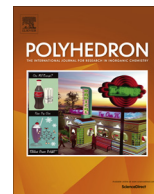




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Catalytic dehydrogenation of cyclooctane and triethylamine using aliphatic iridium pincer complexes

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Dedicated to John Bercaw on the occasion of his 70th birthday

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ABSTRACT

The majority of the known pincer iridium based catalysts for dehydrogenation of alkanes has arene-based backbones. Here, the catalytic activity of aliphatic iridium pincer complexes, viz. the cyclohexane-based phosphine complex (PCyP)IrHCl (**4**) (PCyP = {*cis*-1,3-bis-[(di-*tert*-butylphosphino)methyl]cyclohexane}[−]) and the 2-methylpropane-based phosphinite complex (POCOP)IrHCl (**5**) (POCOP = 1,3-bis-(di-*tert*-butylphosphinito)-2-methylpropane[−]), in dehydrogenation of cyclooctane and triethylamine was studied. They give TONs that are in the range of 0–200. In addition, improved procedures for synthesis and metallation of the PCyP ligand (**3**) are presented.

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1. Introduction

The conversion of cheap and abundant, but relatively inert, alkanes into more reactive olefins is an industrially important process [1]. Significant efforts have been made to develop catalysts that provide selective alkane dehydrogenation under mild conditions [2–5], and iridium PCP pincer complexes have been dominating the field for the last two decades [6]. The majority of the ligands studied are composed of an arene backbone, e.g. benzene [7–13], anthracene [12,14] or a 7-6-7 fused-ring based systems (Fig. 1) [15]. In contrast, iridium pincer complexes with aliphatic backbones have received relatively little attention and their performance in catalytic dehydrogenation of alkanes has not been reported. To fill this gap, we here present a study on the catalytic activity of a cyclohexane-based (PCyP)IrHCl complex (**4**) (PCyP = {*cis*-1,3-bis-[(di-*tert*-butylphosphino)methyl]cyclohexane}[−]) [16], and a 2-methylpropane-based phosphinite complex (POCOP)IrHCl (**5**) (POCOP = 1,3-bis-(di-*tert*-butylphosphinito)-2-methylpropane[−]) [17]. We also report on an improved synthesis of compound **4**.

2. Experimental

2.1. General experimental procedures

All manipulations were carried out under an Ar or N₂ atmosphere using standard Schlenk or glovebox techniques, unless otherwise stated. All catalytic experiments were performed under Ar. Hydrocarbon solvents were degassed and distilled from Na/benzophenone. Chlorinated solvents and triethylamine were degassed and distilled from CaH₂. Commercially available reagents were used as received. NMR spectra were recorded on a Varian Unity INOVA 500 MHz instrument and referenced to the residual solvent peaks for ¹H and ¹³C measurements, and to external 85% H₃PO₄ for ³¹P measurements. Elemental analyses were performed by H. Kolbe Microanalytisches Laboratorium, Mülheim an der Ruhr, Germany.

2.2. Synthesis of *cis*-1,3-bis(iodomethyl)cyclohexane (**2**)

Iodine (10.24 g, 40.4 mmol) was added portion-wise to a stirred mixture of Ph₃P (10.59 g, 40.4 mmol) and imidazole (2.64 g, 38.8 mmol) in CH₂Cl₂ (200 mL) at 0 °C. The mixture was stirred for 30 min at 0 °C and 1 h at RT, before a solution of *cis*-1,3-bis(hydroxymethyl)cyclohexane (**1**) (2.82 g, 19.6 mmol) in THF (40 mL) was added dropwise at 0 °C. The reaction mixture was allowed to warm to RT and was stirred for an additional hour. Further steps could be done in air. After addition of pentane

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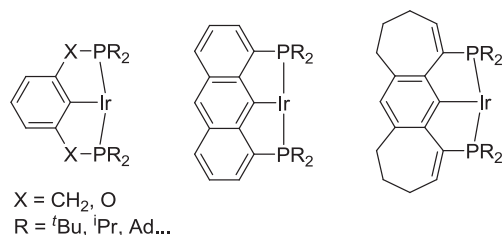


Fig. 1. Arene-based pincer complexes, used in alkane dehydrogenation (14e fragments are shown).

(200 mL) the mixture was filtered through a pad of silica and concentrated in vacuum. The residue was re-dissolved in pentane (60 mL), filtered through another pad of silica and washed out with additional pentane. Concentration in vacuum afforded *cis*-1,3-bis(iodomethyl)-cyclohexane as a colourless oil which readily solidified slightly below RT. Yield: 6.32 g (89%). ($R_f = 0.49$ in hexane). *Anal.* Calc. for C₈H₁₄I₂: C, 26.40; H, 3.88. Found C, 26.41, H, 3.89. ¹H NMR (CDCl₃): δ 3.12 (d, $J = 6.2$ Hz, 4H, $-\text{CH}_2\text{I}$), 2.03 (d of m, $J = 12.6$ Hz, 1H, $1-\text{CH}_A\text{H}_B$), 1.86–1.78 (m, 3H, $3-\text{CH}_A\text{H}_B + 4-\text{CH}_A\text{H}_B$), 1.52–1.44 (m, 2H, $-\text{CH}-$), 1.34 (m, 1H, $4-\text{CH}_A\text{H}_B$), 0.89 (m 2H, $3-\text{CH}_A\text{H}_B$), 0.70 (apparent q, $J = 11.9$ Hz, 1H, $1-\text{CH}_A\text{H}_B$). ¹³C NMR (CDCl₃): δ 40.16 ($1-\text{CH}_2$), 39.73 ($-\text{CH}-$), 33.08 ($3-\text{CH}_2$), 25.48 ($4-\text{CH}_2$), 15.18 ($-\text{CH}_2$).

