

Efficient thermochemical alkane dehydrogenation and isomerization catalyzed by an iridium pincer complex

Fuchen Liu and Alan S. Goldman*

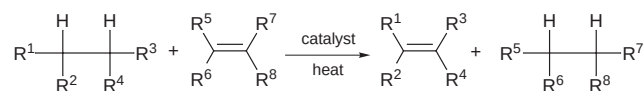
Department of Chemistry, Rutgers University, Piscataway, NJ 08854-8087, USA.
E-mail: goldman@rutchem.rutgers.edu

Received (in Bloomington, IN, USA) 22nd January 1999, Accepted 9th February 1999

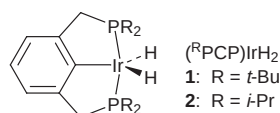
(*i*-PrPCP)IrH₂ is found to be a remarkably effective solution-phase catalyst for the 'acceptorless' thermochemical dehydrogenation of cycloalkanes (and isomerization in the case of cyclodecane), and the first such catalyst reported to effect the dehydrogenation of *n*-alkanes.

Alkanes are the world's most abundant organic resource, yet methods for their conversion to useful chemicals remain extremely limited. Alkenes, by contrast, are probably the single most useful and versatile class of feedstock for commodity-scale organic chemical syntheses. Methods for the dehydrogenation of alkanes to give alkenes are therefore of great interest.¹

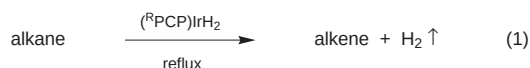
In general, the yields and selectivity afforded by heterogeneous alkane dehydrogenation catalysts are very low.¹ Soluble transition metal complexes, however, have held promise in this respect since the early 1980s when Crabtree and Felkin reported the development of catalysts for transfer-dehydrogenation.²



The initially reported catalysts suffered from ligand degradation which severely limited turnover numbers. Systems were later developed that afforded much higher turnover numbers;³ of these, the most important in the context of the present work was the 'pincer' complex, (*t*-BuPCP)IrH₂ [**1**; *t*-BuPCP = 2,5-C₆H₃(CH₂PBu_t)₂].⁴



Recently [eqn. (1)] it was reported that refluxing alkane solutions of **1** resulted in dehydrogenation with evolution of dihydrogen; no sacrificial hydrogen acceptor was required.⁵ Although this was by far the most efficient catalyst to date for such 'acceptorless' dehydrogenation,^{6,7} the observed rates were still fairly low by the standards of practical catalytic systems.



To a significant extent, the pincer geometry 'holds back' the phosphinoalkyl groups such that they are further removed from the metal, and the molecule is sterically less congested, relative to a hypothetical analogous complex of monodentate ligands [e.g. Ir(PR₂Me)₂(Ph)H₂]. Nevertheless, Milstein and coworkers recently reported that H₂ adds to the carbonyl complex (*i*-PrPCP)Ir(CO)⁸ whereas, in contrast, we find that the *t*-BuPCP analog undergoes no observable addition of H₂ (800 Torr). Thus in spite of the 'pincer effect' the *tert*-butyl groups are apparently still bulky enough to inhibit H₂ addition; this led us to suspect that alkyl hydrides and other presumed intermediates of a

dehydrogenation cycle may be even more sterically disfavored by the *tert*-butyl groups. Accordingly we synthesized[†] and investigated the *i*-PrPCP analog of **1**, i.e. (*i*-PrPCP)IrH₂ (**2**).

