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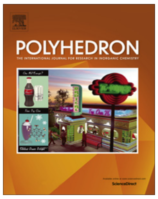

Catalytic dehydrogenation of cyclooctane and triethylamine using aliphatic iridium pincer complexes

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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.

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 N_2 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 CaH_2. 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 ^{13}C measurements, and to external 85% H_3PO_4 for ^{31}P 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 Ph_3P (10.59 g, 40.4 mmol) and imidazole (2.64 g, 38.8 mmol) in CH_2Cl_2 (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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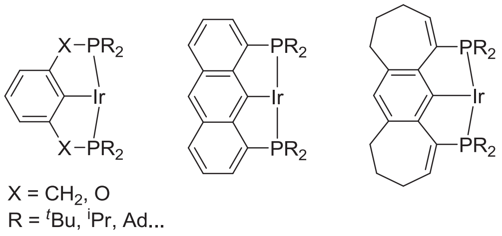


Fig. 1. Arene-based pincer complexes, used in alkane dehydrogenation (14e fragments are shown).

(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 $C_8H_{14}I_2$: C, 26.40; H, 3.88. Found C, 26.41, H, 3.89. ^{1}H NMR ($CDCl_3$): δ 3.12 (d, $J = 6.2$ Hz, 4H, $-CH_2I$), 2.03 (d of m, $J = 12.6$ Hz, 1H, 1-CH_AH_B), 1.86–1.78 (m, 3H, 3-CH_AH_B + 4-CH_AH_B), 1.52–1.44 (m, 2 H, –CH–), 1.34 (m, 1H, 4-CH_AH_B), 0.89 (m 2H, 3-CH_AH_B), 0.70 (apparent q, $J = 11.9$ Hz, 1H, 1-CH_AH_B). ^{13}C NMR ($CDCl_3$): δ 40.16 (1-CH_2), 39.73 (–CH–), 33.08 (3-CH_2), 25.48 (4-CH_2), 15.18 ($-CH_2I$).

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 Et_2O (100 mL) a solution of ^{t}BuLi 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. $^tBu_2PCl$ (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 $MgSO_4$ 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 CH_2Cl_2/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 H_2. The reaction mixture was heated for 5 h at 160 °C under H_2 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 ^{t}BuONa (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 ^{1}H NMR spectroscopy.

2.6. Acceptorless dehydrogenation of cyclooctane by complex 4

Complex **4** (0.0073 g, 0.0116 mmol) and ^{t}BuONa (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.

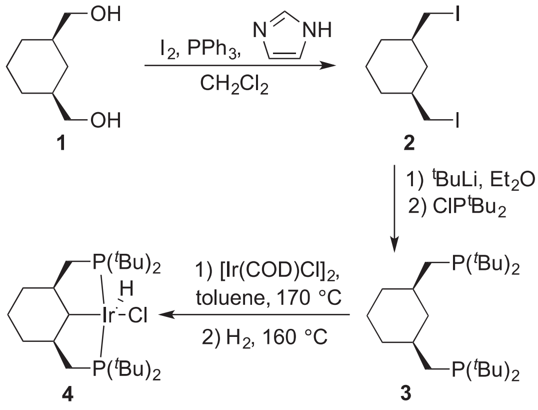
2.7. Dehydrogenation of triethylamine in the presence of tert-butylethylene

In a typical experiment, complex **4** (0.0054 g, 0.0086 mmol) and ^{t}BuONa (0.0012 g, 0.0125 mmol, 1.5 eq) were placed into a Straus flask, and the specified amounts of NEt_3 (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 NEt_3, N,N-diethylvinylamine, N,N-divinylethylamine, TBE and TBA could be detected by ^{1}H 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 reproducability 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, ^{1}H and ^{31}P{^{1}H} 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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To obtain a more stable intermediate in the synthesis of ligand **3** we wanted a good leaving group other than triflate. The diol **1** was made through reduction of commercially available *cis*-1,3-cyclohexanedicarboxylic acid with an excess of BH_3 in THF, according to the previously published procedure [19]. The hydroxyl groups were then iodinated by reaction with PPh_3/I_2/imidazole in anhydrous CH_2Cl_2 [20] (Scheme 1) affording the diiodo compound **2** in 89% yield. In contrast to the corresponding triflate, **2** is air and moisture-stable and can be stored in the freezer for at least several months without any signs of decomposition. Attempts to directly substitute the iodides with HP^tBu_2 failed, but lithiation of **2** followed by reaction with ClP^tBu_2 gave the desired ligand **3** in a 68% yield. The improved metallation protocol includes treatment of the reaction mixture with hydrogen at elevated temperatures. At these conditions, all by-products are converted to complex **4**. Hence very pure **4** is obtained and no further purification is required, except for washing with hexane in order to get rid of traces of grease.

