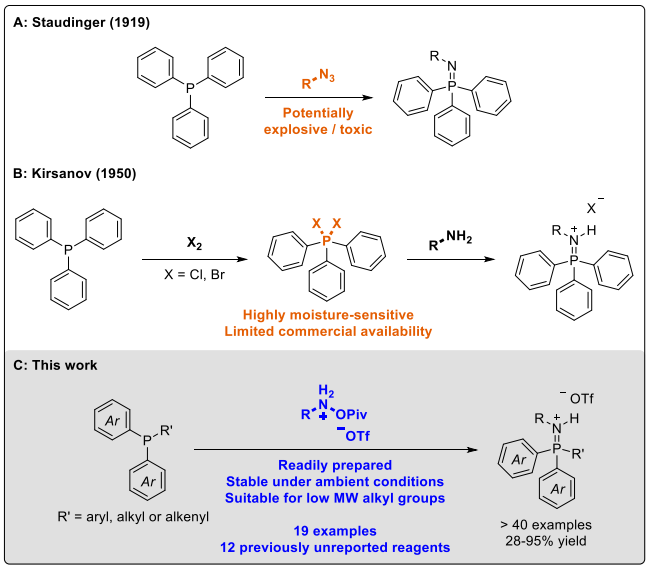
ABSTRACT: A broadly applicable and efficient method for the synthesis of *N*-alkyliminophosphoranes from phosphines that does not use potentially hazardous alkyl azides is reported. Under iron catalysis, a hydroxylamine-derived triflic acid salt oxidizes phosphines to a wide range of iminophosphorane triflic acid salts. Diphosphines afford phosphine-iminophosphoranes, that can serve as ligands in transition metal complexes. The developed method can be employed in the synthesis of mixed diiminophosphoranes and in a traceless Staudinger ligation.

Iminophosphoranes are widely used as versatile intermediates in organic synthesis,[1] as ligands in homogeneous catalysis[2] or as superbases.[3] Recently, our group reported the use of iminophosphoranes in activity-based molecular CO_2 sensing.[4] Key features of iminophosphoranes are the highly polarized P=N bond and the basic nitrogen. Iminophosphoranes first gained attention as the products of the Staudinger reaction, in which an organic azide oxidizes a phosphine (Scheme 1A).[5] While this is a well-established approach for the synthesis of iminophosphoranes, its dependency on organic azides can be problematic. A particularly acute issue are alkyl azides with a low molecular weight as these are usually toxic and explosive, which makes handling them extremely challenging.[6] An alternative method for the preparation of iminophosphoranes from phosphines is the Kirsanov reaction, which involves the oxidation of a phosphine with chlorine or bromine and subsequent treatment of the formed phosphine-dihalide with a primary amine under basic conditions (Scheme 1B).[7] While this method circumvents the use of a potentially explosive organic azide, its practicability suffers from the high moisture sensitivity and limited commercial availability of many phosphine-dihalides. In addition to the aforementioned approaches, several alternative methods for the synthesis of *N*-aryl and *N*-acyliminophosphoranes have been developed.[8] However, methods for the synthesis of highly moisture-sensitive *N*-alkyliminophosphoranes directly from phosphines are scarce and a general and simple method that does not rely on alkyl azides is desirable.

Based on early reports on the reactivity of triphenylphosphine with different *N*-unsubstituted hydroxylamine derivatives[9] and our group's efforts in employing hydroxylamine-derived reagents in aminative reactions of alkenes,[10] arenes[11] and thiols,[12] we hypothesized that *N*-alkylhydroxylamine-derived triflic acid salts could be employed in the oxidation of phosphines to *N*-alkyliminophosphoranes. Hydroxylamine derivatives have been applied in the iron-catalyzed synthesis of *N*-acyliminophosphoranes by Yu, Bao and coworkers,[13] and more recently, by the groups of Chen and Xia.[14] However, those methods were limited to the preparation of *N*-acyl products, and more sensitive *N*-alkyliminophosphoranes were not accessible from hydroxylamine derivatives so far. We reasoned that using triflic acid salts of hydroxylamine derivatives would help to overcome this limitation as the iminophosphorane products would

