

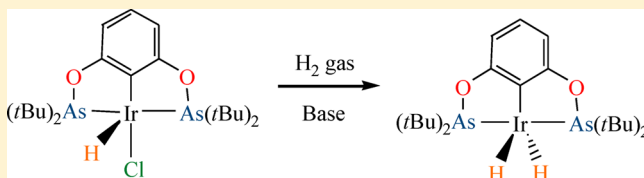
Synthesis, Characterization, and Dehydrogenation Activity of an Iridium Arsenic Based Pincer Catalyst

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S Supporting Information

ABSTRACT: A new arsenic-based pincer (AsOCOAs) dehydrogenation catalyst has been synthesized, $\text{IrHCl}\{2,6\text{-C}_6\text{H}_3\text{-(O-AsBu}^t_2)\}$ (**3**). Treatment with an equivalent of base (NaO-tert-butoxide) under an atmosphere of hydrogen gas affords the dihydride catalyst $\text{IrH}_2\{2,6\text{-C}_6\text{H}_3\text{-(O-AsBu}^t_2)\}$ (**4**). The activity of **3** was explored under transfer dehydrogenation conditions with cyclooctane and *tert*-butyl ethylene, giving a maximum turnover number of 960 at 175 °C in 24 h. Acceptorless dehydrogenations were also explored with pyrrolidine-based molecules, ethylperhydrocarbazole (**5**), methylperhydroindole (**6**), and butylpyrrolidine (**7**), in which all results indicate **3** is roughly half as active as the analogous phosphine-based pincer catalyst **2**. Akin to the phosphine pincer catalysts the activity was seen to steadily improve with increasing temperature, peaking at 175 °C, upon which thermal decomposition sets in.



INTRODUCTION

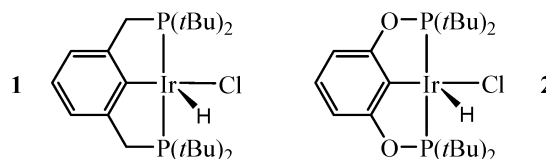
For decades, hydrogen has been targeted as the utopian fuel of the future on account of its abundance and environmental friendliness. However, a major difficulty in the utilization of hydrogen as a fuel is the problem of high-density storage. Thus, a high-density, high-stability method for storing hydrogen is essential to the implementation of fuel cells in all but a few niche applications. Another major concern about hydrogen is implementing a suitable infrastructure. While this could be done for any form of hydrogen carrier, the barrier to implementing a liquid organic carrier (LOC) of hydrogen would be significantly lower than others as it is a similar type of chemical to the current distribution system. In addition to the easy adaption to existing infrastructures, LOCs have many other practical advantages. They are cheap, abundant LOCs that can reversibly release 7–8 wt % hydrogen. They can be economically manufactured in the massive quantities required to meet the anticipated demand and would eliminate the thermal management problems commonly associated with the systems based on solid-state hydrogen-absorbing materials. We have recently discovered catalysts that could potentially enable this technology.^{1–3}

In 1997, the Jensen lab discovered that the “pincer” complex $\text{IrH}(\text{Cl})\{2,6\text{-C}_6\text{H}_3\text{-CH}_2\text{P}(\text{tBu})_2\}_2$ (**1**) catalyzes the dehydrogenation of cycloalkanes to arenes.^{1–3} This was the first report of a homogeneous catalyst for this reaction. The unique reactivity of this especially robust and active catalyst can be ascribed to the tridentate “PCP pincer” ligands, which contain two coordinating, neutral phosphorus centers and an anionic, coordinating carbon site. It has been found that the electronic environment of the catalytic metal center of the pincer complex is highly sensitive to minor changes in the PCP pincer ligand.^{4–6} It is now well established that dihydro POCOP pincer iridium

complexes can selectively dehydrogenate aliphatic groups under much milder conditions than those required for the corresponding heterogeneous catalysts, such as platinum on alumina, without harm to other functional groups of an organic molecule.^{5a,b,6}

