



Dehydrogenation of *N*-ethyl perhydrocarbazole catalyzed by PCP pincer iridium complexes: Evaluation of a homogenous hydrogen storage system

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ABSTRACT

The iridium complexes $\text{IrH}_2\{\text{C}_6\text{H}_3\text{-}2,6\text{-(CH}_2\text{P}^t\text{Bu)}_2\}_2$ (**1**), $\text{IrH}_2\{\text{C}_6\text{H}_3\text{-}2,6\text{-(CH}_2\text{P}^t\text{Pr)}_2\}_2$ (**2**), and $\text{IrHCl}\{\text{C}_6\text{H}_3\text{-}2,6\text{-(OP}^t\text{Bu)}_2\}_2$ (**3**) have been found to be highly active catalysts for the dehydrogenation of *N*-ethyl perhydrocarbazole at 200 °C. However, dehydrogenation to the fully unsaturated ethyl carbazole does not occur in most instances. Complex **3** is the most active catalyst and shows reasonable activity even at 150 °C. No signs of dehydrogenation were found in experiments conducted at 100 °C. This apparently reflects the thermodynamic constraints imposed by the high enthalpy of dehydrogenation of the substrate.

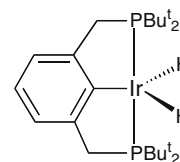
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1. Introduction

A major challenge to achieving the commercial viability of hydrogen fuel cell powered automobiles is the development of a safe and practical method for the onboard storage of hydrogen. Cryogenic hydrogen storage systems are impractical due to volumetric constraints, safety concerns, and/or high costs. There has been an extensive effort to develop hydrogen storage systems based on hydrogen absorbing solids for vehicular application. Unfortunately, no material has been found which has the requisite combination of a high gravimetric hydrogen density; adequate hydrogen-dissociation kinetics and thermodynamic properties; reliability; and low cost [1].

The utilization of liquid aromatic organic compounds as hydrogen carriers has remained a tantalizing but impractical possibility for over 60 years [2–14]. A liquid hydrogen storage media could be economically manufactured in the massive quantities to meet the anticipated demand and eliminate many of the problems commonly associated with systems based on hydrogen absorbing solids including: thermal management on charging and other issues relating to the compatibility with existing infrastructure. In many ways such an onboard energy carrier can be thought of as “recyclable gasoline”. Initial efforts to develop liquid organic hydrogen carriers were primarily fo-

cused on cycloalkanes [2–6]. The dehydrogenation of these cheap and abundant materials to the corresponding aromatic compounds releases approximately 7 wt% hydrogen. However, the large enthalpy of dehydrogenation of cycloalkanes (~60 kJ/mol H₂) is a major drawback to their utilization in practical systems. This thermodynamic constraint mandates that high temperatures (>300 °C) are required to produce equilibrium hydrogen pressure >1 atm. Additionally, the dehydrogenation reaction suffers from extremely slow kinetics and high loadings of heterogeneous precious metal catalysts are required to promote the evolution of hydrogen to rates that meet the demands of an onboard fuel cell. In an attempt to circumvent these difficulties, we developed the “pincer catalyst”, $\text{IrH}_2\{2,6\text{-C}_6\text{H}_3\text{-CH}_2\text{P}^t\text{Bu)}_2\}_2$ (**1**), the first homogenous catalyst for the dehydrogenation of



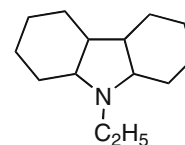
$\text{IrH}_2\{2,6\text{-C}_6\text{H}_3\text{-CH}_2\text{P}^t\text{Bu)}_2\}_2$ (**1**)

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cycloalkanes to arenes [15]. The unique reactivity of this especially robust and active catalyst can be ascribed to the P–C–P pincer ligand that renders the metal center reactive with saturated hydrocarbons but restricts its access to the ligand P–C bonds. We have found that hydrogen can be evolved from solutions of cycloalkanes containing catalytic amounts of **1** at temperatures as low as 100 °C in a system in which the solution is circulated through a “hot-tube” [16]. This “off-equilibrium” approach to cycloalkane dehydrogenation requires the utilization of a Pd/Ag filter-tube that is selectively permeable to hydrogen. Unfortunately, the system cannot supply hydrogen at rates adequate for practical applications.