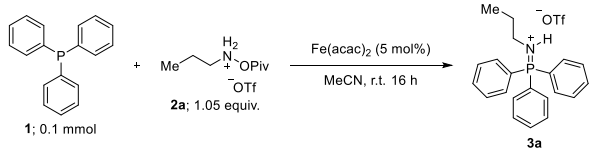
be obtained in their protonated form, which has been shown to be less prone to hydrolysis than the free base.[9a, 15]

Scheme 1. *N*-Alkyliminophosphorane synthesis from phosphines (R = alkyl).



Here, we report a practical synthesis of *N*-alkyliminophosphoranes from phosphines and hydroxylamine-derived triflic acid salts, in which a wide variety of *N*-substituents and phosphines are tolerated (Scheme 1C). Diphosphines are mono-oxidized to phosphine-iminophosphoranes and *in situ* Boc deprotection allows for the synthesis of mixed diiminophosphoranes. The hydroxylamine derivatives serve as a safer alternative to potentially hazardous alkyl azides.

Table 1. Selected optimization results.[a]

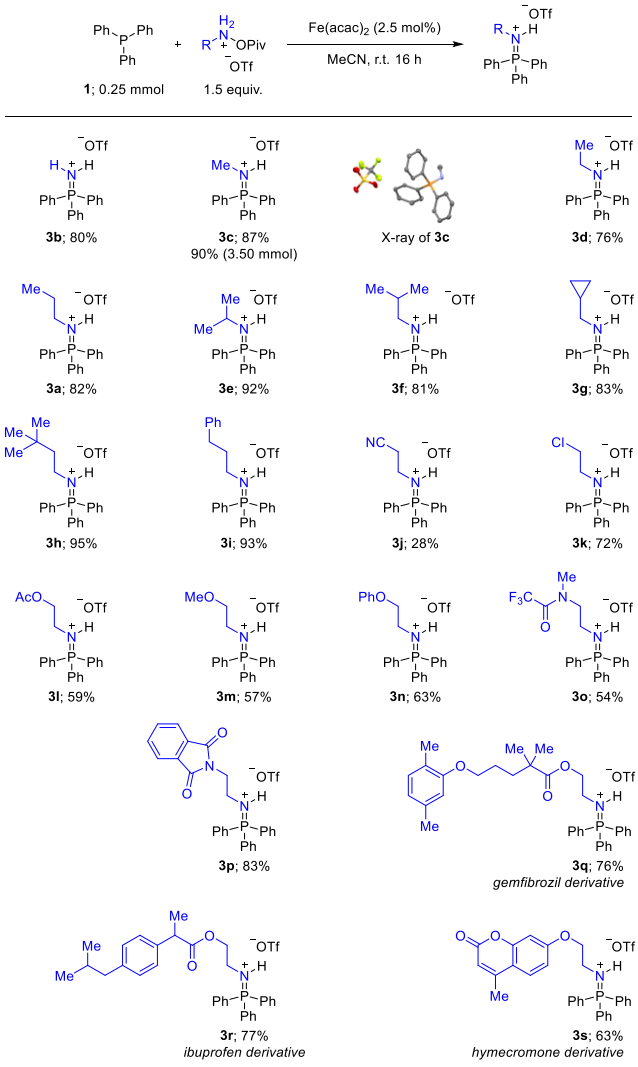


Entry	Deviation from above	Yield (%)[b]
1	none	56%
2	$Fe(OAc)_2$	46%
3	$FeCl_2$	51%
4	without catalyst	34%
5	2.5% catalyst loading	62%
6	10% catalyst loading	54%
7	**2.5% catalyst loading, 1.50 equiv. 2a**	**83%**
8	2.5% catalyst loading, 2.00 equiv. **2a**	70%

[a] Reaction conditions: triphenylphosphine (0.100 mmol), **2a** (0.105 mmol), $Fe(acac)_2$ (0.005 mmol), MeCN (0.4 mL), argon atmosphere. [b] Yields calculated by ^1H NMR using trichloroethylene as internal standard.