More recent reports have described that related POCOP pincer complex **2** is a highly active precatalyst for the dehydrogenation of alkanes and heterocyclic amines, Scheme 1.^{4,7} Previous findings have shown that pyrrolidine-based

Scheme 1. Catalysts **1** and **2**

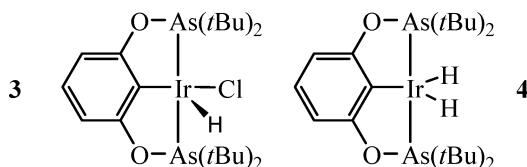


heterocycles are known to have lower ΔH values of dehydrogenation; thus a small family of LOCs was chosen for an initial screening.^{8,9} Seeking to improve this system, we made an alteration to the pincer ligand using arsenic in place of phosphorus as the chelating atoms (AsOCOAs).¹⁰ Herein we formally report the synthesis, characterization, and dehydrogenation activity of the related arsenic-based iridium pincer complexes $\text{IrHCl}\{2,6\text{-C}_6\text{H}_3\text{-(O-AsBu}^t_2)\}_2$ (**3**) and $\text{IrH}_2\{2,6\text{-C}_6\text{H}_3\text{-(O-AsBu}^t_2)\}_2$ (**4**), Scheme 2. To our knowledge only one other arsenic pincer is known of the “ANA” type in which pyridine is the aromatic portion of the pincer, binding through

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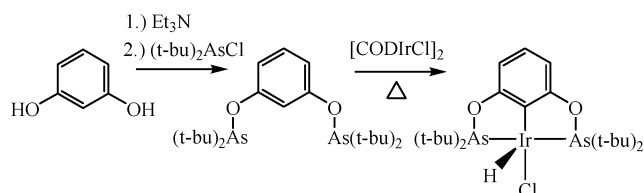
Scheme 2. Catalysts 3 and 4



the nitrogen.¹¹ The molybdenum ANA pincer complex has shown some promise in the area of catalytic nitrogen fixation.¹¹

RESULTS AND DISCUSSION

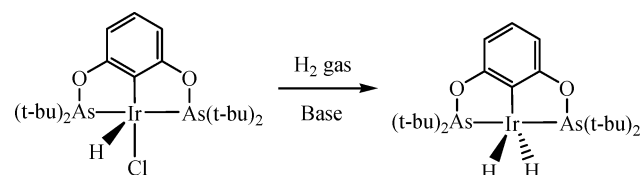
Synthesis. The di-*tert*-butylarsenic chloride was synthesized according to literature procedures.¹² With the di-*tert*-butylarsenic chloride in hand typical iridium pincer protocols were applied to synthesize both 3 and 4.⁶ Resorcinol is reacted with 2 equiv of di-*tert*-butylarsenic chloride and an excess base, for which triethylamine worked best, yielding the *tert*-butyl arsenic pincer, Scheme 3. The ligand can be isolated by

Scheme 3. Synthesis of AsOCOAs^{tBu}, 3

filtration of the ammonium chloride and stripping the solvent; however obtaining high-purity samples of the ligand was troublesome. Instead we preferred to synthesize 3 in a one-pot fashion. The general synthesis of 3 was essentially identical to that of 2, refluxing the AsOCOAs^{tBu} pincer ligand with [IrCl(COD)]₂ in toluene, yielding 91% of a deep reddish-purple solid. The spectroscopic data of 3 are also nearly identical to those of the previously known 2.^{5,13} The aryl and *tert*-butyl peaks shift very little in the ¹H and ¹³C NMR for all of these *tert*-butyl pincer compounds.^{5,13} Thus, the most unique feature of 3 is the iridium hydride resonance at −41.97 ppm, which is slightly farther upfield from the phosphine analogue resonance of 2 at −41.39 ppm.⁵