3.2. Dehydrogenation reactions

A common test reaction used to compare catalytic activity in dehydrogenation of alkanes is the transfer dehydrogenation of cyclooctane (COA) in the presence of *tert*-butylethylene (TBE), which acts as hydrogen acceptor. The reaction is known to be inhibited by both the hydrogen acceptor (TBE) and the dehydrogenation product (cycloctene, COE) [6], and thus it is important to compare activity using the same ratio of catalyst, COA and TBE. Initially, we chose COA/TBE/cat = 3030/3030/1, the same conditions Brookhart and coworkers used for their (POCOP)Ir catalysts such as $[2,6\text{-}(^tBu_2PO)_2C_6H_3]IrHCl$ (**6**) (*cf.* Fig. 2) [8], since most literature data refers to this work. ^tBuONa (1.5 eq) was also added in order to remove HCl from **4** and **5** and generate an active 14e species. All catalytic results are summarised in Table 1. Unfortunately, no products of dehydrogenation were observed when complex **5** was used, indicating a lack of activity (Scheme 2). This result is in line with the poor thermal stability reported for **5** [17] and it is likely that the stability of the catalytically active species is even lower. Complex **4** is more robust (however, dehydrogenation of the cyclohexyl ring (to mono-ene or diene species) in the ligand is noticeable around 200 °C) and thus was expected to show better performance. Indeed, after heating the mixture for 24 h at 200 °C, complex **4** demonstrated a turnover number (TON) of 50, with more than a half (30) of the turnovers observed within the first 10 min of the reaction. Longer heating, as well as raising the temperature to 240 °C did not improve this result. At lower temperature (150 °C) we obtained almost the same TON (45). In comparison, catalyst **6** [8] is reported to give a TON of 1583 in 40 h. To validate our results we performed the reaction using our conditions and **6** as a catalyst, obtaining comparable results. It is known that the catalytic activity can be inhibited by traces of N_2 [21] and given the higher electron-donating nature of aliphatic pincer ligands this effect can be even stronger for these systems.

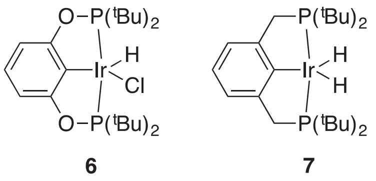
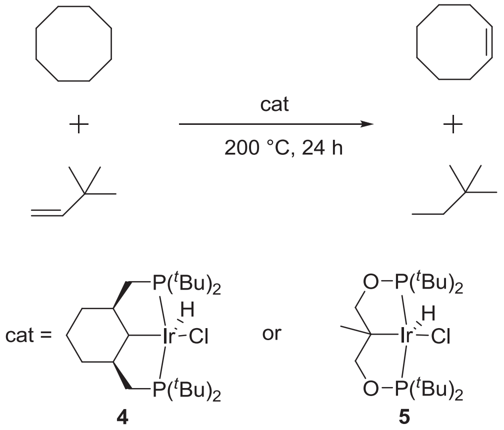


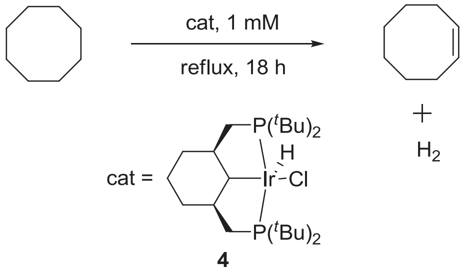
Fig. 2. Benzene-based pincer complexes used in alkane dehydrogenation.

Table 1
Catalytic dehydrogenation using different substrates and iridium catalysts. COA/TBE/cat ratio was 3030/3030/1 unless indicated.

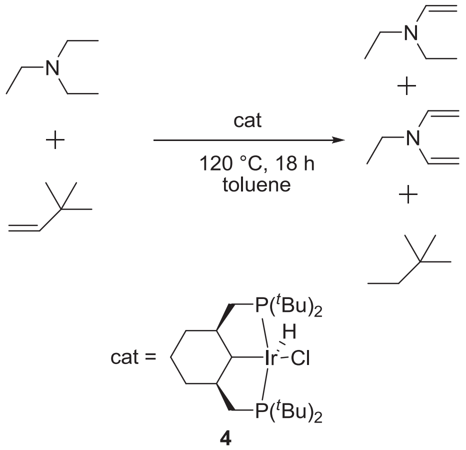
Entry	Catalyst	Substrate	Acceptor	TON	T/°C	Reference
1	**4**	COA	TBE	50	200	this work
2	**5**	COA	TBE	0	200	this work
3	**6**	COA	TBE	1583	200	[8]
4	**6**	COA	TBE	1918	200	this work
5	**4**	COA 7200 eq	TBE 300 eq	60	200	this work
6	**4**	COA 7200 eq	TBE 300 eq	200	120	this work
7	**4**	COA	–	5	150	this work
8	**7**	COA	–	105	150	[22]
9	**4**	NEt_3 100 eq	TBE 200 eq	18.9	120	this work
10	**4**	NEt_3 10 eq	TBE 20 eq	4.3	120	this work
11	**7**	NEt_3 10 eq	TBE 10 eq	6.5	90	[24]
12	**7**	NEt_3 10 eq	TBE 30 eq	11.4	90	[24]



Scheme 2. Transfer dehydrogenation of COA by iridium pincer complexes with aliphatic backbones.



