

Catalytic dehydrogenation of ethylbenzene and tetrahydrofuran by a dihydrido iridium P–C–P pincer complex

Mukta Gupta,^{†a} William C. Kaska^b and Craig M. Jensen^{*a}

^a Department of Chemistry, University of Hawaii, Honolulu, HI 96822, USA

^b Department of Chemistry, University of California, Santa Barbara, CA 93106, USA

The P–C–P pincer complex, [IrH₂{C₆H₃(CH₂PBu_t)₂]-2,6} catalyses the transfer dehydrogenation of the donor-bearing substrates, ethylbenzene and tetrahydrofuran at temperatures as low as 150 °C.

The catalytic dehydrogenation of aliphatic C–H bonds in the presence of functional groups is of major industrial importance. For example, the direct dehydrogenation of ethylbenzene accounts for 85% of the commercial production of styrene.¹ The reaction is carried out commercially at *ca.* 620 °C in the vapour phase over catalysts which primarily consist of iron oxide and potassium salt promoters.¹ Recently there has been considerable interest in the development of higher activity dehydrogenation catalysts which are also more selective for styrene over the degradation products, benzene and carbon.¹ Several soluble metal complexes have been found which catalyse the dehydrogenation of alkanes under moderate conditions.^{2–4} However, none of these species have been reported to effect the catalytic dehydrogenation of aliphatic C–H bonds of functionalized substrates. This is apparently due to catalyst deactivation through strong coordinative interactions with donor groups. For example, [IrH₂{OC(O)CF₃}(PPr_i)₂] effects the dehydrogenation of alkanes to arenes at 150 °C but fails to turnover catalytically since arenes are released from the metal centre only at temperatures at which complex decomposition occurs.⁵

We recently found that the iridium P–C–P pincer complex, [IrH₂{C₆H₃(CH₂PBu_t)₂]-2,6} **1** is a highly active homogeneous catalyst for transfer dehydrogenation of cycloalkanes to alkenes and arenes.⁴ In this system, the P–C–P framework of the catalyst is sufficiently robust that decomposition does not occur at temperatures required to achieve arene elimination. It was therefore of interest to explore whether alkylbenzenes and other weaker donor substrates such as cyclic ethers could be dehydrogenated by this catalytic system. We have found **1** will in fact catalyse the transfer dehydrogenation of ethylbenzene and tetrahydrofuran (thf).

Complex **1** was prepared as previously described.⁴ The catalytic activity was investigated using solutions consisting of 4 ml of substrate (ethylbenzene, 32.6 mmol; thf, 49.3 mmol) *tert*-butylethene (tbe) (0.2 ml, 1.55 mmol) and **1** (3 mg, 0.005 mmol). The orange solutions were sealed in tubes under argon and fully immersed in an oil-bath for the prescribed reaction periods. The solutions became red upon heating and gradually change colour to yellow–orange during the reaction period. The reactivity was unaffected by the addition of metallic mercury to the solution indicating that metallic iridium is not involved in the hydrogen transfer.⁶

The results of the catalytic dehydrogenation experiments are summarized in Table 1. The products were identified by GCMS[†] analysis and quantified by gas chromatography.[‡] Our product quantification balances the number of dehydrogenated C–C bonds within 5% to the amount of the hydrogenated to *tert*-butylethane (tba) in all experiments. No significant difference was found in either the amounts or distributions of products upon increasing the reaction time of the 200 °C experiments beyond 0.5 h. The amounts of products obtained in the 150 °C experiments increase over a longer period of time but are limited to lower levels than the 200 °C experiments. These results indicate that the amounts of products that are obtainable by these systems are restricted by thermodynamics. The direct dehydrogenation of ethylbenzene was explored at higher temperatures where a hydrogen acceptor such as tbe is not thermodynamically required. Unfortunately, **1** rapidly decom-

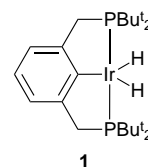


Table 1 Catalytic dehydrogenations with **1**

Substrate	<i>t</i> /h	<i>T</i> /°C	Products (mol/mol of 1)	Dehydrogenated/ hydrogenated C–C bonds
thf	1.0	150	Dihydrofurans: 2,3 (46); 3,4 (<1) furan (31), tba (103)	1.05
thf	3.0	150	Dihydrofurans: 2,3 (41); 3,4 (5), furan (57), tba (154)	1.04
thf	0.5	200	Dihydrofurans: 2,3 (84); 3,4 (5), furan (54), tba (190)	1.04
thf	1.0	200	Dihydrofurans: 2,3 (86); 3,4 (6), furan (53), tba (192)	1.03
Ethylbenzene	1.0	150	Styrene (8), tba (8)	1.00
Ethylbenzene	12.0	150	Styrene (10), tba (10)	1.00
Ethylbenzene	0.5	200	Styrene (50), tba (51)	0.98
Ethylbenzene	1.0	200	Styrene (50), tba (52)	0.96
Ethylcyclohexane	1.0	150	Ethylcyclohexenes (3,5), ethylbenzene (8), styrene (7), tba (84)	1.04
Ethylcyclohexane	12.0	150	Ethylcyclohexenes (47), ethylbenzene (18), styrene (35), tba (274)	1.05
Ethylcyclohexane	0.5	200	Ethylcyclohexenes (58), ethylbenzene (35), styrene (34), tba (310)	0.97
Ethylcyclohexane ^a	1.0	200	Ethylcyclohexenes (13), ethylbenzene (43), styrene (76), tba (441)	1.01

^a An additional 0.2 ml (1.55 mmol) of tbe was added to the reaction mixture after 0.5 h.

poses at temperatures in excess of 200 °C and no dehydrogenation activity was observed.

