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Zirconium-Catalyzed Hydroarsination with Primary Arsines

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Keywords: Hydroarsination, zirconium, arsenic, catalysis, photocatalysis

Abstract

The zirconium compound, $[\kappa^5-N,N,N,N,C-(Me_3SiNCH_2CH_2)_2NCH_2CH_2NSiMe_2CH_2]Zr$ (1), catalyzes the hydroarsination of alkenes with primary arsines, previously unknown substrates for this transformation. Irradiation in the ultraviolet, near-UV, or visible with commercially-available light sources are critical for this catalysis. Styrene substrates are unreactive without irradiation, but Michael acceptors give products in the dark or under irradiation with any source. These observations suggest that the zirconium arsenido intermediate engages in insertion based hydroarsination under photolysis, but the arsenido ligand is nucleophilic without photoexcitation.

Keywords: Hydroarsenation catalysis, zirconium, arsenide, photocatalysis, arsine

1. Introduction

Catalytic heterofunctionalization involving group 15 elements is a proven methodology to generate new C–E bonds for both nitrogen and phosphorus, yet catalytic hydroarsination is rare, with only a handful of reported examples of this reaction.[1-10] Nevertheless, such a strategy offers an atom-economical and direct route to organoarsines, but the transformation is limited to only a handful of substrates and often precious-metal catalysts.[2-4, 9] All reported transformations utilize secondary arsine substrates with the exception of one case that utilizes an arsenylborane.[6] Thus far, hydroarsination with primary arsines to selectively make secondary

arsines remains unreported, but such products are attractive, being available for further functionalization by conventional means.

Organoarsines have found applications in diverse fields including chemistry,[1-3, 11, 12] materials science,[13] agriculture,[14] and as anti-cancer agents.[15, 16] Catalytic chemistry that forms bonds to arsenic chemistry is less developed than that for lighter group pnictogens,[11] but a notable achievement is arsenic-based ligands. Some triarylarsine ligands have outperformed phosphorus analogues in cross-coupling[15, 17, 18] and arsination reactions,[19]

Our previous work on catalytic hydroarsination using $[\kappa^5-N,N,N,N,C-(Me_3SiNCH_2CH_2)_2NCH_2CH_2NSiMe_2CH_2]Zr$ (1) has targeted terminal alkynes and secondary arsines to provide tertiary vinyl arsine products (eqn 1).[7] Critical to that work was establishing facile As–H bond activation at 1, which was primarily exploited for arsine dehydrocoupling but lay the groundwork for additional As–C bond-forming catalysis. However, like the related hydrophosphination catalysis, reactivity with diphenylarsine was ultimately limited and relative rates of catalytic reactions were low.



Development of hydroarsination involving *primary* arsines would be of value. This methodology could selectively generate either secondary or tertiary arsines from simple precursors. Our previous work in catalytic hydrophosphination of primary phosphines with **1**

demonstrated the selective formation of tertiary phosphine products (eqn 2, double activation).[20] Upon slight modification of the reaction conditions, exclusively *secondary* phosphine products could be achieved (eqn 2, single activation).



For **1**, hydrophosphination catalysis with primary phosphines has been more facile than reactions with secondary phosphines,[20] an idea that may be extended to arsenic. More recent reports showed yet greater catalytic activity and a broadened substrate scope with **1** in the under ultraviolet or visible irradiation.[21] The improved hydrophosphination activity prompted reinvestigation into catalytic hydroarsination using **1** with primary arsines under photocatalytic conditions. The result was the first example of a catalytic hydroarsination utilizing primary arsines and a rare example of a photocatalytic heterofunctionalization reaction for heavier group 15 elements.

2. Materials and Methods

2.1 General methods

All manipulations were performed under a positive nitrogen pressure with standard Schlenk techniques or in a glovebox using dry, oxygen-free solvents. NMR spectra were recorded on a Bruker AXR 500 MHz spectrometer using benzene- d_6 that was distilled under reduced pressure from NaK alloy. NMR spectra are reported with reference to residual solvent signals (C₆D₆, δ 7.16 and 128.0). ESI-mass spectra were collected on an Applied Biosystems 4000QTrap Pro. IR data were

collected on a Bruker Alpha FTIR spectrometer in hexanes. Absorption spectra were recorded with a QuantaMaster 4 fluorescence spectrophotometer (PTI, Edison, NJ, USA) as hexanes solutions. The zirconium compound [κ^5 -*N*,*N*,*N*,*N*,*C*-(Me₃SiNCH₂CH₂)₂NCH₂CH₂NSiMe₂CH₂]Zr (1) was prepared according to the literature method.[22] All other chemicals were obtained from commercial suppliers and dried by conventional means.