All hydrogenation and dehydrogenation reactions were run with precatalyst 3, which then was deprotonated with NaO-*tert*-butoxide to generate the active catalyst. This methodology has been described previously in the literature and is advantageous, as the hydrido chloride species is known to be more stable.^{5,6} Dihydride 4 is obtained by blanketing a solution of 3 and an appropriate base (NaH or NaO-*tert*-butoxide) with an atmosphere of hydrogen gas. Filtration of the sodium chloride and removal of the solvent affords a dark purple solid in 93% yield, Scheme 4. The key spectral feature of dihydride 4 is the peak at −18.81 ppm, which falls within the typical dihydride

Scheme 4. General Synthesis of 4



range for iridium pincer complexes.^{1,6} It should be noted that the syntheses of 3 and 4 were more tedious and challenging than those of 1 and 2. While analogous di-*tert*-butylphosphorus species could be removed under high vacuum, di-*tert*-butylarsenic could not. Also the purity of the commercially bought AsCl₃ starting material was difficult to assess and even more difficult to purify.

Catalyst 4 proved to be less reactive than the phosphino analogue both in dehydrogenation activity (discussed below) and in regard to reactivity with chlorinated solvents. The characterization of 4 by NMR was conducted in CD₂Cl₂ and was observed to be stable in solution for 48 h without reacting with CD₂Cl₂ to re-form 3, which is known to occur with phosphine catalysts 1 and 2. This was fortunate, as X-ray quality crystals could successfully be grown only from methylene chloride.

X-ray Crystallographic Data. X-ray quality crystals of 4 were grown from the slow evaporation of methylene chloride over a 24 h period. Complex 4 crystallizes in the P2₁/c space group. The predicted trans geometry of the arsenic atoms about the iridium center is observed, and the pincer ligand is very planar, as commonly seen throughout the literature in analogous pincer complexes.^{5,14} The As–Ir–As bite angle is 160.73°, which is only a single degree bigger than comparable phosphine analogues.⁵ Both of the Ir–As distances are essentially identical at 2.35 Å, which as expected is slightly longer than typical phosphine pincers (Ir–P 2.29 Å) due to arsenic's increased atomic radius, Table 1. Both O–As–Ir

Table 1. Selected Bond Lengths (Å) and Angles (deg) of 4

Ir–As1	2.354	Ir–As2	2.355	As1–Ir–As2	160.7
C14–Ir	2.087	Ir–As1–O1	102.7	Ir–As2–O2	102.6

angles are 102.70°, which is comparable to phosphorus pincer angles O–P–Ir (typical range of 102.3–104.9°).^{5,14} Analysis of this compound showed that it is extremely similar to phosphorus pincer complexes. Due to the close proximity to the iridium, the hydrides could not be reliably located and were omitted from Figure 1. Efforts are currently under way in hopes of elucidating the positions of the hydrides in 4.

Dehydrogenation and Catalyst Stability. Initial studies with iridium pincer catalyst were carried out with the isolated dihydride. However, subsequent reports describe the convenient route in which the active catalyst is generated in situ from the more stable iridium hydrochloride, Scheme 5.^{5,7} All dehydrogenation reactions were run at 1:3000 equiv of catalyst

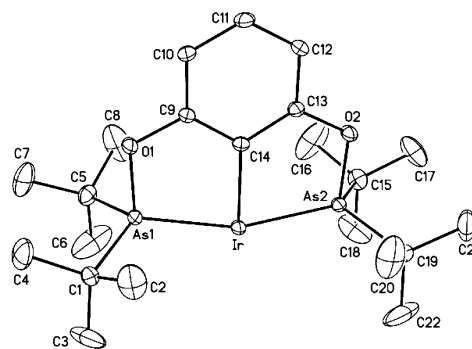
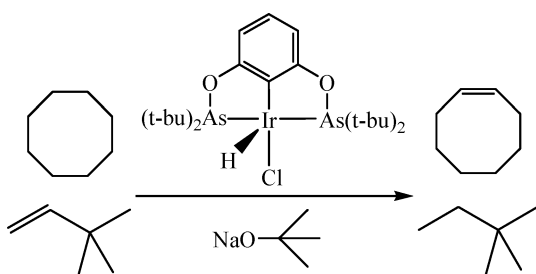


Figure 1. ORTEP diagram for compound 4. Hydrogen atoms are omitted for clarity; 30% thermal ellipsoids are shown.