We started our investigation using triphenylphosphine (**1**) and aminating reagent **2a** under iron(II) catalysis (Table 1). $Fe(acac)_2$ was found to be the optimal catalyst for the reaction (entries 1-3). Without catalyst, the reaction still took place, but afforded iminophosphorane **3a** in a diminished yield (entry 4).[16] The catalyst loading could be decreased to 2.5 mol% which even increased the yield slightly (entry 5), whereas increasing the catalyst loading to 10 mol% had no effect on the reaction outcome (entry 6). The yield of **3a** could be further improved by increasing the equivalents of aminating reagent **2a** (entries 7 and 8). During the optimization process, we did not observe significant amounts of product hydrolysis, even though the products were exposed to air and non-anhydrous solvents for the work-up and analysis. This confirmed that iminophosphorane triflic acid salts are significantly more stable toward hydrolysis than non-protonated *N*-alkyliminophosphoranes, which have been reported to rapidly hydrolyze when exposed to air.[17]

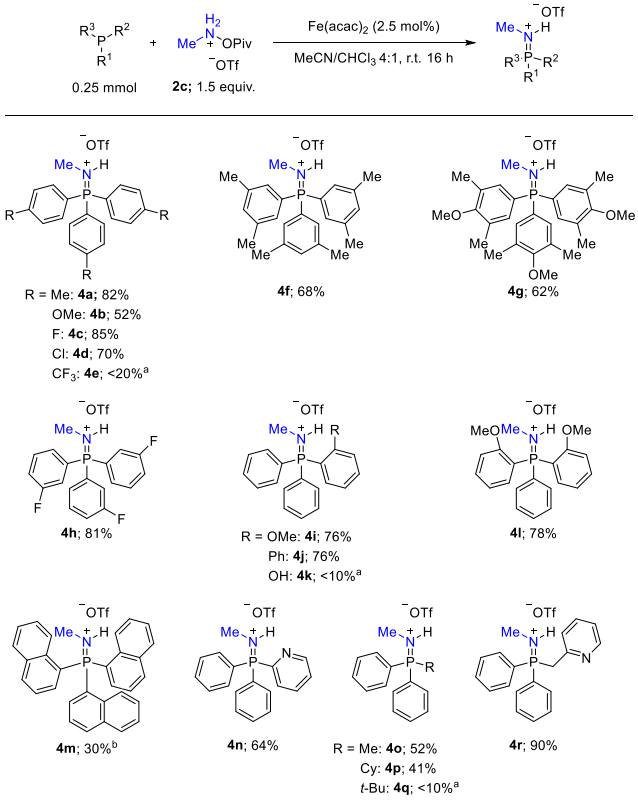
Scheme 2. Aminating reagent scope of the reaction.



Yields are of isolated products. Reaction conditions: triphenylphosphine (0.250 mmol), aminating reagent (0.375 mmol), $Fe(acac)_2$ (2.5 mol%), MeCN (1.0 mL), argon atmosphere.

Having the optimized reaction conditions in hand, we set out to investigate the generality of the transformation. 19 hydroxylamine-derived aminating reagents (**2a–s**), including 12 examples that have not been previously reported (**2a, f, h, i, l–s**), were reacted with triphenylphosphine (**1**) under iron catalysis to yield the corresponding iminophosphorane triflic acid salts (Scheme 2). The hydroxylamine derivatives could be prepared according to simple and robust synthetic procedures in 3–4 steps from commercial starting materials. *O*-Pivaloylhydroxylamine triflic acid (**2b**) was converted to the unsubstituted iminophosphorane **3b** in good yield. The preparative value of the methodology was demonstrated by the gram-scale synthesis of *N*-methyl iminophosphorane **3c**, obtained in an even slightly higher yield than on small scale (90% versus 87%). Different alkyl substituents of low molecular weight, including sterically hindered isopropyl (**3e**), isobutyl (**3f**) or cyclopropyl groups (**3g**), were tolerated in the reaction and the corresponding products were obtained in good to excellent yields. Aminating reagents bearing electrophilic groups such as alkyl nitriles (**2j**), chlorides (**2k**) or acetates (**2l**) were also compatible (**3j–l**). Furthermore, ethers, trifluoroacetamides and phthalimides were also tolerated and the corresponding products **3m–p** were obtained in moderate to good yields. To show the applicability of the developed method to more complex substrates, aminating reagents derived from three pharmaceuticals, gemfibrozil (**2q**), ibuprofen (**2r**) and hymecromone (**2s**), were reacted with triphenylphosphine to afford the corresponding iminophosphoranes **3q–s** in good yields.