Pez et al. have calculated the enthalpy of formation of hydrogenation for a variety of aromatic heterocycles and their saturated analogs [8]. Their calculations show that ΔH of dehydrogenation is significantly lowered upon introduction of a hetero-atom into the ring system as it significantly reduces the aromaticity of the dehydrogenated molecule. This has led several groups to explore the dehydrogenation of heterocyclic aromatic compounds [7–15]. Pez et al. were able to achieve the reversible dehydrogenation of *N*-ethyl perhydrocarbazole (EPHC) using a

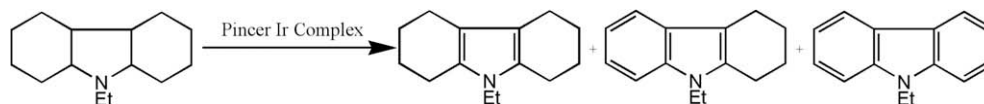


N-ethyl perhydroethylcarbazole

combination of heterogeneous hydrogenation (Ru on C) and dehydrogenation (Pd on lithium aluminate) catalysts [8]. While this system holds some promise for onboard hydrogen storage applications, very high (5 wt%) precious metal catalyst loadings and heating to 200 °C are required in order to obtain only 4 wt% hydrogen at rates that would be adequate for operation of an onboard PEM fuel cell. Thus the 100 °C exhaust heat of a PEM fuel cell is inadequate to drive the dehydrogenation half-cycle of storage apparatus based on this system.

Homogenous catalytic systems typically operate at significantly lower temperatures than their heterogeneous counterparts. It has

Table 1
Dehydrogenation of *N*-ethyl perhydrocarbazole using pincer catalysts.



Entry	Catalyst	T (°C)	Time (h)	Yield ^{a,b} (%)			TON ^c
				EOHC	ETHC	EC	
1	1	200	3	8	0	0	16
2	1	200	6	14	3	0	40
3	1	200	9	17	4	0	50
4	1	200	12	21	5	0	62
5	1	200	24	51	13	0	154
6	1	200	48	65	19	0	206
7	1	200	72	73	23	0	238
8 ^d	1	200	96	69	31	0	262
9	2	200	3	16	0	0	32
10	2	200	6	34	0	0	68
11	2	200	9	36	5	0	92
12	2	200	12	47	12	0	142
13	2	200	24	58	24	0	212
14 ^d	2	200	48	65	35	0	270
15	2	200	72	62	38	0	276
16	3	200	3	23	26	0	150
17	3	200	6	58	30	0	236
18 ^d	3	200	9	70	30	0	260
19	3	200	12	66	34	0	268
20	3	200	24	60	40	0	280
21 ^e	3	200	18	72	28	0	512
22	3	200	216	0	82	18	436
23 ^f		200	24	no reaction			0
24 ^g	3	200	24	no reaction			0
25	3	150	3	9	0	0	9
26	3	150	9	23	2	0	27
27	3	150	12	28	5	0	38
28	3	150	18	48	10	0	68
29	3	150	24	65	11	0	87
30	3	150	36	78	13	0	104
31	3	150	48	90	10	0	110
32	3	150	72	85	15	0	115

^a Average of three runs as determined by GC–MS.

^b EOHC is *N*-ethyl octahydrocarbazole; ETHC is *N*-ethyl tetrahydrocarbazole; EC is *N*-ethyl carbazole.

^c TON is the molar ratio between the generated hydrogen gas and the catalyst.

^d All of the substrate, EPHC, has been consumed.

^e Initially, the reaction was set up according procedure B. After 9 h, another batch of EPHC (100 equivalent) was introduced into the reaction and heated for another 9 h.

^f The reaction was set up according procedure B without **3**.