Scheme 5. Transfer Dehydrogenation of COA and TBE with 3



to cyclooctane (COA) and hydrogen acceptor *tert*-butyl-ethylene (TBE). Table 2 shows the time lapse of the

Table 2. Transfer Dehydrogenation of COA with TBE Catalyzed by 2 and 3 at 200 °C

catalyst (0.033 mol %)	time (h)	substrate	yield (%)	TON
2	0.5	COA/TBE	29	870
2	1	COA/TBE	31	930
2	2	COA/TBE	33	990
2	12	COA/TBE	45	1350
2	24	COA/TBE	48	1440
3	0.5	COA/TBE	10	300
3	1	COA/TBE	19	570
3	2	COA/TBE	26	780
3	12	COA/TBE	28	840
3	24	COA/TBE	31	930

dehydrogenation reactions run at a constant temperature of 200 °C. During all time periods catalyst 2 is nearly twice as active as 3. For example, after the first hour the turnover numbers (TONs) were 930 and 570, respectively, and after 24 h the TONs were 1440 and 930. Both 2 and 3 show a leveling off in catalyst activity. This trend of inhibition has been seen for iridium pincer compounds and is attributed to the system approaching equilibrium as the product concentrations of COE and TBA increase.^{2,5,15,16} Although this inhibition is certainly occurring, we believe that catalyst decomposition is a more significant factor contributing to the decline in activity of 3. After only 1 h at 200 °C the appearance of an unidentifiable black precipitate was consistently observed.

To further explore this thermal decomposition, the activity was investigated by steadily increasing the temperature, Table 3. The activity of the 3 topped off as the temperature was increased to 200 °C, peaking at 175 °C. Any increases in temperature produced further unidentifiable decomposition products. As this type of decomposition is not seen during dehydrogenations with 1 and 2 or when the reaction is kept

Table 3. Transfer Dehydrogenation of COA with TBE Catalyzed by 2 and 3 after 24 h

catalyst (0.033 mol %)	temp (°C)	substrate	yield (%)	TON
2	150	COA/TBE	41	1230
3	125	COA/TBE	11	330
3	150	COA/TBE	20	600
3	165	COA/TBE	32	720
3	175	COA/TBE	32	960
3	185	COA/TBE	31	930
3	200	COA/TBE	31	930

under 175 °C, it is presumably due to the weaker As–O and/or As–Ir bonds. Two separate experiments were conducted to explore the homogeneity and potential nanoparticle activity of the unknown decomposition products. A test of homogeneity was run in the manner of previous reports, in which a typical dehydrogenation reaction was run with the presence of Hg, yielding nearly identical TONs.¹⁷ The second experiment was exploring the decomposition products, in which the unknowns were isolated and rerun in the typical dehydrogenation acceptor fashion, yielding no dehydrogenation.¹⁷

Liquid Organic Carriers. Pyrrolidine-based LOCs were selected from our previous reports to directly compare the dehydrogenation activity of catalysts 2 and 3, Table 4.^{7,18} In

Table 4. Acceptorless Dehydrogenation of Pyrrolidine-Based Substrates Catalyzed by 3 and 2 (1% catalyst loading, 24 h, and 180 °C)

Substrate	Product	yield ^a
EPHC 5		25 (52)%
MePHI 6		12 (25)%
BuPy 7		23 (44)%

^aYield with phosphino catalyst 2 in parentheses.

each of these cases the arsenic catalyst 3 proved to be less active. Catalyst 3 displayed roughly 50% the activity of 2 regardless of the LOC substrate or conditions. Table 4 shows the acceptorless dehydrogenation results of LOCs 5–7; the yields of 2 are displayed in parentheses. When catalyst 3 is directly compared to 2 using COA/TBE or LOCs 5–7, the dehydrogenation activity was always lower, ~50% (TON or % yield), Tables 2, 3, and 4.