Vigorously refluxing (151 °C) a cyclooctane solution of **2** (1.0 mM) leads to the formation of 47 mM cyclooctene (47 turnovers) after 30 min. The reaction rate subsequently levelled off; 105 mM cyclooctene was present after 15 h. This initial dehydrogenation rate (> 94 turnover h⁻¹) may be compared with 11 turnover h⁻¹ resulting from cyclooctane dehydrogenation catalyzed by **1** under similar conditions,⁵ and 1.41 turnover h⁻¹ reported for IrH₂(O₂CCF₃)(PCy₃)₂.⁷

Cyclodecane, with a reflux temperature of 201 °C, undergoes dehydrogenation at a much greater rate than cyclooctane: for example 460 turnovers cyclodecene are obtained after 1 h of reflux, (*cis*:*trans* ratio of 4.6:1; see Table 1). This compares, for example, with 170 turnover after 4 h obtained from the use of catalyst **1**.⁵ The isopropyl derivative **2** is thus an extremely efficient catalyst for acceptorless dehydrogenation of cycloalkanes, yielding turnover rates a full order of magnitude greater than the *tert*-butyl derivative.

The dehydrogenation enthalpy of cyclooctane, and probably that of cyclodecane as well, is anomalously low.^{9–12‡} Accordingly, with *n*-alkanes, the *t*-BuPCP catalyst **1** gave no observable yields of acceptorless dehydrogenation product. By contrast, **2** is able to catalyze the acceptorless dehydrogenation of *n*-alkanes, though the efficiency is less than that with cyclodecane. Refluxing an *n*-undecane solution of **2** (1.0 mM; 196 °C) yields 35.4 mM undecenes, as a mixture of internal isomers (not fully characterized), after 0.5 h. Unfortunately, the yield quickly levelled off and after 1 and 45 h the respective concentrations of undecenes were 42.3 and 44.1 mM. This represents the first report of a homogenous catalytic system for the dehydrogenation of *n*-alkanes.

To determine whether product concentrations level off due to catalyst decomposition or product inhibition, we allowed an *n*-decane solution of **2** to reflux (174 °C) until the decene concentration reached a constant value. Volatiles (decenes and decane) were then removed and fresh *n*-decane was added; upon refluxing, the kinetics of decene production were identical to those of the initial run indicating that the catalyst did not decompose. This result is similar to that obtained previously for **1**-catalyzed dehydrogenation of cyclooctane.⁵ In the case of *n*-alkanes, however, the removal of product, if sufficiently rapid, could have an additional and very significant benefit. When *n*-alkane dehydrogenation is conducted (at 150 °C) using a

Table 1. Dehydrogenation and isomerization of cyclodecane catalyzed by **2**^a

t/h	<i>cis</i> -Cyclodecene	<i>trans</i> -Cyclodecene	<i>cis</i> -DEC ^b	<i>trans</i> -DEC
1	378	82	16	10
4	619	145	38	59
8	692	163	42	79
20	700	163	43	81

^a Refluxing cyclodecane; 1.0 mM **2**; values are turnover numbers (equal to concentration/mM). ^b DEC = diethylcyclohexane.

sacrificial acceptor, the major kinetic product is the terminal (α) olefin which then undergoes isomerization to the more stable internal olefins.¹³ Presumably the same kinetic product is formed in the absence of an acceptor but isomerization is much more rapid relative to dehydrogenation; accordingly, added dec-1-ene is rapidly isomerized (> 99% in 2.5 min) in refluxing *n*-undecane. Thus, efficient dynamic removal of product from the mixture might lead not only to high turnover numbers, but also to high regioselectivity for α -olefins in the case of *n*-alkanes.

Returning to the 2-catalyzed dehydrogenation of cyclodecane, two intriguing products other than *cis*- and *trans*-cyclodecene are observed to accumulate in significant concentration (by GC and GC-MS); GC-MS and ¹H NMR data indicate them to be diethylcyclohexanes (DEC). When *cis*- and *trans*-1,2-DEC were independently generated by the hydrogenation of 1,2-diethylbenzene; ¹H NMR, GC and GC-MS data were in complete agreement with those of the cyclodecane reaction products.