^g The reaction was set up according procedure B without NaOBu^t.

been reported that **1** and related iridium “PCP pincer” complexes catalyze dehydrogenation of secondary and tertiary amines to imines and enamines [17,18] and ammonia borane [19]. We were therefore interested in exploring **1** as a catalyst for the dehydrogenation of perhydrocarbazoles in a homogeneous systems. We report here the results of our investigation of the activity of **1** and the related complexes, $\text{IrH}_2\{\text{C}_6\text{H}_3\text{-}2,6\text{-(CH}_2\text{PPr}^i_2)_2\}$ (**2**), and $\text{IrH}_2\{\text{C}_6\text{H}_3\text{-}2,6\text{-(OPBu}^t_2)_2\}$ (**3**), as catalysts for the dehydrogenation of EPHC to *N*-ethyl octahydrocarbazole (EOHC) and *N*-ethyl tetrahydrocarbazole (ETHC).


 $\text{IrH}_2\{\text{C}_6\text{H}_3\text{-}2,6\text{-(CH}_2\text{PPr}^i_2)_2\}$ (**2**)

 $\text{IrH}_2\{\text{C}_6\text{H}_3\text{-}2,6\text{-(OPBu}^t_2)_2\}$ (**3**)

2. Results and discussion

Complexes **1** and **2** were synthesized and purified by the literature methods [20,21]. Complex **3** was generated from the *in situ* reaction of $\text{IrHCl}\{\text{C}_6\text{H}_3\text{-}2,6\text{-(OPBu}^t_2)_2\}$ with NaOBu^t [22]. It has been established the pincer complexes all show significant activity as catalysts for the dehydrogenation of cycloalkanes at 200 °C [20–22]. Therefore, our initial kinetic comparison studies were conducted at that temperature. The results of the studies of the catalytic activity of the pincer complexes are summarized in Table 1. All three catalysts show the ability to dehydrogenate EPHC completely to EOHC and to further dehydrogenate 30–40% of the EOHC to ETHC. In the case of complex **3**, as shown in entry 21, the catalyst was found to be capable of dehydrogenating a second loading of EPHC after the initial loading has been consumed without loss of activity or any significant difference in the distribution of products. Furthermore, product inhibition, a common problem in acceptorless aliphatic alkane dehydrogenation systems [20–22], was **not** observed in the catalytic dehydrogenation of EPHC.

Fig. 1 compares the kinetics observed for the dehydrogenation reactions catalyzed by the pincer complexes. While similar turnover numbers (TON, molar hydrogen/catalyst ratio) were achieved for all three complexes, the consumption of the full charge of EPHC

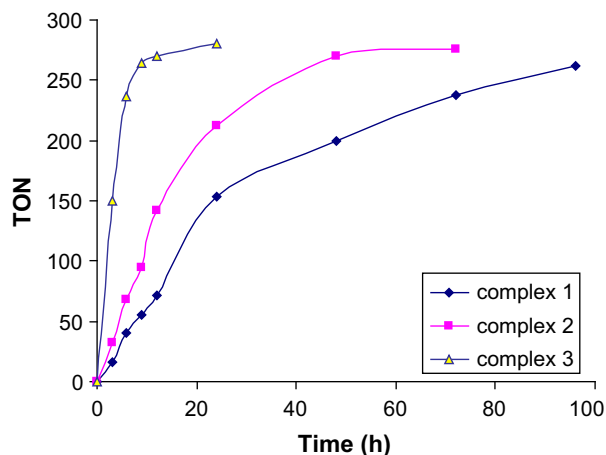


Fig. 1. Dehydrogenation of EPHC catalyzed by complexes **1–3** at 200 °C.