Rehydrogenation. Using the same protocol and reactor type for heterogeneous hydrogenations, we attempted rehydrogenation reactions in the presence of the activated AsOCOAs pincer complex 3. Many hydrogenation attempts were made using the fully unsaturated molecules in Table 4, ethylcarbazole, methylindole, and butylpyrrole. However, no hydrogenated products were observed regardless of the time of reaction, temperature, or hydrogen pressure (limited by the tank pressure limited at ~2100 psi or ~140 atms).

CONCLUSION

The previously unknown arsenic pincer hydrochloride catalyst 3 has been synthesized and characterized. Upon treating the catalyst with an equivalent of base, sodium hydride, or sodium *tert*-butoxide and then blanketing with an atmosphere of hydrogen gas, 4 is obtained. Catalyst 3 was explored under transfer dehydrogenation conditions with COA and TBE, giving a maximum TON of 960 at 175 °C in 24 h. Acceptorless dehydrogenations were also explored with pyrrolidine-based LOCs, ethylperhydrocarbazole, methylperhydroindole, and

butylpyrrolidine. All data indicated that the analogous phosphine pincer catalyst **2** is substantially more active (~50%). Akin to other pincer catalysts, dehydrogenation activity improves as the temperature is increased; however the activity of **3** peaked at 175 °C, as significant thermal decomposition occurs at higher temperatures. In contrast to the phosphine-based iridium pincers, the arsenic pincer **3** reported here showed not only lower dehydrogenation activity but also less thermal stability.

EXPERIMENTAL SECTION

General Procedures. All solvents used were reagent grade, and anhydrous solvents were distilled from calcium hydride. All other chemicals were purchased from Aldrich and used as received. Where anaerobic techniques were required, glovebox and standard Schlenk techniques were used. ¹H and ¹³C NMR spectra were recorded at ambient temperatures with chemical shifts specified in ppm relative to the specified solvent. NMR solvents were distilled over calcium hydride and degassed prior to use. Elemental analyses were performed by Desert Analytics (Phoenix, AZ, USA). Di-*tert*-butylchloroarsine was prepared according to literature procedures.^{12,19} The iridium arsenic pincer catalyst **3** (IrHCl{C₆H₃-2,6-(OAsBu^t)₂}) was made with a modification of the literature procedures for phosphorus derivatives.⁶ The identity and purity of the LOC and products in general were determined using a GC HP 5890 Series II gas chromatograph with an HP 5971 (GC-MS) mass selective detector, equipped with an HP-1MS capillary column (30 m) from Hewlett-Packard.

Standard Catalytic Activity. The activity of the iridium catalysts was always checked before use and followed the format outlined by Gottker-Schnetmann et al., in which the active catalyst is generated in situ from the hydrido chloride compound with sodium *tert*-butoxide.⁶

General Preparation of Perhydro LOC Compounds. The desired LOC (~5 g) was loaded into a Parr bomb reactor along with palladium on carbon (1 g). The vessel was purged for 20 min with hydrogen gas, then pressurized to 100+ bar with hydrogen gas, and heated to ~100 °C. The reaction was left to stir for 2 days. The reactor was then allowed to cool to room temperature and depressurized, and the palladium on carbon was filtered out by washing with hexanes. The hexanes were removed in vacuo, upon which the LOC was stored over molecular sieves in an argon dry glovebox. The perhydro LOCs' purity was confirmed by both GC-MS and ¹H NMR prior to use.

Acceptorless Dehydrogenation of 5–7. The desired LOC (0.85 mmol) and premixed pincer complex with sodium *tert*-butoxide (0.0085 mmol) were washed with pentane into a 10 mL Schlenk flask with an integrated water condenser. The integrated flask was connected to an oil bubbler and purged with argon, and the pentane was boiled off at ~60 °C over the course of 20 min. Upon removal of the pentane, the flask was completely immersed in an oil bath at the prescribed temperature (range explored from 140 to 200 °C depending on LOC). After a specified period of time (2 to 48 h), the reaction mixture was removed from the flask and the products were characterized by GC-MS.