The unprecedented isomerization of cyclodecane to *cis*- and *trans*-1,2-DEC might seem to suggest the involvement of a cyclodecane C-C bond activation step. It is difficult, however, to envisage such a mechanism that would account for the selectivity of this ring-contraction. Furthermore, the formation of DEC's appeared to be a secondary reaction since the ratio of the DEC's to cyclodecenes significantly increased with time (Table 1). This leads us to propose, for the overall isomerization reaction, the mechanism of Scheme 1 which receives strong additional support from the following observations:

(i) A mixture of **2** (1.0 mM) and cyclodecene (200 mM) in *n*-undecane solvent was refluxed (196 °C). After 30 min, 4.2 mM diethylcyclohexane had appeared (*ca.* 2:1 *trans*:*cis*);[¶] in addition, *ca.* 50% of the cyclodecene had been transfer-hydrogenated to cyclodecane (with commensurate formation of undecenes), while 98 mM cyclodecene remained. This rate of DEC formation (8.4 turnover h⁻¹; 149 mM time-averaged concentration of cyclodecene) is proportional to the time-averaged concentration of cyclodecene present in the reactions that began with cyclodecene only; *i.e.* this result is entirely consistent with the DEC being derived from cyclodecene (not directly from cyclodecane).

(ii) *trans,trans*-1,5-cyclodecadiene has been reported to undergo a thermal Cope rearrangement to give *trans*-1,2-divinylcyclohexane.^{14¶} Extrapolating the rate data to 201 °C gives a rate of 1.2 s⁻¹,^{14**} which is clearly consistent with Scheme 1 and the lack of build-up of observable quantities of the cyclodiene. Presumably, cyclodecadienes other than the 1,5-isomers are initially formed and these undergo isomerization to the 1,5-diene which then undergoes rearrangement.

(iii) Since divinylcyclohexane is not formed in an observable quantity, the mechanism of Scheme 1 requires that this intermediate is rapidly hydrogenated under the reaction conditions. Accordingly, when a cyclodecane solution of **2** (1.0 mM) and added vinylcyclohexane (100 mM) was refluxed, after only 10 min 100% conversion to ethylcyclohexane was observed.

In summary, we describe the first homogeneous catalyst system to dehydrogenate alkanes at rates that might be considered suitable for a practical and useful system. It would appear that efficient removal of the olefin product, by either physical or chemical means, might lead to dramatically increased yields and even regioselectivity. The formation of DEC represents a novel example of catalytic alkane functional-

ization proceeding via dehydrogenation and a secondary olefin reaction.

Support by the Division of Chemical Sciences, BES, OER, US Department of Energy is gratefully acknowledged. We thank Johnson-Matthey for a generous loan of iridium.

Notes and references

† The protonated *i*-PrPCP ligand was synthesized according to Milstein⁸ and reacted with [Ir(cyclooctene)₂Cl] in refluxing toluene for 3 days. The resulting (*i*-PrPCP)IrHCl was isolated and converted to (*i*-PrPCP)IrH₂ using the procedure previously reported for (*n*-BuPCP)IrH₂.⁴

‡ The dehydrogenation enthalpy of cyclooctane is *ca.* 23.8(5) kcal mol⁻¹ as determined by either direct measurement of hydrogenation or on the basis of enthalpies of formation.^{9,10} The value for cyclodecane is less certain. Based on available data for enthalpies of formation it would appear to be rather high, at least 30 and 33 kcal mol⁻¹ for formation of *cis*- and *trans*-cyclodecene respectively.⁹⁻¹¹ However, direct hydrogenation measurements yield values of -20.7(1) and -24.0(9) kcal mol⁻¹, respectively, in acetic acid solvent.¹² Enthalpies of other cycloalkene hydrogenations in acetic acid, determined by the same workers, are *ca.* 1.3 kcal mol⁻¹ less negative than reliable values in hydrocarbon solvent.^{9,12} Thus, 22 and 25 kcal mol⁻¹ are probably the best estimates for the dehydrogenation of cyclodecane to give *cis*- and *trans*-cyclodecene respectively.