Preparation of *p***-tolylarsine** A Schlenk flask containing 520 mg (13.7 mmol, ~2.5 equiv) of lithium aluminum hydride was suspended in diethyl ether and cooled to -78 °C. Slowly, via cannula, a solution of 1.274 g (5.38 mmol) of *p*-tolyldichloroarsine in diethyl ether was added. The reaction stirred at -78 °C for 1 h, then gradually warmed to ambient temperature and stirred overnight. The crude mixture was quenched with degassed water, and the solution was filtered via cannula. Diethyl ether was removed by distillation under nitrogen. The product was slowly sublimed from the crude reaction mixture at ambient temperature under nitrogen atmosphere (416 mg, 2.47 mmol, 46%). ¹H NMR: δ 7.28 (d, *J* = 8 Hz, 2 H, C₆H₄CH₃), 6.85 (d, 8 Hz, 2 H, C₆H₄CH₃), 3.49 (s, 2 H, AsH₂), 2.03 (s, 3 H, C₆H₄CH₃). ¹³C{¹H}: δ 137.7 (s, C₆H₄CH₃), 136.0 (s, C₆H₄CH₃), 129.7 (s, C₆H₄CH₃), 126.0 (s, C₆H₄CH₃), 21.0 (s, C₆H₄CH₃). MS calcd for C₇H₉As: m/z 168.1. Found: 168.8.

Preparation of (N₃N)Zr(*p***-tolyl)AsH (2)**. A scintillation vial was charged with 41.4 mg (0.246 mmol) of *p*-tolylarsine, 112.1 mg (0.247 mmol) of **1**, and ca 4 mL of toluene to give a deep golden-orange solution. This solution stirred for twenty minutes, and then the toluene was removed under reduced pressure. The crude reaction mixture was dissolved in pentane and cooled to -20 °C to afford orange crystals after 3 d (110 mg, 0.178 mmol, 72%). Anal. Calcd for C₂₂H₄₇AsN₄Si₃Zr Calc: C, 42.75; H, 7.67; N, 9.07. Found: C, 43.01; H, 7.55; N, 8.92. ¹H NMR: δ 7.71 (d, 8 Hz, 2 H, C₆H₄CH₃), 6.97 (d, 8 Hz, 2 H, C₆H₄CH₃), 3.38 (s, 1 H, AsH), 3.20 (t, *J* = 5

Hz, 6 H, CH₂), 2.16 (s, 3 H, CH₃), 2.13 (t, J = 5 Hz, 6 H, CH₂), 0.29 (s, 27 H, Si(CH₃)₃). ¹³C{¹H}: δ 139.8 (s, C₆H₄CH₃), 135.3 (s, C₆H₄CH₃), 133.3 (s, C₆H₄CH₃), 129.1 (s, C₆H₄CH₃), 64.0 (s, CH₂), 47.8 (s, CH₂), 21.1 (s, C₆H₄CH₃), 1.2 (s, Si(CH₃)₃). UV-vis (toluene, λ_{max} nm): 375 (ϵ = 367(9) M⁻¹ cm⁻¹).

2.2 General procedure for catalytic hydroarsination reactions

A borosilicate NMR tube was charged with 0.1 mmol *p*-tolylarsine and 0.1 mmol alkene in the presence of 5 mol % of **1** in benzene- d_6 solvent. The consumption of substrate to product was monitored by ¹H NMR spectroscopy. Conversions were determined by integration of ¹H NMR spectra.