Transfer Dehydrogenation of 5–7. The desired LOC (0.85 mmol) and premixed pincer complex with sodium *tert*-butoxide (0.0085 mmol) were placed in a sealable flask. A varying amount (1–12 equiv) of 3,3-dimethyl-1-butene was then added. The tube was sealed and completely immersed into a hot silicon oil bath at the desired temperature (150 to 200 °C). After stirring for a specified time (6–48 h), the reaction mixture was removed and the product was characterized by GC-MS.

Synthesis of AsOCOAs^{tBu}. A solution of resorcinol (0.340 g, 1.89 mmol) and triethylamine (10 mL) was charged into an oven-dried round-bottom flask, flushed with argon, and cooled to 0 °C. Dry THF (30 mL) was then syringed into the flask and stirred for an hour. Di-*tert*-butylchloroarsenide (0.686 g, 1.89 mmol) was then added dropwise over a 10 min period. The reaction was then left to stir for an hour. THF was removed and pentane syringed into the flask and filtered. The pentane was stripped off under reduced pressure, yielding

0.580 g (53%) of a thick, light yellow oil. ¹H NMR (300 MHz, toluene-*d*₈): 7.02 (m, 1 H, Ar-H); 6.72 (m, 2 H, Ar-H); 6.53 (m, 1 H, Ar-H); 1.14 (br s, 36 H, –CH₃). ¹³C NMR (126 MHz, toluene-*d*₈): 164.49, 130.21, 111.82, 110.58, 31.02, 28.02.

Synthesis of Ir(H)(Cl)(AsOCOAs^{tBu}) (3**).** AsOCOAs^{tBu} (0.274 g, 0.5633 mmol) and [IrCl(COD)]₂ (0.228 g, 0.2817 mmol) were charged in a Schlenk flask in an argon glovebox. Toluene (40 mL) was added, and the solution was heated to 50 °C and stirred vigorously for an hour. The solvent was removed, and dry benzene was cannula transferred into the Schlenk flask. The benzene was removed via lyophilization, yielding 0.363 g (90.1%) of a powder soft, reddish-purple solid. ¹H NMR (300 MHz, C₆D₆): 6.12 (m, 3 H, Ar-H); 1.31 (m, 36 H, –CH₃); –41.97 (s, 1 H, Ir-H). ¹³C NMR (126 MHz, CDCl₃): 169.12, 147.41, 128.53, 103.01, 30.95, 27.76 (–CH₃). Anal. Calcd for C₂₂H₄₁As₂O₂Ir: C, 38.88; H, 6.08. Found: C, 38.90, H 6.06.

Synthesis of Ir(H)₂(AsOCOAs^{tBu}) (4**).** **3** (0.173 g, 0.2422 mmol) and sodium hydride (0.006 g, 0.2422 mmol) were charged in a Schlenk flask in an argon glovebox. Benzene (50 mL) was added, and the solution was blanketed with an atmosphere of hydrogen gas and stirred overnight. The solvent was removed via lyophilization, yielding 0.153 g (92.9%) of a reddish-purple solid. ¹H NMR (300 MHz, C₆D₆): 6.13 (m, 3 H, Ar-H); 1.30 (m, 36 H, –CH₃); –18.81 (s, 2 H, Ir-H). ¹³C NMR (126 MHz, C₆D₆): 168.12, 146.91, 128.11, 104.12, 31.91, 27.13. Anal. Calcd for C₂₂H₄₀As₂O₂ClIr: C, 37.00; H, 5.65. Found: C, 37.03, H 5.63.

Crystal Isolation. Ir(H)₂(AsOCOAs^{tBu}) (~50 mg) was dissolved in CH₂Cl₂ and allowed to slowly evaporate to dryness, yielding good sized deep red crystals suitable for X-ray crystallographic studies.

ASSOCIATED CONTENT

Supporting Information

Crystallographic data (CIF) for this paper, CCDC deposit number 997803. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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