2.3. Synthesis of *cis*-1,3-bis-[(*di-tert-butylphosphino*)methyl]cyclohexane, (PCyP)H (3)

To a -78 °C solution of *cis*-1,3-bis(iodomethyl)-cyclohexane (5.37 g, 14.8 mmol) in Et₂O (100 mL) a solution of ^tBuLi in pentane (1.6 M, 46.2 mL, 74.0 mmol) was slowly added. The reaction mixture was stirred for 1 h at 0 °C and 2 h at RT. ^tBu₂PfCl (8.43 mL, 44.4 mmol) was added dropwise at -78 °C and the reaction was stirred at RT overnight. The solvent was removed under vacuum before hexane (400 mL) and degassed water (100 mL) were added, and the resulting mixture was stirred for 10 min. The organic phase was separated, dried over MgSO₄ and concentrated in vacuum. The residue was dried for ca. 5 h at 50 °C under 10^{-3} mbar vacuum to give a pale yellow oil, which solidifies upon standing. This material was crystallized from CH₂Cl₂/MeOH and dried under vacuum to give a white powder. Yield: 4.0 g (68%). NMR spectra are consistent with the literature [18].

2.4. Synthesis of (PCyP)IrHCl (4)

The (PCyP)H ligand **3** (1.500 g, 3.74 mmol) and [Ir(COD)Cl]₂ (1.258 g, 1.87 mmol) were placed into a Straus flask inside a nitrogen glovebox and 35 ml of toluene was added. The flask was sealed, fully immersed into an oil bath and heated for 6 h at 170 °C. After reaching RT, the solution was degassed, cooled to -196 °C and the flask was refilled with H₂. The reaction mixture was heated for 5 h at 160 °C under H₂ atmosphere. The volatiles were evaporated and the resulting red powder was washed with cold hexane and dried in vacuum to give 2.261 g (96%) of **4**. NMR spectra are consistent with the literature data [16].

2.5. Dehydrogenation of cyclooctane in the presence of *tert*-butylethylene

In a typical experiment, the catalyst (0.0116 mmol) and ^tBuONa (0.0017 g, 0.0177 mmol, 1.5 eq) were placed into a Straus flask and specified amounts of cyclooctane (COA) as well as *tert*-butylethylene (TBE) were added. The flask was sealed and fully immersed

into a pre-heated oil bath with the specified temperature for 24 h. After that, the flask was cooled by a stream of air and the sample was analysed by NMR spectroscopy. Two runs were performed to determine average TONs. No compounds other than COA, cyclooctene (COE), TBE and *tert*-butylethane (TBA) could be detected by ¹H NMR spectroscopy.

2.6. Acceptorless dehydrogenation of cyclooctane by complex 4

Complex **4** (0.0073 g, 0.0116 mmol) and ^tBuONa (0.0017 g, 0.0177 mmol, 1.5 eq) were placed into a Schlenk flask and COA (1.56 ml, 11.6 mmol, 1000 eq) was added. The flask was connected to a reflux condenser, immersed into an oil bath pre-heated to 170 °C and the mixture was refluxed for 18 h while passing a slow flow of argon above the reflux condenser. After cooling with a stream of air, the sample was analysed by NMR spectroscopy.

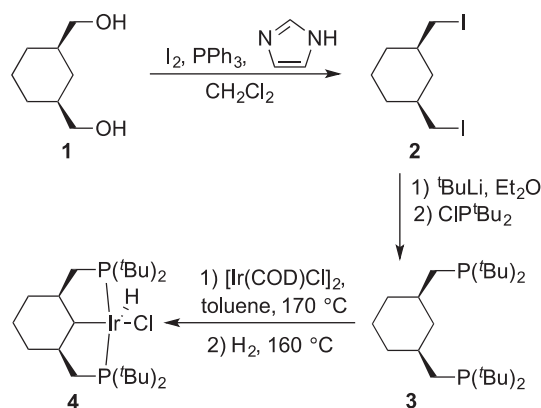
2.7. Dehydrogenation of triethylamine in the presence of *tert*-butylethylene

In a typical experiment, complex **4** (0.0054 g, 0.0086 mmol) and ^tBuONa (0.0012 g, 0.0125 mmol, 1.5 eq) were placed into a Straus flask, and the specified amounts of NEt₃ (10 or 100 eq), TBE (20 or 200 eq) as well as 1.5 ml of toluene were added. The flask was sealed and fully immersed into a pre-heated oil bath at 120 °C for 18 h. Subsequently, the flask was cooled by a stream of air and the sample was analysed by NMR spectroscopy. An average of two runs were performed to determine TONs. No compounds other than NEt₃, N,N-diethylvinylamine, N,N-divinylethylamine, TBE and TBA could be detected by ¹H NMR spectroscopy.

3. Results and discussion

3.1. Improved synthesis of 4

While the previously reported procedure [18] can give good yields of the cyclohexane-based pincer ligand **3**, difficulties in the handling of the highly unstable *cis*-1,3-bis[(trifluoromethylsulfonyloxy)methyl]cyclohexane intermediate [19] makes the synthesis inconsistent in the reproducibility of the yields. For the same reason it is also impractical for large-scale synthesis. Metallation of **3** according to the literature procedure gives **4** in a moderate yield (62%) [16]. In addition, ¹H and ³¹P{¹H} NMR spectra indicate that this protocol always gives trace impurities in the resulting samples of **4**, and thus we wanted to develop an over-all more robust and convenient route to **4**.



Scheme 1. New synthetic route to (PCyP)IrHCl (**4**).

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