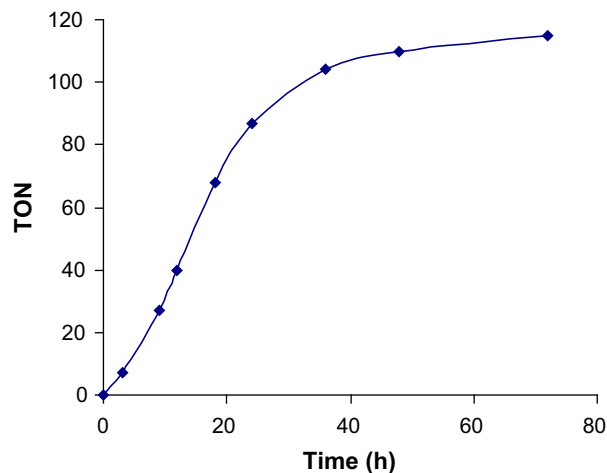


Fig. 2. Dehydrogenation of EPHC catalyzed by **3** at 150 °C.

occurred in only 9 h when the reaction was catalyzed by **3** compared to the 78 and 48 h required when **1** and **2** were used, respectively. This finding is consistent with the earlier observation that among the three pincer complexes, **3** catalyzes the transfer dehydrogenation of cyclooctane at the fastest rate [22].

A further study of the catalytic activity of the **3** was conducted at 150 °C, a temperature that is much closer to the operating temperatures that are required for a practical hydrogen storage system. As seen in Table 1 and Fig. 2, **3** catalyzes the dehydrogenation of EPHC to EOHC at 150 °C. However, much lower catalytic activity was observed at the lower temperature. For example, the dehydrogenation of a full charge of EPHC (50% of the charged used in the 200 °C experiments) requires 48 h. Additionally, analysis of the product mixture shows it to consist of only 10% ETHC and 90% EOHC as opposed 30% ETHC, 70% EOHC distribution observed at the time of total consumption EPHC. Thus only 104 molar equivalents H_2 were released in 48 h as opposed to 260 molar equivalents in 9 h at 200 °C.

The activity of complex **3** was also studied 100 °C. After two weeks time no dehydrogenated products were observed in the reaction mixture. This finding is consistent with the calculations of Pez et al. that predict the lowest thermodynamically allowed dehydrogenation temperature is 120 °C [8].

3. Conclusions

These three iridium complexes **1–3**, all exhibit excellent activity as catalysts for the dehydrogenation of *N*-ethyl perhydrocarbazole at 200 °C. However, dehydrogenation to the fully unsaturated ethyl carbazole does not occur in most instances. Complex **3** is the most active catalyst and shows a reasonable activity even at 150 °C. No signs of dehydrogenation were found in experiments conducted at 100 °C. This apparently reflects the thermodynamic constraints imposed by the high enthalpy of the substrate.

4. Experimental

4.1. General details

All manipulations were carried out under an argon atmosphere, using either glovebox or double-manifold Schlenk techniques. Pentane (Fisher Scientific) was distilled from lithium aluminum hydride under nitrogen. Temperatures were maintained to within ± 5 °C using a silicon oil bath. All dehydrogenation reactions were performed in re-sealable glass vessels equipped with one or several

3-mm Teflon vacuum stopcocks (Rotaflor or Kontes). These reaction vessels were immersed into a hot silicon oil bath during the reactions and the reaction mixtures were stirred with small Teflon-coated stirring bars.

Identity and purity of the products were examined by gas chromatography with a gas chromatograph GC HP 5890 Series II with a mass selective detector HP 5971 (GC–MS), equipped with a HP-1MS capillary column (30 m) from Hewlett Packard.

4.2. Preparation of *N*-ethyl perhydrocarbazole

EPHC was prepared by a slight modification of the literature method [8]. About 5 g (30 mmol) of *N*-ethylcarbazole was added to a 150 mL autoclave along with 1 g of a 5% Ru/C catalyst. The reactor was pressurized with H₂ and vented 3 times to purge the system of oxygen. The reactor was then pressurized again with 50 bar H₂ pressure and the autoclave was heated to 160 °C stirred for two days. The resulting yellow oil was extracted twice with 50 mL acetone and dried in vacuo overnight. GC–MS analysis showed this procedure produces >99% *N*-ethylperhydrocarbazole (EPHC) in nearly quantitative yield.