3. Results and Discussion

Prior work with **1** and primary arsines considered sterically bulky primary arsines for dehydrocoupling reactivity to make new As–As bonds with concomitant formation of H₂.[7] Although small, polar, unsaturated substrates could readily insert into a family of zirconium arsenide derivatives, the arsines used in this report were too sterically encumbered for optimal catalytic turnover.[7] For this work *p*-tolylarsine was chosen for its NMR handle and ease of synthesis. The precursor *p*-tolyldichloroarsine was synthesized through modifications of literature procedures (Scheme 1).[7, 23]



Scheme 1: Synthesis of *p*-tolylarsine

Reduction of *p*-tolyldichloroarsine afforded the desired arsine, albeit in low yields (<50%) due to the high volatility of *p*-tolylarsine. Treatment of **1** with stochiometric *p*-tolylarsine in toluene converts colorless **1** to the anticipated yellow zirconium-arsenido product, $(N_3N)ZrAsHTol$ (**2**; $N_3N = N(CH_2CH_2NSiMe_3)_3^{3-}$, Tol = *p*-tolune; eqn 3). The isolated yield of **2** is 72%, but observation of the reaction by ¹H NMR spectroscopy reveals quantitative conversion to **2**, indicating that yield is a function of crystallization. The spectroscopic data for **2** is similar to the broader family of triamidoamine-supported zirconium-arsenido and -phosphido derivatives.[7, 22, 24, 25] Of note, the arsenic proton and the *p*-toluene methyl protons resonate as a singlet at δ 3.38 and a triplet at δ 2.16 in the ¹H NMR spectrum of **2**, respectively.



Treatment of a 1:1 benzene- d_6 solution of *p*-tolylarsine and styrene with 5 mol % of **1** resulted in quantitative, immediate formation of **2** and only trace formation of the single activation hydroarsination product, (Tol)AsHCH₂CH₂Ph, over a period of 24 hours (Table 1). It was hypothesized that, as with hydrophosphination catalysis using **1**, photolysis would enhance reactivity.[21, 26] Running this reaction under irradiation in the visible, near ultraviolet, and in a UV reactor all provided substantially improved conversions, and importantly, the control reaction in strict darkness failed to give any turnover (Table 1). Likewise, reactions in the absence of **1** failed to give appreciable products under these conditions.

Table 1: Zirconium-catalyzed hydroarsination of styrene under different light sources.Conditions: Twenty equiv. of *p*-tolylarsine, twenty equiv. of styrene, one equiv. of 1, ambient
temperature. Percent conversions were measured by ¹H NMR spectroscopy.

+	AsH ₂ $5 \mod \% 1$ $5 \mod \% 1$ C_6D_6 , 24 h	h As Tol
Entry	Irradiation	% Conversion
1	visible	44
2	near UV	48
3	253.7 nm	54
4	ambient light	trace
5	dark	0

The increased catalytic activity of hydroarsination reactions run under ultraviolet or visible irradiation suggests that hydroarsination may be operative via an analogous photoexcitation and LMCT event as noted for catalytic hydrophosphination with **1** (vide infra).[21] Photocatalysis is an attractive route to pnictanes because visible light irradiation suggests that sunlight could be utilized, but more pragmatically, highly efficient photon sources such as LED bulbs can be utilized rather than heating. While there was improvement in the conversion by movement to higher energy sources, there was still good conversion with visible irradiation. A transition at 375 nm was measured in the UV-vis spectrum of **2**. Based on the similarity in energy and extinction coefficient ($\varepsilon = 367(9)$ M⁻¹ cm⁻¹) to the related phosphido derivative,[26] we tentatively assign this transition as arsenic–zirconium charge transfer.

Previous studies on the catalytic hydrophosphination of styrene derivatives with **1** showed selective formation of tertiary phosphine products, depending on reaction conditions.[27] In this hydroarsination catalysis with **1**, however, only secondary arsine products were detected (Table 1, entries 1-3). Evidence for the secondary product comes from the ¹H NMR spectra. For example, the ¹H NMR spectrum of (Tol)AsHCH₂CH₂Ph contains an As–H triplet at δ 3.72. This catalysis is the first example of a hydroarsination with a primary arsine and selectivity to form secondary arsine products.

Additional styrene derivatives were considered for photocatalytic hydroarsination with **1** to make the desired secondary arsine products. Hydroarsination of styrene derivatives under visible or ultraviolet irradiation shows comparable conversions for all styrene substrates, regardless of electronic factors (Table 2, entries 1-3). There did appear to be slightly greater reactivity for

electron-rich styrenes, and a linear free-energy experiment was performed to test this preference. Hammett competition experiments indeed showed greater reactivity of styrene derivatives bearing electron-donating substituents, consistent with similar experimentation for catalytic hydrophosphination. In that work, it was suggested that this reactivity was consistent with insertion-based hydrophosphination.[26]

Table 2: Catalytic hydroarsination with 1. Conditions: Twenty equiv. of *p*-tolylarsine, twentyequiv. of substrate, one equiv. of 1, near UV irradiation, ambient temperature. Percentconversions are measured by ¹H NMR spectroscopy.