The catalytic activity of **1** for the dehydrogenation of the functionalized substrates is significantly lower than previously found for cycloalkanes.^{3,4} This suggests that arene and oxygen donor interactions with the metal centre inhibit the catalytic system. The findings of product inhibition and the concentration sensitivity in the transfer dehydrogenation of cyclooctane and cyclohexane also suggest that the catalytic activity of **1** is inhibited by species bearing donor groups.³ In order to probe this possibility, the activity of **1** for the transfer dehydrogenation of ethylcyclohexane was investigated. As seen in Table 1, significantly higher styrene production was observed than in the case of ethylbenzene. This is apparently due to the reduced arene concentration in the ethylcyclohexane experiments. Nitrogen has been found to poison the transfer dehydrogenation of cyclooctane by **1**.³ Similarly, no dehydrogenation of either ethylbenzene or thf was observed in experiments conducted under 1 atm of N₂ in place of argon at 150 °C. Thus the catalytic system is sensitive to even the weak donor, N₂.

Despite the limitations of this catalytic system, it represents a step forward in the development of improved catalysts for the production of styrene. It is also the first report of a homogeneous catalytic system for dehydrogenation of saturated C–H bonds in presence of functionalization. Modified catalysts of this type could provide an entrance into new chemical processes through previously inaccessible catalytic pathways.

The support of this research by the US Department of Energy Hydrogen Program is gratefully acknowledged.

Footnotes

† 1995 J. J. Zuckermann fellow.

‡ GC analyses were performed on a temperature programmed (ethylbenzene, 70 °C isothermal for 1 min, 5 °C min⁻¹ to 130 °C; thf, 35 °C

isothermal for 1 min; 1 °C min⁻¹ to 45 °C; ethylcyclohexane, 60 °C isothermal for 1 min, 5 °C min⁻¹ to 150 °C) Hewlett Packard 5890 gas chromatograph using a 250 µm × 25 m OV-1 capillary column. For GCMS analyses the column was coupled to a VG 70SE dual sector high-resolution mass spectrometer.

References

- 1 D. H. James and W. M. Castor, in *Ullmann's Encyclopedia of Industrial Chemistry*, 5th edn., ed. B. Elvers, S. Hawkins and W. Russey, VCH Verlagsgesellschaft, Weinheim, 1994, p. 332.
- 2 D. Baudry, M. Ephritikhine and H. Felkin, *J. Chem. Soc., Chem. Commun.*, 1983, 788; H. Felkin, T. Fillebeen-Khan, R. Holmes-Smith and J. Zakrzewski, *Tetrahedron Lett.*, 1984, **25**, 1279; H. Felkin, T. Fillebeen-Khan, R. Holmes-Smith and Y. Lin, *Tetrahedron Lett.*, 1985, **26**, 1999; M. W. Burk, R. H. Crabtree and D. V. McGrath, *J. Chem. Soc., Chem. Commun.*, 1985, 1829; M. W. Burk and R. H. Crabtree, *J. Am. Chem. Soc.*, 1987, **109**, 8025; K. Nomura and Y. Saito, *J. Chem. Soc., Chem. Commun.*, 1988, 161; K. Nomura and Y. Saito, *J. Mol. Catal.*, 1989, **54**, 57; T. Sakakura, T. Sodeyama and M. Tanaka, *New J. Chem.*, 1989, **13**, 737; J. A. Maguire, W. T. Boese and A. S. Goldman, *J. Am. Chem. Soc.*, 1989, **111**, 7088; T. Sakakura, T. Sodeyama, F. Abe and M. Tanaka, *Chem. Lett.*, 1991, 297; J. A. Maguire and A. S. Goldman, *J. Am. Chem. Soc.*, 1991, **113**, 6706; J. A. Maguire, A. Petrillo and A. S. Goldman, *J. Am. Chem. Soc.*, 1992, **114**, 9492; T. Fujii and Y. Satio, *J. Chem. Soc., Chem. Commun.*, 1990, 757; T. Fujii, Y. Higashino and Y. Satio, *J. Chem. Soc., Dalton Trans.*, 1993, 517; T. Aoki and R. H. Crabtree, *Organometallics*, 1993, **12**, 294; J. A. Miller and L. K. Knox, *J. Chem. Soc., Chem. Commun.*, 1994, 1449; J. Belli and C. M. Jensen, *Organometallics*, 1996, **15**, 1532.
- 3 M. Gupta, C. Hagen, W. C. Kaska, R. Flesher and C. M. Jensen, *Chem. Commun.*, 1996, 2083.
- 4 M. Gupta, W. C. Kaska, R. Cramer and C. M. Jensen, *J. Am. Chem. Soc.*, 1997, **119**, 840.
- 5 D. R. Anton and R. H. Crabtree, *Organometallics*, 1982, **2**, 855.

Received, 29th October 1996; Com. 6/07381F