4.3. Dehydrogenation of *N*-ethylperhydrocarbazole

Procedure A: A solution of **1** or **2** (0.0085 mmol) in 2 mL of pentane was combined with a solution of *N*-ethylperhydrocarbazole (176 mg, 0.85 mmol) in 2 mL of pentane and placed into a 10 mL Schlenk flask with an integrated water condenser. The flask was connected to an oil bubbler, and the pentane was boiled off at 55 °C over 30 min. After the pentane was removed, the flask was placed in an oil bath at 200 °C. After a prescribed period of reaction time, the reaction mixture was removed from the flask and analyzed by GC–MS.

Procedure B: A solution of **3** (5.3 mg, 0.0085 mmol) and NaOBu^t (1.0 mg, 0.01 mmol) in 2 mL of pentane was combined with a solution of *N*-ethyl perhydrocarbazole (176 mg, 0.85 mmol) in 2 mL of pentane and placed into a 10 mL Schlenk flask with an integrated water condenser. The flask was connected to an oil bubbler, and

the pentane was boiled off at 55 °C over 30 min. After the pentane was removed, the flask was placed in an oil bath at 200. For the reactions carried out at 150 °C the half the amount of *N*-ethyl perhydrocarbazole (88 mg, 0.42 mmol) was used in the reaction mixture. After the prescribed reaction time, the reaction mixture was removed from the flask and analyzed GC–MS.

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References

- [1] S.-I. Orimo, Y. Nakamori, J.R. Eliseo, A. Zuttel, C.M. Jensen, Chem. Rev. 107 (2007) 4111.
- [2] R.P. Linstead, S.L.S. Thomas, J. Chem. Soc. (1940) 1127.
- [3] N.F. Grunenfelder, T.H. Schucan, Int. J. Hydrogen Energy 14 (1989) 579.
- [4] J.K. Ali, E.J. Newson, D.W.T. Rippen, Chem. Eng. Sci. 48 (1994) 2120.
- [5] N. Meng, S. Shinoda, Y. Saito, J. Hydrogen Energy 22 (1997) 361.
- [6] C.M. Jensen, in: Proceedings of the 1997 US DOE Hydrogen Program Review, Herndon, VA.
- [7] S. Hodoshima, S. Takaiwa, A. Shono, K. Satoh, Y. Saito, Appl. Catal. A 282 (2005) 235.
- [8] G.P. Pez, A. Scott, A. Cooper, H. Cheng, United States Patent 7101530, 2006.
- [9] D.E. Schwarz, T.M. Cameron, P.J. Hay, B.L. Scott, W. Tumas, D.L. Thorn, Chem. Commun. (2005) 5919.
- [10] Y. Okada, E. Sasaki, E. Watanabe, S. Hyodo, H. Nishijima, Int. J. Hydrogen Energy 31 (2006) 1348.
- [11] A. Moores, M. Poyatos, Y. Luo, R.H. Crabtree, New J. Chem. 30 (2006) 1675.
- [12] R.B. Biniwalea, S. Rayalua, S. Devotta, M. Ichikawab, Int. J. Hydrogen Energy 33 (2008) 360.
- [13] R.H. Crabtree, Energy Environ. Sci. 1 (2008) 134.
- [14] Y. Cui, S. Kwok, A. Bucholtz, B. Davis, R.A. Whitney, P.G. Jessop, New J. Chem. 32 (2008) 1027.
- [15] M. Gupta, C. Hagen, W.C. Kaska, R.E. Cramer, C.M. Jensen, Am. Chem. Soc. 119 (1997) 840.
- [16] C.M. Jensen, United States Patent 6074447, 2002.
- [17] X.Q. Gu, W. Chen, D. Morales-Morales, C.M. Jensen, J. Mol. Catal. A 119 (2002) 189.
- [18] X. Zhang, A. Fried, S. Knapp, A.S. Goldman, Chem. Commun. (2003) 2060.
- [19] C.M. Jensen, Chem. Commun. (1999) 2443.
- [20] M.C. Denney, V. Pons, T.J. Hebden, D.M. Heinekey, K.I. Goldberg, J. Am. Chem. Soc. 128 (2006) 12048.
- [21] F. Liu, A.S. Goldman, Chem. Commun. (1999) 655.
- [22] I. Göttker-Schnetmann, P. White, M. Brookhart, J. Am. Chem. Soc. 126 (2004) 1804.