Thermochemical alkane dehydrogenation catalyzed in solution without the use of a hydrogen acceptor

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(PCP)IrH$_2$ [PCP = η^3-C$_6$H$_3$(PBu$^t{}_2$)$_2$-1,3] catalyzes the efficient (several hundred mol product/mol catalyst) dehydrogenation of alkanes under reflux to give the corresponding alkenes and dihydrogen.

The development of effective systems for the functionalization of alkanes is one of the major goals in the field of homogeneous catalysis.[1] Conversion of alkanes to the corresponding alkenes is a particularly valuable functionalization reaction in view of the great versatility of alkenes as organic feedstock. Crabtree *et al.* first showed in 1979 that transition-metal phosphine complexes could effect stoichiometric dehydrogenation of alkanes;[2] this was later extended to catalytic dehydrogenation.[3,4] The high endothermicity of dehydrogenation was compensated for by either the use of a sacrificial hydrogen acceptor or by UV irradiation.[5]

Such systems were all plagued by ligand decomposition, however, and it was not until 1988 that the first 'high-turnover' (> *ca.* 100 turnovers) dehydrogenation system was discovered: Rh(PMe$_3$)$_2$(CO)Cl under UV irradiation.[6] This robust catalyst was later found to yield efficient thermochemical dehydrogenation through the use of sacrificial hydrogen acceptors and, surprisingly, added dihydrogen; unfortunately, the presence of H$_2$ atmosphere resulted in the hydrogenation of more than one mole sacrificial acceptor per mole dehydrogenated product.[7]

Most recently, the development of the first 'high-turnover' thermochemical catalysts not requiring H$_2$ atmosphere was reported: complexes of the 'pincer' ligand η^3-C$_6$H$_3$(CH$_2$P-Bu$^t{}_2$)$_2$-1,3 (PCP), including (PCP)RhH$_2$ or, more effectively, (PCP)IrH$_2$.[8]

The key to the effectiveness of the PCP-based catalysts appears to be their long-term stability at very high temperatures (*e.g.* 200 °C).[9] We considered that such temperatures are sufficiently high, in principle, to overcome the large positive enthalpy of dehydrogenation without the use of a sacrificial acceptor.†[10] This was indeed found to be the case and the remarkable stability of the catalyst is maintained under such conditions. Herein, we report the first example of efficient alkane dehydrogenation catalyzed homogeneously without the use of either light or a sacrificial hydrogen acceptor.

Refluxing a cyclooctane solution of (PCP)RhH$_2$ (10 mM) while passing a stream of argon above the condenser results in negligible rates of cyclooctene formation, (< 2 mM after 24 h). As was found when sacrificial acceptors were used, the iridium analog is much more effective for 'acceptorless' dehydrogenation. Under similar conditions [2 mM (PCP)IrH$_2$], the initial rate of cyclooctene (COE) formation is 11 turnovers h^{-1}.‡

After 44 h, 104 turnovers are obtained; after 120 h, 190 turnovers are produced. These results may be compared with the most effective soluble 'acceptorless' dehydrogenation catalyst reported to date: IrH$_2$(O$_2$CR)(PCy$_3$)$_2$ (1.25 mM) was reported to yield 1.41 turnovers h^{-1} COE, with a maximum of 28.5 turnovers obtained after 48 h.[11]

The high endothermicity of alkane dehydrogenation is obviously a key factor involved in the challenge of developing alkane dehydrogenation catalysts, particularly in developing an acceptorless dehydrogenation system. In this respect cyclooctane is anomalous, since its dehydrogenation enthalpy of 23.3 kcal mol^{-1} contrasts with *ca.* 28–30 kcal mol^{-1} required for the elimination of two secondary C–H bonds from more typical alkanes.[10] Extrapolation to typical alkanes, based on behavior observed with cyclooctane, is therefore, *a priori*, quite tenuous. We find, however, that the catalytic efficacy of (PCP)IrH$_2$ with other alkanes is at least comparable to that with cyclooctane and the higher reflux temperatures of less volatile solvents permit significantly greater rates. For example, in refluxing cyclodecane (201 °C), 170 and 360 turnovers cyclodecene are obtained after 4 and 24 h, respectively (*ca.* 3 : 1 *cis : trans*; 1.0 mM catalyst; see Fig. 1). This rapid dehydrogenation occurs in spite of the high dehydrogenation enthalpy of cyclodecane (30 and 33 kcal mol^{-1} to form *cis*- and *trans*- cyclodecene, respectively).[10]

The decrease in the rate of alkene formation which invariably occurs with time is probably not due to inevitable decomposition of the catalyst but may be caused by build-up of alkene product. Accordingly, a fresh solution of catalyst in cyclooctane, to which had been added 10% COE, showed no increase in COE concentration upon reflux. The mechanism by which the alkene product inhibits the reaction remains to be determined.

