Enantioselective Hydrophosphination of Terminal Alkenyl aza-Heteroarenes

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Hydrofunctionalizations

Enantioselective Hydrophosphination of Terminal Alkenyl Aza-Heteroarenes

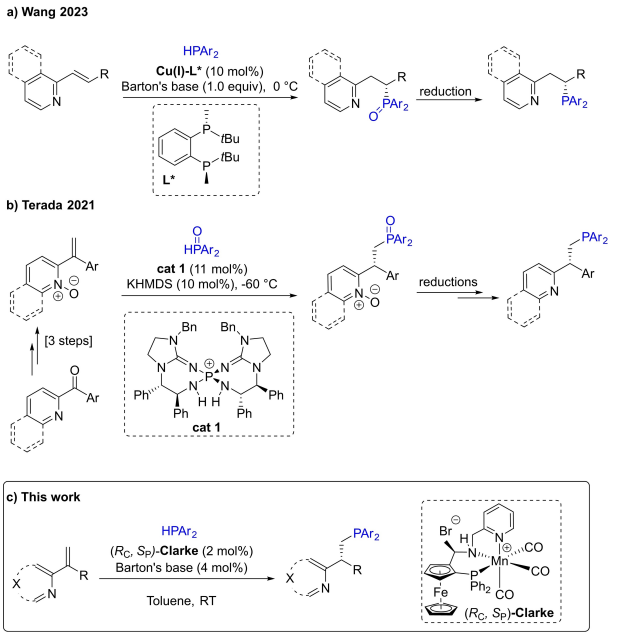
*Esther G. Sinnema, Tizian-Frank Ramspoth, Reinder H. Bouma, Luo Ge, and Syuzanna R. Harutyunyan**

Abstract: This paper presents a Mn(I)-catalysed methodology for the enantioselective hydrophosphination of terminal alkenyl aza-heteroarenes. The catalyst operates through H–P bond activation, enabling successful hydrophosphination of a diverse range of alkenyl-heteroarenes with high enantioselectivity. The presented protocol addresses the inherently low reactivity and the commonly encountered suboptimal enantioselectivities of these challenging substrates. As an important application we show that this method facilitates the synthesis of a non-symmetric tridentate P,N,P-containing ligand like structure in just two synthetic steps using a single catalytic system.

Introduction

Chiral phosphorus containing compounds are of importance for applications in biologically active pharmaceuticals, agrochemicals and asymmetric catalysis.[1] In the latter case, phosphorus compounds are often used as standalone chiral organocatalysts or as chiral ligand components of metal complexes used in transition metal catalysis.

Stereoselective hydrophosphination is an appealing approach for direct access to chiral phosphorus containing compounds and recent years[2] have witnessed rapid development in catalytic asymmetric hydrophosphination methodologies using chiral catalysts derived from transition metals, for example Pt,[3] Pd,[4] Ni,[5] or Cu[6] complexes. However, despite these advances, enantioselective hydrophosphination is still largely limited to conventional Michael acceptors. In contrast, little progress has been made in utilizing alkenyl-aza-heteroarene acceptors, most likely due to their relatively low reactivity and difficulties to control the product stereochemistry. This is unfortunate since hydrophosphination of alkenyl aza-heteroarenes opens a direct route to chiral P,N ligand-like structures, most of which currently require multistep synthesis, often using chiral resolution to obtain enantioenriched products.[7] The recent report by Wang et al.[8a] represents an important step forward in this context. At the same time, it emphasizes the difficulties associated with reactions involving α-substituted terminal alkenes. (Scheme 1a). Their only example of hydrophosphination of terminal alkenyl quinoline shows significantly lower enantioselectivity (53 % *ee*) compared to their β-substituted counterparts (up to 92 % *ee*). The β-substituted alkenes generate a carbon stereocenter upon forming a bond with a phosphorus atom. In contrast, when using α-substituted terminal alkene, the carbon stereocenter is formed upon C–H bond formation (formal stereospecific protonation) which is known to be more challenging to control. In this context, Terada et al. reported catalytic enantioselective hydrophosphinylation of N-oxide analogues of α-substituted terminal alkenyl aza-heteroarenes. (Scheme 1b).[8b] However, this method requires multiple steps to arrive at the target chiral phosphine products. Furthermore, both reported protocols require relatively high catalysts loadings. These observations collectively under-



Scheme 1. Literature precedents on enantioselective synthesis of chiral aza-heteroaromatic phosphines with a carbon stereocenter and our work.

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score the unique challenges associated with enantioselective synthesis of chiral aza-heteroaromatic phosphines with a carbon stereocenter and the need for new strategies.