Scheme 3. Monophosphine scope of the reaction.



Yields are of isolated products. Reaction conditions: phosphine (0.250 mmol), **2c** (0.375 mmol), $Fe(acac)_2$ (2.5 mol%), $MeCN/CHCl_3$ 4:1 (2.5 mL), argon atmosphere. [a] Yields calculated by ^1H NMR using trichloroethylene as internal standard. [b] $MeCN/CHCl_3$ 1:4 used as solvent mixture.

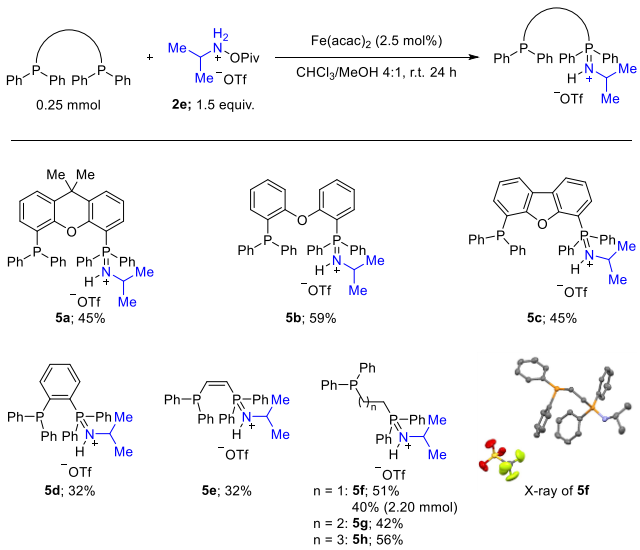
We next investigated the phosphine scope (Scheme 3). Due to the low solubility of some phosphines in acetonitrile, a 4:1 mixture of acetonitrile and chloroform was used as reaction solvent to ensure the homogeneity of the reaction mixture. First, triarylphosphines with different substitution patterns were examined. Electron-donating substituents like methyl (**4a**) or methoxy (**4b**) as well as mildly electron-withdrawing substituents like halides (**4c** and **4d**) were all well-tolerated in the *para* position, whereas strongly electron-withdrawing substituents resulted in low conversion (**4e**). Electron-donating (**4f** and **4g**) as well as electron-withdrawing (**4h**) substituents

in the *meta* position were also suitable in this process. *Ortho*-substituents like methoxy (**4i**) or phenyl (**4j**) were tolerated on one or two of the aryl groups, but if all three aryl groups bore an *ortho*-substituent, poor conversion of the phosphine was observed. Other aryl substituents like naphthyl or pyridyl were also compatible with the developed methodology (**4m** and **4n**). Besides triarylphosphines, alkyldiphenylphosphines were also suitable substrates. A methyl (**4o**) or cyclohexyl (**4p**) substituent on the phosphine was tolerated and the corresponding iminophosphoranes were obtained in moderate yields. A phosphine with a methylene substituent bearing a pyridine was also converted to iminophosphorane **4r**, a potential bidentate ligand, in excellent yield.

In terms of limitations, we observed that increasing steric bulk around the phosphorous atom decreases reactivity. Furthermore, stabilization by at least two aryl groups seems to be required, as dialkylphenylphosphines and trialkylphosphines provided the corresponding iminophosphorane in low yields (see supporting information for more details). Phosphines with very electron-withdrawing substituents and therefore low oxidation potentials were also found to be unsuitable substrates due to low conversion.