Significant amounts of cyclooctane can also be dehydrogenated to give COE and molecular hydrogen in reactions carried out in a closed system under reduced pressure. In a typical experiment, a solution of cyclooctane (4.0 ml) and (PCP)IrH$_2$ (3 mg, 0.005 mmol) was sealed in a tube under 0.007 mbar of argon and fully immersed in a 200 °C oil bath. After 0.5 h, 10 turnovers of COE had been produced. The production of H$_2$ was confirmed by gas chromatographic analysis† of the vapor above

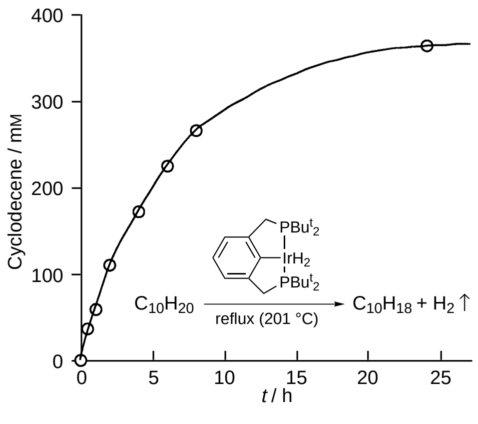

Fig. 1 Cyclodecene formation (total, *ca.* 3 : 1 *cis*:*trans*) *vs.* time; (PCP)IrH$_2$ in refluxing cyclodecane (1.0 mM, 201 °C)

the reaction mixture. Increased levels of cyclooctane dehydrogenation were not observed in solutions which were heated for longer reaction times. However, additional dehydrogenation activity was achieved in solutions which had been heated to 200 °C for 0.5 h by removing the resulting H_2 by freeze–pump–thaw degassing. A total of 36 turnovers of COE were obtained in an experiment in which H_2 was removed four times through this procedure. These results demonstrate that under these conditions the catalysis is limited by equilibrium constraints rather than catalyst stability.

The PCP ligand clearly bears a close relationship (at least formally) to the ligand set in the putative catalytically active fragments $M(PR_3)_2Cl$ (M = Rh,[7] Ir[12]). In the case of the chloride complexes, rhodium has proven to be the more effective metal (for both transfer- and photo-dehydrogenation).[13] Thus the much greater efficacy of Ir *vs.* Rh in the case of the PCP complexes presents an issue which merits attention.

Although complexes $Rh(PR_3)_2ClH_2$ are classical dihydrides,[14] Milstein has reported the T_1 of $H_2Rh[\eta^3\text{-}HC(CH_2CH_2PBu^t{}_2)_2]$ to be 30–60 ms (−40 °C, 400 MHz)[15] strongly indicating the presence of a dihydrogen ligand. The closely related $(PCP)RhH_2$[16] is apparently also a dihydrogen complex: we find a T_1 value of 46 ms at 293 K (500 MHz)[17] and an H–D coupling constant of 33 Hz for (PCP)RhH(D).

We have previously reported that addition of H_2 to $Rh(PPr^i{}_3)_2Cl$ [to give $H_2Rh(PPr^i{}_3)_2Cl$] is highly exothermic ($\geqslant$ 33 kcal mol^{-1}).[18] The fact that H_2 addition to Rh(PCP) does not even cleave the H–H bond suggests that addition is much less favorable. Indeed, *ab initio* electronic structure calculations¶ yield remarkably different reaction energies for H_2 addition to the model fragments $Rh(PH_3)_2Cl$ and $Rh(PH_3)_2Ph$: −28.5 and −4.2 kcal mol^{-1}, respectively (producing dihydride and dihydrogen complexes, respectively, in accord with observation). In the case of Ir, the additions are much more exothermic though the difference between chloride and phenyl complexes is similar; respective values are $Ir(PH_3)_2Cl$: −54.1 kcal mol^{-1} and $Ir(PH_3)_2Ph$: −23.0 kcal mol^{-1}.¶ These computational results strongly suggest a simple explanation for the very high catalytic activities of the $Rh(PR_3)_2Cl$ and Ir(PCP) fragments as compared with the 'converse' pair [*i.e.* Rh(PCP) and $Ir(PR_3)_2Cl$]. For Rh, the PCP complex adds H_2 too weakly. This implies not only that transfer of H_2 from alkane to rhodium is unfavorable, but it also suggests that C–H addition may be unfavorable, since H_2 normally adds much more favorably than C–H bonds. For Ir, H_2 addition to the chloride complex is highly exothermic; this may inhibit thermal loss of H_2 or even transfer of H_2 to a sacrificial acceptor. Thus, the similar affinities of the $Rh(PR_3)_2Cl$ and Ir(PCP) fragments for H_2 (*viz.*, −28.5 and −23.0 kcal mol^{-1}) may help explain their similarly high catalytic activities. In the case of the Rh complex, however, H_2 is needed to cleave the μ-Cl bridge and catalyst decomposition is observed at very high temperatures ($\gg$ 100 °C).[7] In the case of the Ir(PCP) unit, formation of analogous anion-bridged dimers is not possible and presumably the rigidity of the PCP ligand endows the complex with resistance to decomposition that is highly unusual for a transition-metal phosphine complex. Apparently, ligand stability and the appropriate (but unremarkable) energetics of oxidative addition to the Ir(PCP) fragment are the key factors resulting in the unprecedented ability to effect efficient alkane dehydrogenation without the use of light or a sacrificial acceptor.

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Footnotes and References

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† For example, if $\Delta G^{\neq}$ = 30.0 kcal mol (1 cal = 4.184 J), at 200 °C the catalytic turnover rate would be 500 h^{-1}. Since the dehydrogenation enthalpy of typical alkanes is on the order of 28–30 kcal mol^{-1},[10] reasonable rates could be obtained (in principle) even if the favorable reaction entropy does not make any contribution in the transition state. Of course, a significant concentration of alkene can only be obtained by allowing hydrogen to escape, thereby permitting entropy to predominate over enthalpy.

‡ Addition of liquid Hg to the solution has no measurable effect on the rate of COE formation, indicating that the catalyst is not colloidal iridium: D. R. Anton and R. H. Crabtree, *Organometallics,* 1983, **2**, 855.

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