In recent years, complexes based on the earth-abundant metal Mn(I) have emerged as remarkably successful catalysts for reductive transformations of carbonyl compounds, including asymmetric variants.[9] Apart from these reports, we have recently demonstrated that catalytic H–P bond activation of diarylphosphines can also be achieved by Mn(I)-(R_C, S_P)-**Clarke** catalyst.[10] This specific catalyst uniquely utilizes metal-ligand cooperativity (MLC) to activate the H–P bond, setting it apart from other catalysts in the field of catalytic hydrophosphinations. Our previous studies of α,β-unsaturated nitriles led us to the conclusion that for these compounds the MLC mode of bond activation is advantageous both for the enantioselective delivery of the phosphorus moiety in the case of internal alkenes as well as for the enantioselective protonation in the case of terminal alkenes.[10a] These results prompted us to investigate Mn(I)-complexes as catalysts for asymmetric hydrophosphination of the less reactive and less explored terminal alkenyl aza-heteroarenes (Scheme 1c).

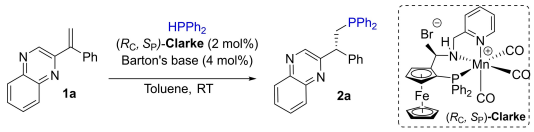
Here, we describe a general protocol for Mn(I)-catalysed asymmetric hydrophosphination of a diversity of α-substituted alkenyl aza-heteroarenes. This method enables the synthesis of P,N and P,N,P scaffolds in a single step and non-symmetric P,N,P motives in two steps.

Results and Discussion

We initiated our studies by investigating the model reaction between diphenylphosphine and alkenyl quinoxaline **1a** in toluene at room temperature using Mn(I)-Clarke catalyst in the presence of Barton's base (Table 1). The reaction proceeded promptly, suggesting that our catalytic system is capable of activating the reactants efficiently towards the formation of the desired product **2a** (Entry 1). The presence of Barton's base alone in the absence of catalyst is also sufficient for the reaction to proceed, although longer reaction times are required, highlighting the importance of carefully controlling the amount of base in the catalytic system (compare Entries 1–3). Similar outcomes were obtained using *t*PentOK instead of Barton's base (Entry 4), in line with our previous study with Mn(I)-catalysed hydrophosphination. Inorganic bases facilitated the reaction as well, but with diminished enantioselectivity (Entries 5 and 6). When testing different solvents (Entries 7–11), we observed high yields and good enantioselectivity with MeCN, THF, and DCM. Interestingly, even though the carbon stereocenter in this reaction is formed via a formal stereospecific protonation, there was hardly any deterioration of enantiomeric excess in a protic solvent such as *i*PrOH. However, the use of Et_2O as the solvent caused a significant decrease in enantiopurity. Lastly, we observed that a decrease in temperature resulted in a slightly increased enantioselectivity (Entry 12).

With the optimised reaction conditions in hand, we proceeded to investigate the scope of this methodology

Table 1: Optimisation of the reaction conditions for hydrophosphination of **1a**.[a]

