A highly active alkane dehydrogenation catalyst: stabilization of dihydrido rhodium and iridium complexes by a P–C–P pincer ligand

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The novel P–C–P pincer complex, [$IrH_2\{C_6H_3(CH_2PBu^t_2)_2$-2,6}] has long-term stability at 200 °C and catalyses the transfer dehydrogenation of cyclooctane to cyclooctene at the rate of 12 turnovers min^{-1}.

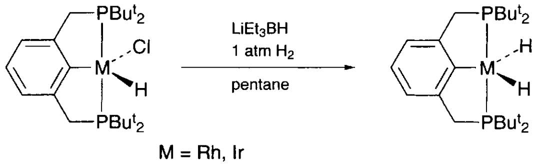
Several soluble metal complexes catalyse the dehydrogenation of alkanes.[1–7] Systems have been reported that are driven by the hydrogen transfer from alkanes to hydrogen acceptors (transfer dehydrogenation),[1–5] photoirradiation,[5,6] and the thermal evolution of hydrogen.[7] However, the utility of these reactions is generally limited by very slow rates, low numbers of turnovers, and catalyst instability under the reaction conditions.[1–3,5–7] A system with significantly improved activity has been reported by Goldman and coworkers but it requires the sacrificial hydrogenation of a 4–20 fold excess of an acceptor alkene in conjunction with the alkane dehydrogenation.[4]

Iridium and rhodium dihydrido complexes containing P–C–P pincer ligands have unusually high thermal stabilities. {For example, [$IrH_2\{HCC_2H_4P(Bu^t_2)_2\}$] is stable at 200 °C.}[8] Dihydrido iridium bisphosphine complexes have been found to catalyse the transfer-dehydrogenation of alkanes.[2,3,5] It was therefore of interest to explore the reactivity of rhodium and iridium P–C–P pincer complexes with alkanes in the presence of the hydrogen acceptor *tert*-butylethylene (tbe).

The complexes [$RhH_2\{C_6H_3(CH_2PBu^t_2)_2$-2,6}] **1** and [$IrH_2\{C_6H_3(CH_2PBu^t_2)_2$-2,6}] **2** were prepared in >85% yield through treatment of the corresponding hydrido chloride complexes[9] with a thf solution of $LiBEt_3H$ at 25 °C under an atmosphere of H_2 as shown in Scheme 1. Complex **1** was previously prepared in inferior yield by the reaction of the hydrido chloride complex with KH.[10] The complexes were purified and isolated upon recrystallization from pentane.‡

Solutions of cyclooctane (4.0 ml, 37.0 mmol) and tbe (0.2 ml, 1.6 mmol) were charged with **1** (10 mg, 0.019 mmol), in sealed tubes under argon, and fully immersed in an oil-bath for the prescribed reaction times. The reaction mixtures did not darken or discolour upon heating to 150 °C for periods as long as 1 week. The long-term maintenance of catalyst integrity contrasts the short, *ca.* 12 h halflives generally found for dehydrogenation catalysts at this temperature. The production of cyclooctene was quantified by gas chromatography§ and the rate of catalysis was determined to be 0.8 turnovers h^{-1}. The rate increases to 1.8 turnovers h^{-1} at 200 °C but significant decomposition of **1** is apparent after 24 h.

Strikingly higher activity is observed in solutions of cyclooctane (4.0 ml, 37.0 mmol), tbe (0.2 ml, 1.6 mmol), and the iridium complex **2** (3 mg, 0.0051 mmol). At 150 °C the dehydrogenation of cyclooctane proceeds at the rate of 82 turnovers h^{-1} while a rate of 12 turnovers min^{-1} is observed at 200 °C. Appreciable activity (20.5 turnovers h^{-1}) is found even at 100 °C. The solutions containing **2** show no signs of complex decomposition up to 1 week of reaction at all temperatures studied and remain active to the limit of complete hydrogenation of the hydrogen acceptor. The reaction is unaffected by the addition of metallic mercury to the mixture indicating that metallic iridium is not involved in the hydrogen transfer.[11] Comparable high levels of catalytic activity have previously been achieved only in systems catalysed by [$RhCl(PMe_3)_2(CO)$] which require the sacrificial hydrogenation of 6–8 equiv. of norbornene and 68 atm of H_2.[4] Our finding of far greater activity with **2** than **1** is in accordance with a recent theoretical study by Goddard and coworkers which identified Ir^+ as the most efficient transition metal for the dehydrogenation of methane.[12] The differences in the catalytic activities of **1** and **2** are possibly related to the ability of iridium to form stronger M–C and M–H bonds and the availability of the Ir^V oxidation state.



Scheme 1

At high concentration, both tbe and the hydrogenated product, *tert*-butylethane (tba) inhibit the catalytic reaction. Diminished rates of catalysis are found in solutions containing >300 : 1 ratio of tbe to catalyst. Thus, high turnover numbers can be achieved only in solutions containing a limited amount of tbe which must be periodically added to the reaction mixture. Following incremental additions of tbe (0.2 ml, 1.6 mmol), the dehydrogenation of cyclooctane is observed to again proceed at the rate of 12 turnovers min^{-1}. However, pronounced product inhibition of the catalytic system is observed after 1000 total turnovers.

We have also found that the catalytic activity is strongly inhibited by N_2. In order to achieve the maximum catalytic rates, the solutions must be freeze–pump–thaw degassed prior to heating to remove any vestiges of N_2. Apparently, N_2 coordination is competitive with alkane coordination. This explanation is supported by the findings that **1**, **2** and [$Rh(H_2)\{HCCH_2CH_2P(Bu^t)_2)_2\}$] coordinate N_2 when placed under an atmosphere of N_2.[13]

In conclusion, **2** catalyses the transfer-dehydrogenation of cyclooctane at rates which are two orders of magnitude greater than those of previously reported for catalytic systems which do not require the sacrificial hydrogenation of a large excess of hydrogen acceptor[1–3,5] Furthermore, the P–C–P pincer complexes have unprecedented, long-term stabilities under catalytic conditions.

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Footnotes

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‡ The ^1H and ^{31}P NMR spectra of **1** obtained through this procedure were identical to those previously reported.[10] For **2**: ^1H NMR (400 MHz, [$^2H_8$]toluene), δ 7.43, (m, 1 H, *p*-C), 7.19, (br, s, 2 H, *m*-C, 3.36 (vt, J_{PH} 3.7

Hz, 4 H, CH$_2$), 1.24 (vt, J_{PH} 6.7 Hz, 18 H, CH$_3$), −9.01 (J_{PH} 9.8 Hz IrH). $^{31}P\{^1H\}$ NMR (161.9 MHz, [$^2H_8$]toluene), δ 73.1. Anal. Calc: C, 49.04; H, 7.72. Found: C, 49.12; H, 8.21%.

§ GC analysis was performed on a temperature programmed (85 °C isothermal for 1 min; 5 °C min^{-1} to 200 °C) Hewlett Packard 5890 gas chromatography using a 250 μm × 25 m OV-1 capillary column.

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