We next turned our attention to diphosphines as substrates (Scheme 4). Xantphos, DPEPhos and DBFPhos, bidentate ligands regularly used in homogeneous catalysis, were all oxidized to afford the corresponding iminophosphorane product in moderate yields (**5a**–**c**). Interestingly, the main product that was observed was a phosphine-iminophosphorane, whereas diiminophosphoranes were only observed in minor amounts even though an excess of aminating reagent was employed.[18] Phosphine-iminophosphoranes are a substance class that has attracted attention as hemilabile bidentate ligands in homogeneous catalysis.[2] Diphosphines with a benzene (**5d**) or ethylene linker (**5e**) were also tolerated in the process. Furthermore, diphosphines with alkyl linkers of various lengths were all transformed to the corresponding iminophosphorane-phosphine products (**5f**–**h**).

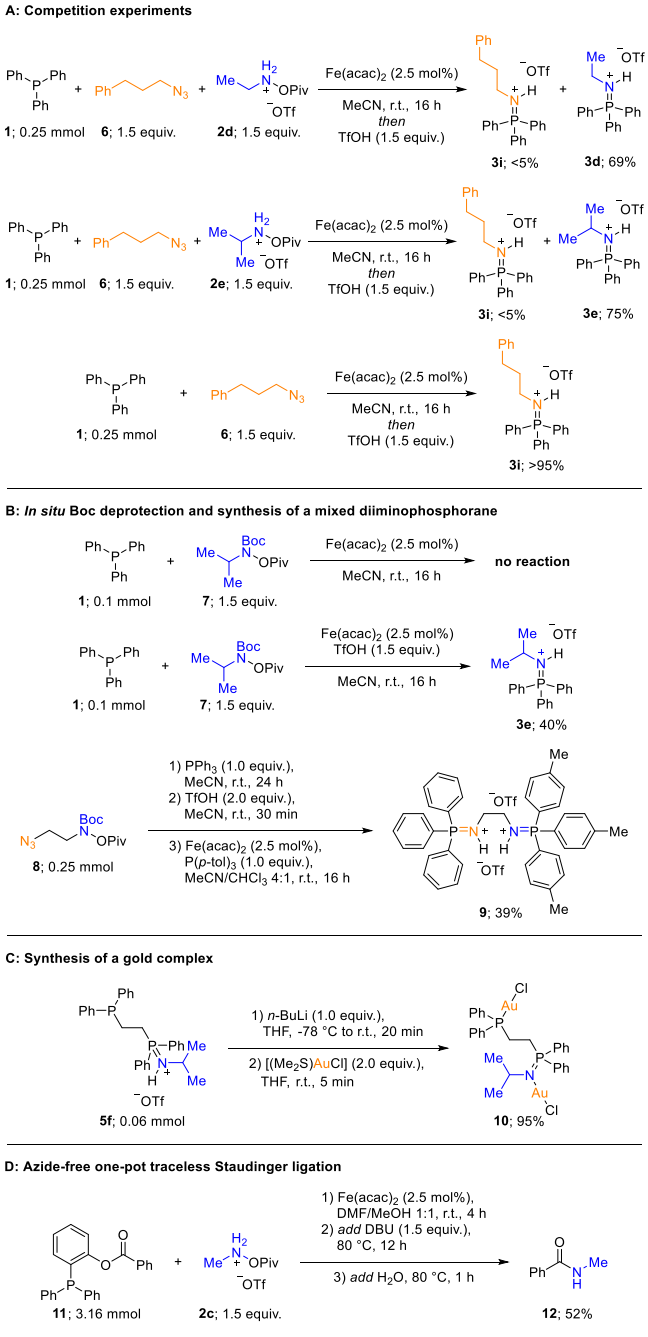
Scheme 4. Diphosphine scope of the reaction.