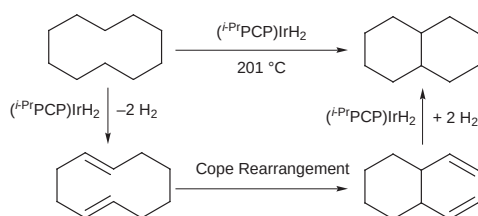
§ An attempt to dehydrogenate *n*-decane using catalyst **1** gave no detectable decene. It is difficult to set an upper limit on the amount of decene produced since as many as eight major isomers could be formed. Nevertheless, the reaction of *n*-decane catalyzed by **2**, unlike that of **1**, gave very easily detectable decene GC peaks indicating total concentrations of 14.4 and 16.1 mM after 0.5 and 5 h respectively.

¶ Both our dehydrogenations and our independent synthesis gave mixtures of the two DEC's; we are unable to assign their respective stereochemistry with high confidence. However, the ratio changes with time during the cyclodecane dehydrogenation and we tentatively assign the product that relatively increases in concentration as the more stable *trans*-DEC.

|| The product of the uncatalyzed reaction of 1,5-*trans,trans*-cyclodecadiene is exclusively the *trans*-DEC isomer in contrast with our observation of a mixture of *trans* and *cis*. However, MOPAC calculations indicate that the 1,5-*cis,trans*-cyclodecadiene is the more stable diene; molecular modeling suggests that this isomer would yield *cis*-1,2-diethylcyclohexane. Furthermore, Cope rearrangements can be metal-catalyzed which might represent another pathway leading to the *cis* isomer.

** The measured rates (40–90 °C) give the following activation parameters: $\Delta H^\ddagger = 24.32$ kcal mol⁻¹; $\Delta S^\ddagger = -7.81$ cal mol⁻¹ K⁻¹.¹⁴

- P. N. Rylander, in *Ullmann's Encyclopedia of Industrial Chemistry*, ed. B. Elvers, J. F. Rounsaville and G. Schulz VCH Verlagsgesellschaft, Weinheim, 1989, p. 494.
- D. Baudry, M. Ephritikine, H. Felkin and R. Holmes-Smith, *J. Chem. Soc., Chem. Commun.*, 1983, **788**; M. J. Burk, R. H. Crabtree, C. P. Parnell and R. J. Uriarte, *Organometallics*, 1984, **3**, 816.
- J. A. Maguire and A. S. Goldman, *J. Am. Chem. Soc.*, 1991, **113**, 6706.
- M. Gupta, C. Hagen, R. J. Flesher, W. C. Kaska and C. M. Jensen, *Chem. Commun.*, 1996, 2083; M. Gupta, C. Hagen, W. C. Kaska, R. E. Cramer and C. M. Jensen, *J. Am. Chem. Soc.*, 1997, **119**, 840.
- W. Xu, G. P. Rosini, M. Gupta, C. M. Jensen, W. C. Kaska, K. Krogh-Jespersen and A. S. Goldman, *Chem. Commun.*, 1997, 2273.
- T. Fujii, Y. Higashino and Y. Saito, *J. Chem. Soc., Dalton. Trans.*, 1993, 517.
- T. Aoki and R. H. Crabtree, *Organometallics*, 1993, **12**, 294.
- B. Rybtchinski, A. Vigalok, Y. Bendavid and D. Milstein, *Organometallics*, 1997, **16**, 3786.
- NIST Standard Reference Database Number 69, 1996, <http://webbook.nist.gov/chemistry/>
- D. R. Stull, E. F. Westrum and G. C. Sinke, *The Chemical Thermodynamics of Organic Compounds*, Robert E. Kreiger Publishing, Malabar, FL, 1987.
- J. B. Pedley and J. Rylance, *Computer Analysed Thermochemical Data: Organic and Organometallic Compounds*, University of Sussex, Brighton, UK, 1977.
- R. B. Turner and W. R. Meador, *J. Am. Chem. Soc.*, 1957, **79**, 4133.
- F. Liu, E. B. Pak, B. Singh, C. M. Jensen and A. S. Goldman, *J. Am. Chem. Soc.*, in press.
- P. S. Wharton and D. W. Johnson, *J. Org. Chem.*, 1973, **38**, 4117.



Scheme 1

Communication 9/00631A