Scheme 3. Acceptorless dehydrogenation of COA by complex **4**.



Scheme 4. Transfer dehydrogenation of triethylamine by complex **4**.

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Indeed, carrying out the catalysis under high vacuum (10^{-3} mbar) instead of an Ar atmosphere raised the TON, but only slightly; 70 equivalents of COE were observed. The reason behind the inferior performance of **4** is the poor thermal stability of the catalytically active species derived from it; monitoring the reaction mixture by means of ^{31}P NMR-spectroscopy after activation with ^{t}BuONa indicate complete decomposition of the catalytically active species after several hours at 150 °C. It seems likely that some of the activity of **4** with ^{t}BuONa belongs to an unsaturated, more active species. Removal of HCl from **4** is fairly slow, and at 200 °C some amount of **4** seems to undergo an intramolecular dehydrogenation prior to dehydrochlorination. Indeed, when a mixture of **4**, COA and TBE were heated for 1 h at 210 °C prior to activation with ^{t}BuONa, the overall turnover number increased to 130. A thorough investigation of the decomposition routes of complex **4** is currently in progress.

A direct comparison of the activity of saturated species derived from **4** with their aromatic counterparts is possible using 7200/300/1 COA/TBE/cat ratio, for which literature data for low temperature exists. Under these conditions, the result of complex **4** at 200 °C is almost unchanged (60 TON), reflecting the rapid decomposition. At 120 °C, however, the active species are more stable. Thus, an initial rate of 10 TON/h was observed, slowly diminishing to give a total turnover number of 200 after 36 h, whereupon the reaction was almost over. At slightly lower temperature (100 °C) and the same reactant ratio the benzene-based complex $[2,6\text{-}(^t\text{Bu}_2\text{PCH}_2)_2\text{C}_6\text{H}_3]\text{IrH}_2$ (**7**) was reported to demonstrate nearly twice the reaction rate (20.5 TON/h) [7]. Thus, under all conditions the activity of **4** seems to be lower than that of arene-based catalysts.

Acceptorless dehydrogenation of COA by **4** resulted in 5 turnovers (Scheme 3), which can be compared to 105 for benzene-based complex $[2,6\text{-}(^t\text{Bu}_2\text{PCH}_2)_2\text{C}_6\text{H}_3]\text{IrH}_2$ (**7**) (*cf.* Fig. 2) [22]. Probably the decomposition of **4** is quite fast already at the COA boiling point of 149 °C [23].

Considering the low thermal stability of active species derived from **4**, we decided to test it in a reaction that does not require high temperature such as the dehydrogenation of tertiary amines, which was reported to proceed at 90 °C with **7** as a catalyst [24]. A toluene solution instead of neat reactants was used to suppress inhibition by the generated products. In the case of complex **4**, the reaction was too slow at 90 °C, but heating a 100/200/1 NEt_3/TBE/cat mixture in toluene at 120 °C afforded a TON of 18.9, with the yields of N,N-diethylvinylamine and N,N-divinyl-ethylamine being 15.7 and 1.6%, respectively (Scheme 4). Complex **7** has been reported to give a TON of 6.5 and 65% yield of N,N-diethylvinylamine using a 10/10/1 NEt_3/TBE/cat ratio and a TON of 11.4 with 64% yield of N,N-diethylvinylamine and 25% yield of N,N-divinylethylamine using a 10/30/1 NEt_3/TBE/cat ratio [24]. For a more direct comparison with literature data, we carried out the dehydrogenation using 10/20/1 NEt_3/TBE/**4** ratio, and 4.3 turnovers with 43% yield of N,N-diethylvinylamine was observed. NMR monitoring showed that in this case interactions with the toluene lead to formation of a catalytically inactive species prior to complete decomposition of the catalyst.[1] Thus, the low TON presumably reflects a kinetic competition between these unwanted processes and interaction with NEt_3. When COA was used as a solvent, competition between dehydrogenation of COA and NEt_3 was observed; on a per mol basis, selectivity is around 1:10. However, in view of the large excess of COA, high yields of vinylamines could not be achieved.

4. Conclusions

In conclusion we have presented an improved synthetic route to the cyclohexane-based PCyP ligand **3**, suitable for multigram scale, and improved the metallation procedure for the complex (PCyP)IrHCl (**4**). The latter, together with the aliphatic phosphinite complex **5**, was tested for several catalytic dehydrogenations. The activity was found to be relatively low compared to the corresponding aromatic complexes, and this is primarily due to the low thermal stability of the catalytically active species.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2014.06.016.

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[1] NMR spectra indicate the formation of a tolyl hydride presumably through oxidative addition of toluene to the 14e Ir(I) fragment as previously reported [25,26], which further undergoes transformations leading to catalytically inactive species.