Yields are of isolated products. Reaction conditions: phosphine (0.250 mmol), **2e** (0.375 mmol), $Fe(acac)_2$ (2.5 mol%), $CHCl_3$/MeOH 4:1 (2.5 mL), argon atmosphere.

To gain further insights into the characteristics of the developed reaction, we performed intermolecular competition experiments between (3-azidopropyl)benzene **6** and different aminating reagents (Scheme 5A). When triphenylphosphine was subjected to equimolar amounts of azide **6** and aminating reagent **2d** or **2e** under the standard reaction conditions, the main products were **3d** or **3e**, respectively, which resulted from the hydroxylamine derivatives. Azide-derived product **3i** was only observed in trace amounts in both cases (<5%). A control experiment, in which triphenylphosphine was exposed to the azide **6** in the absence of any hydroxylamine derivatives, resulted in near-quantitative formation of **3i**. This demonstrates that, under our optimized reaction conditions, *N*-alkylhydroxylamine-derived triflic acid salts outcompete alkyl azides in the reaction with triphenylphosphine.

Scheme 5. Further investigations and applications of the developed methodology.



Boc-protected hydroxylamine-derivatives such as **7** are inert under standard reaction conditions (Scheme 5B). However, when triflic acid is added to the reaction mixture, **7** undergoes *in situ* Boc deprotection to form **2e**, which then can react with triphenylphosphine to afford iminophosphorane salt **3e**. This feature was leveraged to prepare mixed diiminophosphoranes. We designed substrate **8** that bears both an azide and an *N*-Boc-*O*-pivaloylhydroxylamine group. When a phosphine is added, it selectively undergoes a Staudinger reaction with the azide, forming the first iminophosphorane. After Boc-deprotection with triflic acid, a second phosphine can be added that selectively reacts with the deprotected *N*-alkylhydroxylammonium species to form the second iminophosphorane. We applied this strategy for the one-pot synthesis of the mixed diiminophosphorane **9** in 39% overall yield. The preparation of diiminophosphoranes has previously been reported employing the Kirsanov reaction, but was limited to symmetrical diiminophosphoranes,[19] whereas the presented method allows for a one-pot synthesis of mixed diiminophosphoranes and therefore allows facile access to an underexplored chemical space.

The ability of phosphine-iminophosphoranes to coordinate to transition metals[2,15,19] was demonstrated in the synthesis of the dinuclear gold complex **10** from **5f** (Scheme 5C). After deprotonation of the iminophosphorane triflic acid salt **5f** with *n*-BuLi, complex **10** was obtained in a high yield of 95% after ligand exchange with 2 equivalents of [(Me$_2$S)AuCl].

We furthermore applied the developed methodology in an azide-free version of the traceless Staudinger ligation (Scheme 5D).[20] We envisioned the aminating reagent and the phosphine form an iminophosphorane triflic acid salt, which, after deprotonation by DBU, would attack the carbonyl group of the attached ester, thereby cleaving the carbon-oxygen bond. After hydrolysis, the desired amide would be obtained. Indeed, as a proof of concept, we could synthesize *N*-methylbenzamide (**12**) from aminating reagent **2c** and phosphine **11** in 52% yield.

In conclusion, we have developed a method for the iron-catalyzed synthesis of *N*-alkyliminophosphoranes from phosphines and hydroxylamine-derived aminating reagents under mild reaction conditions. The employed aminating reagents can be readily prepared and offer a safer alternative to organic azides, particularly for alkyl groups of low molecular weight. Besides monophosphines, diphosphines are suitable substrates and are mono-oxidized to afford phosphine-iminophosphoranes. The developed methodology was applied in the synthesis of mixed diiminophosphoranes, a gold complex, and in an azide-free traceless Staudinger ligation.

ASSOCIATED CONTENT

Data Availability Statement. The data underlying this study are available in the published article and its Supporting Information.

Supporting Information. General procedures, experimental details, characterization data, crystal data and NMR spectra.
This material is available free of charge via the Internet at http://pubs.acs.org

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The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

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