Conversions for the hydroarsination reactions of styrene derivatives as measured by NMR spectoscopy are modest but consistent among all styrenes tested (Table 2, entries a–c). Reactions

run for 48 hours show a slight improvement in conversion to the hydroarsination product, but the catalysis is sluggish overall. Heating the reactions under irradiation did not substantially impact catalysis, as anticipated from previous studies on catalytic hydrophosphination.

Michael acceptors were excellent candidates for catalytic hydroarsination (Table 2, entries d-f). These substrates proceeded smoothly to give high conversions to the secondary arsine products after only one hour. Reactions with 1-hexene (Table 2, entry g) failed to provide detectable levels of products after 48 hours, whereas 1-hexene with PhPH₂ and catalytic **1** provides ~50% conversion to the hydrophosphination product after 24 hours under irradiation.[26]

Many aspects of this system are similar to hydrophosphination catalysis with **1** including the light-dependence, which is doubtlessly related to the similar electronic spectra of the $(N_3N)ZrER$ (E = P, As) derivatives in question. Studies on photocatalytic hydrophosphination with **1** found that photoexcitation promoted catalytic bond-formation by excitation to state with significant Zr–P antibonding character and substantial Zr–P bond lengthening, which lead to the hypothesis that insertion is facilitated by the weakening Zr–P bond under photolysis.[21] Given the similar UV-vis absorbance spectra of both **2** and the analogous phosphido derivatives, it is likely that a related charge transfer event occurs during photocatalytic hydroarsination, which appears to accelerate hydrophosphination of styrene derivatives but is not sufficiently activated for 1-hexene. The latter observation is consistent with greater reactivity of styrene substrates versus simple alkenes in photocatalytic hydrophosphination using **1**.

Nevertheless, there is a substantial difference in this reactivity. Control hydroarsination reactions of the Michael acceptors in the dark provide similar if not the same conversions as reactions run under irradiation. This observation harkens back to early work with trimaidoamine-supported zirconium and arsines in which unsaturated substrates readily insert into the Zr–As bond

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of the zirconium-arsenide compound $(N_3N)ZrAsHMes$ (Mes = 2,4,6-Me₃C₆H₂).[7] The observed increased activity of Michael acceptors over styrenes is consistent with previous study. The indifference toward light for the catalytic hydroarsination with **1** of Michael acceptors as compared to styrene derivatives that require photolysis argues for separate mechanisms in this catalysis. It appears that the arsenido ligand of **2** is acting as a nucleophile for polar substrates but it can be activated upon photolysis for insertion of less polar unsaturated molecules.

4. Conclusions

Compound **1** is a pre-catalyst for hydroarsination of alkenes with a primary arise substrate and provides exclusively secondary arsines with high selectivity for the *anti*-Markovnikov product. These results are one in the limited set of catalytic hydroarsination reactions, and this is the first report with primary arsines. An observed intermediate in the catalysis, (N₃N)ZrAsHTol (**2**), was independently prepared and spectroscopically characterized. The spectroscopic features of **2** and light dependence in the hydroarsination of styrene substrates is similar to hydrophosphination photocatalysis with **1**. For Michael acceptors, the hydroarsination catalysis is no longer light dependent. These observations suggest nucleophilic hydroarsination with activated substrates and insertion-based hydroarsination for unactivated substrates, but only with Zr–As bond activation under photolysis. This kind of divergent reactivity is to be important in further developing metal-arsenido chemistry, and as is this new example of photocatalytic heterofunctionalization.

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Dedication

To Prof. William Jones, a patient teacher and thoughtful scientist, on the occasion of his 65th

birthday.

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TOC graphic



Synopsis: A simple zirconium compound catalyzed the hydroarsination of alkynes with primary arsines, RECORDERATED MANUSCRIP which appears to have insertion or nucleophilic behavior based on the unsaturated substrate.