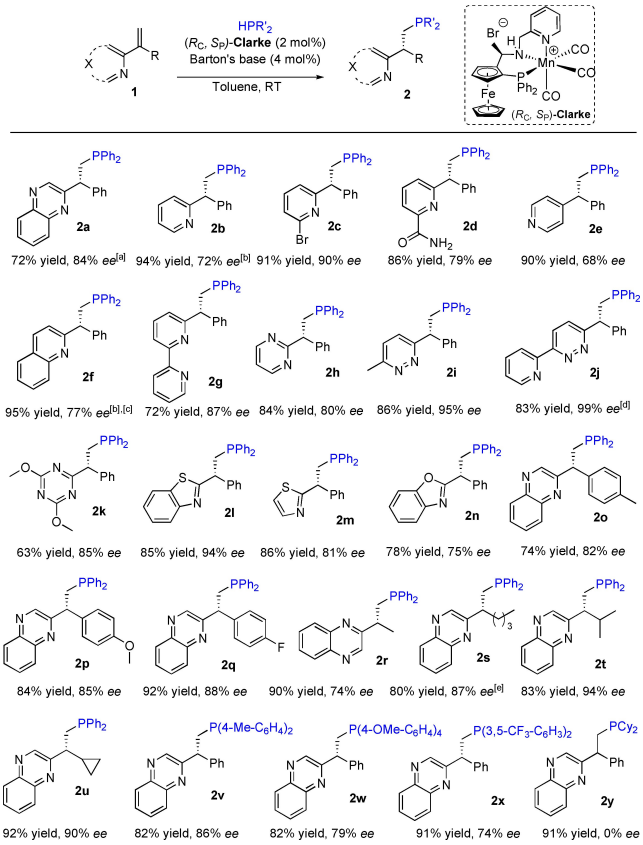


Entry	Deviation from standard conditions	Conv. [%][b]	ee [%][c]
1	None	>99	79
2	Without Mn(I)-Clarke catalyst	50	–
3	8 mol% Barton's base	>99	71
4	tPentOK instead of Barton's base	>99	79
5	LDA instead of Barton's base	>99	72
6	K_2CO_3 instead of Barton's base	>99	77
7	MeCN instead of toluene	>99	75
8	THF instead of toluene	>99	78
9	DCM instead of toluene	>99	77
10	*i*PrOH instead of toluene	>99	79
11	Et_2O instead of toluene	>99	66
12	0 °C instead of RT	>99 (72)[d]	84

[a] General conditions: **1a** (0.1 mmol), (R_C, S_P)-**Clarke** (2 mol%), Barton's base (4 mol%), $HPPh_2$ (0.1 mmol) in toluene (1 mL) at RT for 16 h. [b] Determined by ^{1}H NMR of reaction crude. [c] Determined by SFC on a chiral stationary phase. [d] Isolated yield.

(Scheme 2). We initially focused on the use of alkenes with various heteroaromatic rings, an aspect that has been notably absent from the existing literature, starting with derivatives of alkenyl-pyridines. Phosphinated products **2b** and **2e** were obtained from 2- and 4-alkenyl pyridine substrates with enantiomeric purities slightly lower than that obtained in the model reaction with alkenyl quinoxaline **1a**. Interestingly, substrates with electron withdrawing substituents, such as bromine and amide gave the corresponding products **2c** and **2d** with higher enantiomeric purities (90 and 79% respectively). In all cases full conversion and high yields were obtained and importantly no specific measures were required to prevent possible oxidation of the phosphine moiety of the products into their corresponding phosphine oxides. As expected, no reaction occurred when placing alkenyl substituents in the 3-position of the pyridine ring, as conjugation with the nitrogen atom is required for the reactivity. Moving away from pyridine substrates, we found that alkenyl quinoline undergoes hydrophosphination smoothly as well, resulting in product **2f** with 77% *ee*. We then continued our scope studies with the investigation of heteroarenes containing multiple nitrogen atoms within the aromatic ring, finding that they also undergo hydrophosphination successfully with good to excellent enantioselectivity and full conversion towards the corresponding products (**2g**–**2k**). Particularly noteworthy is the exceptional enantioselectivity observed for pyridazine containing products (**2i** and **2j** with 95 and 99% *ee*, respectively). Alkenyl heteroarenes including benzothiazole, thiazole and benzoxazole rings were also suitable substrates for this reaction, yielding the corresponding products **2l**–**2n** with good to high enantioselectivies.

Subsequently, we turned our attention to the exploration of the effect of the phenyl substituent on the alkene.

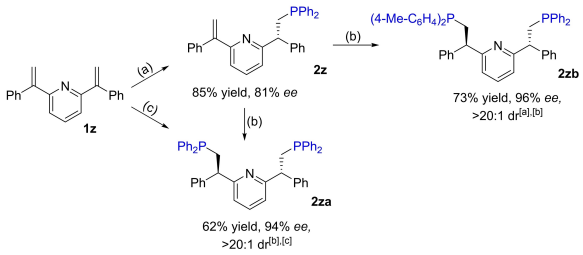


Scheme 2. Scope of the reaction between phosphine and alkenyl aza-heteroarene. General conditions: **1** (0.1 mmol), (R_C, S_P)-**Clarke** (2 mol%), Barton's base (4 mol%), phosphine (0.1 mmol) in toluene (1 mL) at RT for 16 h. [a] Reaction performed at 0 °C. [b] Reaction performed in *i*PrOH with *t*PentOK at 0 °C. [c] The absolute configuration was determined for compound **2f** (see SI). The configuration of other compounds were assigned by analogy. [d] Reaction also performed at gram-scale. [e] 3 days reaction time.

Introducing *p*-Me, *p*-OMe, and *p*-F substituents into the phenyl ring of quinoxaline containing substrates resulted in products **2o**–**2q** with high enantiomeric excess (*ee* 82–88%). The reaction tolerated various aliphatic groups such as methyl, butyl, isopropyl, and cyclopropyl, furnishing the corresponding products (**2r**–**2u**) with high yields and good to high enantioselectivities.

Finally, a screening of various phosphine reagents was performed. Hydrophosphination with (p-Me–C_6H_4)$_2$PH, (p-MeO–C_6H_4)$_2$PH and (3,5-CF_3–C_6H_3)$_2$PH led to the corresponding products **2v**, **2w** and **2x**, with good yields and enantiomeric purities. However, racemic product was obtained with the aliphatic phosphine Cy_2PH (**2y**), revealing a limitation of the protocol.

Having established the scope of the reaction, we wondered whether our methodology allows access to tridentate P,N,P scaffolds. For this purpose, we synthesized heteroaromatic diene **1z** and subjected it to our hydrophosphination protocol (Scheme 3). By using one equivalent of diphenylphosphine, we were able to selectively produce the monophosphinated alkene **2z** from the symmetric substrate **1z**. The resulting alkene **2z** can subsequently

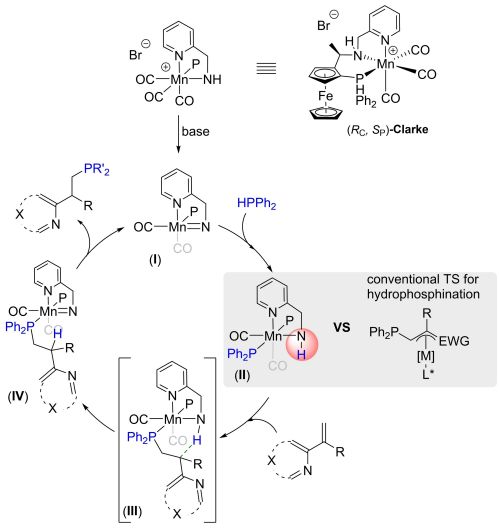


Scheme 3. Hydrophosphination of alkene **1z** to yield P,N, symmetric and asymmetric P,N,P scaffold. Reaction conditions; (a) **1z** (0.1 mmol), (R_C, S_P)-**Clarke** (4 mol%), Barton's base (8 mol%), phosphine (0.1 mmol) in toluene (1.0 mL) at RT for 16 h; (b) **2z** (0.1 mmol), (R_C, S_P)-**Clarke** (4 mol%), Barton's base (8 mol%), phosphine (0.1 mmol) in toluene (0.5 mL) at RT for 16 h, Reported yields and enantiopurities are obtained after crystallization, see SI; (c) **1z** (0.1 mmol), (R_C, S_P)-**Clarke** (10 mol%), Barton's base (20 mol%), phosphine (0.1 mmol) in toluene (0.5 mL) at RT for 16 h.

undergo further hydrophosphination to yield either **2za** when diphenylphosphine is used or the corresponding non-symmetric P,N,P product **2zb** when (p-Me-C_6H_4)$_2$PH is used as the phosphine substrate. Product **2za** can also be obtained directly from substrate **1z** by increasing the phosphine concentration and the catalyst loading.

Building upon our previous findings with α, β-unsaturated nitriles,[10b] we propose the following catalytic cycle for our hydrophosphination protocol (Scheme 4). We hypothesize that the catalyst is first activated by a base (**I**), after which the H–P bond is activated (species **II**) upon addition of diphenylphosphine. These events result in both the phosphorus and the hydrogen atoms ending up within the chiral environment of the Mn(I)-complex (species **II**).

Subsequently, the reaction with the alkenyl-heteroarene can take place through the nucleophilic addition of the phosphide moiety to the β-carbon of the alkene, forming species **III**. This is followed by fast stereospecific intramolecular protonation of the resulting carbanion at the α-



Scheme 4. Proposed catalytic cycle.

carbon by the N–H moiety of the Mn(I) complex, thus promoting the catalytic hydrophosphination through enantioselective protonation. Stereospecific proton transfer from the chiral ligand bound to the metal is what distinguishes our catalytic system from all other approaches used in hydrophosphinations, in which the proton originates from an achiral source, such as baseH^+. As a result, our system allows for a more general method with enhanced enantioselectivities, reactivities and substrate scope. Further studies to expand the scope of our catalytic system and to get detailed mechanistic insights are underway.

Conclusion

We have developed the first Mn(I)-catalysed, general protocol for the enantioselective hydrophosphination of alkenyl aza-heteroarenes. The phosphine group of the resulting products exhibit reduced susceptibility to oxidation, rendering them notably stable and better accessible for further synthesis and applications. The method supports a wide variety of alkenyl aza-heteroarenes, substrates that are considered challenging due to their inherently low reactivity and the difficulty of controlling their enantioselective transformation. Importantly, our method offers an efficient route to access non-symmetric P,N,P ligand like structures through a single catalytic system within two synthetic steps.

Supporting Information

The authors have cited additional references within the Supporting Information.[11–22]

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Asymmetric Catalysis · Hydrophosphination · Manganese(I)-Catalysis · Terminal Alkenyl Hetereoarenes

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